1681

Orientational Anisotropy in the Total Collision Cross Section of State Selected NO Molecules

S. Stolte

**ORIENTATIONAL ANISOTROPY
IN THE TOTAL COLLISION CROSS SECTION
OF STATE SELECTED NO MOLECULES**

PROMOTOR PROF DR A DYMANUS
COREFERENT DR J. REUSS

**ORIENTATIONAL ANISOTROPY
IN THE TOTAL COLLISION CROSS SECTION
OF STATE SELECTED NO MOLECULES**

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE WISKUNDE EN NATUURWETENSCHAPPEN
AAN DE KATHOLIEKE UNIVERSITEIT TE NIJMEGEN
OP GEZAG VAN DE RECTOR MAGNIFICUS,
DR. CH. M. A. KUIJPER,
HOOGLERaar IN DE FACULTEIT
DER WISKUNDE EN NATUURWETENSCHAPPEN,
VOLGENS BESLUIT VAN DE SENAAAT
IN HET OPZAKENBAAR TE VERDULDIGEN
OP VRIJDAG 26 MEI 1972
DES NAMIDDAGS TUSSEN 2 UUR PRECIJS

DOOR

STEVEN STOLTE

GEBOREN TE UTRECHT

1972

THOBI NOUFS TE NIJMEGEN

Allen, die hebben bijgedragen tot het tot stand komen van dit proefschrift, wil ik gaarne bedanken.

Enkelen wil ik in het bijzonder noemen:

Dr. H.L. Schwartz voor de goede samenwerking en de vele steun, die ik gedurende de laatste twee jaar van hem heb ondervonden.

Drs. G. Schonk en Drs. L. van Deursen, die gedurende hun afstudeerperiode aan dit onderzoek hebben medegewerkt en op wie ik ook daarna nooit tevergeefs een beroep heb gedaan.

C. Sikkens, J. Hermsen en F. van Rijn, voor hun technische hulp bij de opbouw van de apparatuur.

Drs. J.W. Kuijpers en Drs. W.L. Meerts voor het berekenen van het Zeeman- en Stark-effect van NO.

De dienstverlenende afdelingen wil ik graag bedanken in de personen van de Heren J.G.M. van Langen en W. van Rooyen.

De figuren in dit proefschrift werden vervaardigd door de afdeling illustratie onder leiding van de Heer J. Gerritsen.

*Voor
mijn vader en moeder
en Janneke*

CONTENTS

CHAPTER 1:	
INTRODUCTION	11
1.1. Motivation	11
1.2. Description of Thesis Content	14
CHAPTER 2:	
EXPERIMENTAL METHOD	17
2.1. Configuration of the Apparatus	17
2.2. General Features of State Selection	17
2.3. Orientation of Molecules and their Attenuation in the Scattering Region	21
CHAPTER 3:	
TECHNICAL DETAILS OF THE APPARATUS	25
3.1. Multi-Chamber Arrangement	25
3.2. Source	25
3.3. Rabi-magnet	25
3.4. Six-pole	27
3.5. The Secondary Beam	28
3.6. The Helmholtz Coils	30
3.7. The Velocity Selector	32
3.8. The Detector	33
CHAPTER 4:	
RESULTS ON STATE SELECTION OF NO	37
4.1. The Focusing Spectrum	37
4.2. The Focused Spot	39

CHAPTER 5:	
THEORY	41
5.1. The Intermolecular Potential	41
5.2. Distorted Wave Approximation .	48
5.3. The Landau-Lifshitz Approximation	55
5.4. Discussion of the Approximations	59
5.5. Small Angle Scattering	63
 CHAPTER 6:	
FORMAL TRANSFORMATION OF EXPERIMENTAL DATA INTO PHYSICAL QUANTITIES	67
6.1. The Total Collision Cross Section in a Magnetic Field	67
6.2. Experimental Correction Factors	70
6.3. Evaluation of $C_{\Delta B}$ and $C_{\hat{B}}$. . .	71
6.4. The Influence of the Target Motion	74
6.5. The Influence of Finite Angular Resolution .	77
 CHAPTER 7:	
SCATTERING RESULTS	81
7.1. Determination of the Total Collision Cross Section . .	81
7.2. Velocity Dependence of the Total Collision Cross Section	83
7.3. The Anisotropy Effect	87
7.3.1. Data Collection	87
7.3.2. Data Evaluation	88
7.3.3. Results	91
 CHAPTER 8:	
DISCUSSION OF THE RESULTS AND CONCLUDING REMARKS	99
8.1. Glory Undulations	99
8.2. Analysis of the Experimental Results	102
8.3. Theoretical Aspects	104
8.4. Discussion of the Bonn Results	105
8.5. Concluding Remarks and Future Possibilities	107

APPENDIX:	
PROPERTIES OF NO	109
A1. NO without Field	109
A2. Stark Effect of NO	110
A3. Zeeman Effect of NO	111
 SAMENVATTING	 113
 REFERENCES	 117

INTRODUCTION

1.1 MOTIVATION

The interaction between two molecules is usually described by an intermolecular potential (I P). Generally, such a potential depends in a complicated way on the distance r between the molecules. For practical purposes it is customary to consider the I P as composed of two parts, a long-range and a short-range part. Both parts are electrostatic in origin. The long-range part consists of potential terms which describe the interaction of two molecules at distances where overlap of electron clouds can be neglected and the interaction is only a small perturbation on the two free molecules. The short-range part, on the contrary, determines the interaction at distances where overlap effects are important. At thermal energies, both the long-range and the short-range parts of the I P determine the collision phenomena.

The long- and short-range parts of I P each consist of isotropic terms, and of anisotropic (or angle-dependent) terms which depend on the molecular orientations. The isotropic part of the I P is well known now for many atomic systems from precision scattering experiments. It is usually described by a Lennard-Jones type of potential or by some modification of it. The angle-dependent part of the I P is less known. The knowledge normally is restricted to only such long-range terms as are determined by the molecular dipole and quadrupole moments and the polarizability. These quantities may be often known to high precision from spectroscopic measurements.

In this thesis we present an investigation of the angle-dependent terms of the I P. These terms play a role in such processes as the thermal relaxation of gases, chemical reactions, the Senftleben-Beenakker effect, broadening of microwave spectral lines, supersonic flow of molecules and population inversion mechanisms in gas masers.

Unfortunately, a quantitative link between information obtainable from these collision processes and the angle-dependent I P is not well estab-

lished Even if one had a complete knowledge of the I P he would still be unable to calculate these processes*) A 'practical' scattering theory, which allows the calculation of inelastic and/or differential (large angle) cross sections, does not yet exist A partial wave expansion, for instance, leads to a large set of coupled differential equations which cannot be solved within reasonable computer time Solution of the reverse problem, the extraction of the anisotropic I P from these collision processes, is then entirely out of the question

However, presently, there is some theoretical progress towards a 'practical' scattering theory (e g JOH 66, LES 67, GOR 69, SAM 69, FRE 70, RAB 71) Optimistically, we assume that realistic I P 's will be needed in the near future Therefore, our goal is to furnish some quantitative information about the anisotropic terms of the I P We decided to measure the influence of the anisotropy of the I P on the *total* collision cross section, because it is only in this case that interpretation of results with aid of an angle-dependent I P looks straight forward

The influence of anisotropic forces upon the *total* collision cross section is rather small ($< 1\%$) and can be treated by perturbation theory The total collision cross section is mainly a measure of the largest impact parameter at which a molecule is scattered into a state quantum mechanically different from the incoming state Anisotropic potential terms normally add a small correction to the isotropic potential at large impact parameters Therefore, the anisotropy of the I P can be treated as a perturbation, in the well established distorted wave approximation (e g MES 64)

The influence of the anisotropy on the total collision cross section can be observed directly if measurements are done with two different orientations of at least one collision partner The orientation is determined by the quantum numbers of the rotational state Orientational preference can be produced in a molecular beam by using inhomogeneous electric and/or magnetic fields, which serve as state selectors for a particular rotational state. The trajectories of the molecules through the state selector and through the rest of the beam machine depend on the effective electric and/or magnetic

*) Assuming the cross sections were calculated, one then has to average over the velocity of the collision partners and the various initial states to obtain the desired result

dipole moments of the molecules which in turn depend on the rotational quantum numbers. By using properly placed slits it is possible to filter through the molecules in the selected state and to stop all unwanted molecules in other states. Once the molecular beam consists of molecules in a pure rotational state, we may vary the molecular orientation in the scattering region in order to compare the total collision cross section for two different orientations. This is accomplished by changing the direction of an external homogeneous magnetic field, which provides a unique quantization axis along which the magnetic quantum number is defined. The observed relative difference between the total collision cross sections for two orientations of the molecule is what we call the anisotropy in the total collision cross section.

This anisotropy was measured earlier by only the Bonn group (BEN 64) for TIF, later followed by measurements on CsF (BEN 69, BEN 69a and BEN 69b). A new generation of experiments has been started here in Nijmegen on H_2 (MOE 70 and MOE 71) and on NO (STO 71, STO 72); the second experiment is presented in this thesis.

We wanted to probe the angle-dependent forces with a molecule of well known properties. In case of the TIF (CsF) molecule, the important anisotropy parameter $(\alpha_{\parallel} - \alpha_{\perp})/3\alpha$ (the anisotropy in the electric polarizability) is unknown from other experiments. In this respect the NO molecule looked quite suitable because $(\alpha_{\parallel} - \alpha_{\perp})/3\alpha$ has been accurately determined in an optical depolarization experiment (BRI 66). Moreover the moderate weight and small electric dipole moment of NO help to reduce the probability of inelastic collisions. In addition, NO has a $^2\Pi$ ground state and rotates as a symmetric top because of the non-vanishing electronic angular momentum. The consequence of this behaviour looked interesting to be studied.

From an experimental point of view NO also looked suitable. It has an almost linear Stark effect and can be focused by a six-pole with large acceptance angle. This focusing can be combined with magnetic deflection because of its large magnetic dipole moment. Detection with a mass spectrometer is simplified by the low background at mass 30.

In the course of the preparation of the present experiment it became clear that state selection of a $^2\Pi$ -molecule is rather difficult. There is only a small difference in effective moments between different rotational states.

Consequently, the early goal of this work was to produce for the first time a state selected NO beam with a reasonably strong signal to noise ratio. The second step was to perform scattering experiments with the state selected beam in order to determine the magnitude of the anisotropy of the total collision cross section. The third step was to establish a simple formalism to describe the results of the measurements.

1.2 DESCRIPTION OF THESIS CONTENT

In Chapter 2 we give a general description of the present experimental method for state selection and for determination of the anisotropy in the total collision cross section. This Chapter still has an introductory character.

The details of the apparatus are given in Chapter 3.

In Chapter 4, we report the first result: the production of a state selected NO beam by a combination of focusing and deflection technique. Details are reported of the focusing spectrum (Sect. 4.1) and the profile of the focused beam (Sect. 4.2). Especially the achievement of a sharply focused image was necessary before we could start with scattering experiments. The properties of NO, which form the basis of the method used, are described in the Appendix.

In Chapter 5, we develop the theory necessary to interpretate the scattering results. The surprising result is that although the IP contains many angle-dependent terms from the outset, the anisotropy in the total collision cross section turns out to be determined in first order distorted wave approximation by only one term.

In Chapter 6, we give the formulae for the necessary correction factors which transform the experimental results into physically meaningful quantities. Those formulae look unattractive, but they change the measured anisotropy less than 25%. As follows from the theoretical discussion of small angle scattering in Sect. 5.6, a correction for finite angular resolution, similar to the one applied to the measured total collision cross section, has to be applied to the anisotropy effect on the total collision cross section (Sect. 6.5).

In Chapter 7, the results of the scattering measurements are collected

For the non-state selected NO beams, the influence of finite angular resolution (Sect 7.1) and the velocity dependence of the total collision cross section (Sect 7.2) are investigated. In the energy region of the present measurements, the absence of glory structure and the approximately $v^{-2/5}$ velocity dependence is proved for the investigated systems, at least as long as no state selection is introduced. In Section 7.3 the measured anisotropies are given, together with the description of the data evaluation.

In Chapter 8, we discuss the results obtained, and comment on the future possibilities of the present scattering machine.

EXPERIMENTAL METHOD

2.1 CONFIGURATION OF THE APPARATUS

A schematic view of the molecular beam apparatus (as seen from above) is shown in Fig. 2.1. The NO molecules emerging from the source (s) pass through a magnetic Rabi field (m) and an electrostatic six-pole field (p6). The purpose of these two fields is to select NO molecules in a particular state and to focus these onto the detector slit (s_5). The envelope of the state selected beam is shown in the Figure.

After the state selecting fields, the molecules enter the scattering region (sv). Here a shower of secondary beam molecules crosses the NO beam. In the scattering region the NO molecules can be oriented in an arbitrary direction by the field of two pairs of Helmholtz coils. The difference in attenuation of the NO beam, for two mutually orthogonal orientations of the NO molecules, contains the information about the anisotropy effect in the total collision cross section (Sect. 2.3). Finally, the rotating disc velocity selector (rd) is necessary to ensure that a practically mono-energetic state-selected NO beam is sharply focused by the six-pole (p6) onto the detector slit (s_5) before entering the detector (d).

2.2. GENERAL FEATURES OF STATE SELECTION

The approximately linear Stark effect of the NO molecule is given by

$$W_{\text{Stark}} = -\mu_{\text{eff}} \mathcal{E}, \text{ with } \mu_{\text{eff}} \equiv \frac{\Omega}{J(J+1)} \mu_{\text{NO}} \text{ and } \mu_{\text{NO}} = 0.16 \text{ D} \quad (2.1)$$

Here, $\mathcal{E}$ is the external electric field, μ is the electric dipole moment, and μ_{eff} is the effective dipole moment in the $|\Omega, J, m_J\rangle$ state. The quantum numbers

Fig.2.1. Schematic diagram of the molecular beam machine as seen from above with the envelope of the selected beam. source (s) (source slit $0.05 \times 1 \text{ mm}^2$), skimmer (sk), vibrating beam flag (f), Rabi magnet (m), variable slit (s_1), variable slit (s_2), six-pole (p6), scattering volume of secondary beam (sv), rotating disc velocity selector (rd), variable slits (s_3) and (s_4), movable ($1 \times 3 \text{ mm}^2$) detector slit (s_5), and universal detector (d). The horizontal dimensions perpendicular to the beam axis are exaggerated. The capital letters indicate the different vacuum sections described in Table 3.1. The distance of the various components from the source slit is indicated on the horizontal axis.

J, m_J and Ω refer to the total angular momentum J of the molecule and the component of J along a space-fixed and along the molecular axis, respectively.

A six-pole field can be used for focussing molecules with positive and linear Stark effect (KRA 65) like NO. Perpendicularly to its axis the six-pole exerts a harmonic force on an NO molecule that starts an oscillatory motion with frequency ω . In this way a sharp image of the source slit can be obtained for a monochromatic beam (velocity v_1) of NO molecules in a defined state with a unique value of μ_{eff} . The distance (L_2) between the image for a certain state and the exit end of the six-pole, is given by

$$L_2 = \frac{L_0 + \frac{1}{K} \tan(K L_1)}{K L_0 \tan(K L_1)}, \quad (2.2)$$

with $K = \omega/v_1 = (3V\mu_{eff}/ma^3v_1^2)^{\frac{1}{2}}$. V is the voltage between neighbouring rods, a is the inside radius of the six-pole (Fig. 3.1) and m is the mass of the NO molecule. The meaning of L_0 and L_1 can be seen in Fig. 2.1. In the experiment, V is set to such a value that the state with the strongest positive Stark effect is focussed onto the detector slit ($L_2 = L_D = 1355$ mm). According to Eq. (2.1), this state – the selected state – has $J = |m_J| = |\Omega| = 3/2$, $\Omega m_J < 0$.

What happens to the other rotational states with positive Stark effect, can be seen from Fig. 2.2 in which L_2 is shown as a function of K , according to Eq. (2.2). The state with the second-highest μ_{eff} already has $L_2 \approx \infty$. For all states with $\mu_{eff} < 0$, other than the selected state, an increased beam intensity is measured behind the detector slit. The reason is that a positive Stark effect causes a convergence of the beam towards the axis of the six-pole.

On the other hand, for states with $\mu_{eff} > 0$ a decrease in beam intensity occurs. The total effect of the six-pole is an increase of beam intensity for $\mu_{eff} > 0$; the decrease can never exceed 100%, for $\mu_{eff} < 0$ the beam intensity can be increased by a large factor, a factor of about 250 is achieved by us for the selected state.

Normally, those molecules *not* in the selected state are suppressed by use of a beam stop and diaphragms (BEN 64). This method is not practical in the case of NO. As shown in Fig. 2.2, the differences of L_2 -values for the different states of NO (linear Stark effect) are much smaller than in the case of diatomic molecules (quadratic Stark effect).

Fig 2.2. Distance L_2 of focal point from the six-pole exit as a function of $K = [3V \mu_{\text{eff}} / m a^3 v_1^2]^{1/2}$. Negative L_2 corresponds to a virtual image. The distance between detector slit and six-pole exit ≈ 1 m. Therefore, the $2\Pi_{3/2, j=m_j=3/2}$ state is focused onto the detector slit for $K = 2.54 \text{ m}^{-1}$ (corresponding to $V \approx 30 \text{ kV}$ at a molecular velocity $v_1 \approx 540 \text{ m/s}$). The K -values for the molecular states with smaller effective values of the electric dipole moment μ_{eff} , under the same experimental conditions, are also indicated. For comparison, the K -values of a 1Σ -molecule in a four-pole field are also shown for conditions that would focus the $j=1, m_j=0$ state onto the detector slit. This comparison indicates how much more difficult it is to separate out a single NO state.

Our method of state selection is based on the fact that, in the detector plane, the distribution of molecules other than in the selected state is rather uniform over a broad region. The width of the spot formed by the focussed beam molecules in the selected state is about 1.4 mm in the detector plane. Under this condition, the next state ($j = |m_j| = |\Omega| = 5/2$, $m_j \cdot \Omega < 0$) has there already a beam width of about 14 mm. The distribution of molecules in other states is still broader. Consequently, a deflection of molecules over about 2 mm in the detector plane prevents focussed molecules in the selected state from passing through a 1 mm wide detector slit. The beam signal of the molecules in the other states remains practically constant.

Deflection can be achieved by a) a small displacement of the source slit, b) use of an inhomogeneous electric field, or c) use of an inhomogeneous magnetic field. We have chosen c) because molecules in the selected state have the largest magnetic moment ($1.17 \mu_B$), in comparison to the other states ($0.79 \mu_B$, for $j = |m_j| = |\Omega| = 5/2$, for example). The special advantage of this method is that the majority of molecules, which are in the $^2\Pi_{1/2}$ -state, have only a very small magnetic moment. Thus, we can produce a beam signal which is modulated by switching the deflection magnet on-off. The modulation amplitude is proportional to the number of NO-molecules in the selected state.

2.3. ORIENTATION OF MOLECULES AND THEIR ATTENUATION IN THE SCATTERING REGION

For the measurement of the total collision cross section a secondary beam is produced by a multiple array effuser. The effuser has such a length that, with a small pressure at the entrance of the effuser, a 50% attenuation of the primary beam can be achieved. The secondary beam which is produced shows little self-scattering near the exit of the effuser and has a well defined direction in the scattering region. By means of an electromagnetic valve the secondary beam can be switched off and on.

The effuser is placed after the six-pole (Fig. 2.1). The secondary beam molecules pass vertically through the primary beam and are pumped off by a cryo-trap which is placed beneath to prevent pressure bursts from frozen particles falling onto warm surfaces.

Fig 2.3 Scattering for two orientations of the magnetic field in the scattering region, a) $\mathbf{B} \parallel \mathbf{v}_{\text{rel}}$, b) $\mathbf{B} \perp \mathbf{v}_{\text{rel}}$ in the c.m. system

Both the primary and the secondary beam have rather well defined directions so that the direction of the relative velocity is approximately fixed in the laboratory system. The primary beam is velocity selected, the secondary beam has nearly a Maxwellian distribution, with a mean velocity comparable to or smaller than the selected velocity of the primary beam. The Maxwellian distribution causes a small variation of direction of the relative velocity with respect to the most probable direction.

At the end of the six-pole the selected molecules do not have a unique direction of their quantization axis. By means of small magnetic guiding fields the molecules adiabatically acquire a unique direction of quantization and enter the scattering chamber conserving their orientation.

In the scattering region, the quantization axis of the selected beam molecules of the primary beam is made parallel or perpendicular to the most probable direction of the relative velocity by appropriate settings of the current through two perpendicular sets of Helmholtz coils (Fig. 2.3).

If the sharp image of the focussed molecules is deflected off the detector slit, the secondary beam can nevertheless cause some selected mole-

cules to pass through the detector slit. The error from these collisions is small and analogous to the error from the finite angular resolution of the scattering apparatus. These effects work in opposite directions.

In Table 2.1 the different situations are indicated, in which the intensity of the primary beam is measured.

TABLE 2.1
Primary beam intensity in the eight different measuring situations

Intensity	Secondary beam	Six-pole field	Rabi field	Helmholtz field
I_1 (I_5)	off (on)	on	off	$\parallel$
I_2 (I_6)	off (on)	on	on	$\parallel$
I_3 (I_7)	off (on)	on	off	$\perp$
I_4 (I_8)	off (on)	on	on	$\perp$

From the measured intensities, we form (Eq. (7.3))

$$\frac{\sigma_{\parallel}^e - \sigma_{\perp}^e}{\sigma_{\parallel}^e} = \frac{\ln \frac{I_7 - I_8}{I_5 - I_6} \ln \frac{I_3 - I_4}{I_1 - I_2}}{\ln \frac{I_1 - I_2}{I_5 - I_6}} \quad (2.3)$$

where $\sigma_{\parallel}^e$ ($\sigma_{\perp}^e$) is the effective total collision cross section for NO molecules with $j = |m_j| = |\Omega| = 3/2$ colliding with the molecules of the secondary beam, m_j is measured along a direction parallel (perpendicular) to the relative velocity.

TECHNICAL DETAILS OF THE APPARATUS

3.1. MULTI-CHAMBER ARRANGEMENT

The molecular beam machine has total length of about 3 m. It consists of seven separately pumped chambers (Table 3.1 and Fig.2.1). All diffusion pumps are equipped with water cooled baffles. The advantage of the multi-chamber arrangement lies in the fact that all parts are replaceable, interchangeable and removable.

3.2. SOURCE

The primary beam effuses via a source slit from a rectangular copper tube attached to the bottom of a dewar. Its temperature can be regulated between 80 °K and 300 °K, and is normally around 180 °K. The source slit is .05 mm wide and 1 mm high. The normal operating source pressure is about 5 torr.

Earlier attempts to work with a very small nozzle opening (.05 mm diam.) and high source pressure (1 atm.) were unsuccessful. Molecules in the selected state disappeared from the primary beam, probably due to freezing effects during supersonic expansion.

A slit skimmer (0.3 mm wide) is mounted 14 mm downstream from the source slit in order to minimize beam scattering by background molecules. Because of the use of a six-pole with its acceptance angle of about 10^{-2} rad, no other collimating slit could be used. As beam chopper a vibrating flag at 30 Hz is used, which intersects the beam directly behind the skimmer.

3.3. RABI-MAGNET

The Rabi deflection magnet is mounted in the chamber next to the source

TABLE 3.1

Characteristics of the vacuum chambers.

The abbreviations of the first column refer to Fig. 2.1.

Name of chamber		Pumps	Operating pressures	Remarks
S	source chamber	3000 l/s oil diffusion	1×10^{-4} torr	$0.05 \times 1 \text{ mm}^2$ source slit
P ₂	Rabi-magnet chamber	400 l/s oil diffusion	2×10^{-6} torr	inhomogeneous deflection magnet (10 mm long) vibrating beam-chopper
P ₆	six-pole chamber	350 l/s oil diffusion	2×10^{-7} torr	400 mm long electrostatic focuser
Sb	scattering chamber	350 l/s oil diffusion and cryopump	8×10^{-7} torr	secondary beam effuser
V	velocity-selector chamber	350 l/s oil diffusion	2×10^{-7} torr	slotted disc-selector
B	buffer chamber	50 l/s ion getter	3×10^{-8} torr	bakeable
D	detector chamber	200 l/s ion getter	1×10^{-9} torr	ionizer, magnetic mass-spectrometer, bakeable

chamber. Its length is 100 mm, the radius of the convex (concave) pole face is 7 mm (8 mm). The maximum average field on the beam axis is 10 kG; the normal operating field strength is about 6 kG. The focused beam has a width of 5 mm at the end of the deflection magnet. Therefore, the deflection of the focused beam is uniform only within $\pm 35\%$. With the Rabi magnet on, the focused molecules show a displacement of 1.8 mm in the plane of the detector slit during the scattering measurements.

The six-pole is constructed of six polished stainless steel rods (length 400 mm) with a diameter of 7 mm. Their nearest distance from the beam axis is 7 mm. The distance between neighbouring rods is 3.5 mm. The spacing of the rods is effected by two perspex pieces with recessed contact points (Fig 3.1) and long leakage paths (HAW 68). A maximum voltage of 60 kV can be applied.

Fig 3.1 Perspex spacers which support the rods of the six-pole. All dimensions are in mm. Cross section AA shows the recessed areas where the rods enter the spacers. The six-pole can sustain a maximum voltage of 60 kV. The inside diameter is $2a = 14$ mm.

The perspex pieces are mounted on a flat flange ($400 \times 60 \text{ mm}^2$) in such a way that the six-pole can be adjusted horizontally by micrometer screws from outside the vacuum. The vertical position is less critical because we work with an image of the 1 mm high source slit onto a 3 mm high detector slit. (The magnification of the six-pole is about 1.8.)

With the geometry of the apparatus (Fig 2.1) one finds an acceptance angle for the focused beam of 4×10^{-4} sterad, which should be compared to

the acceptance of the detector slit for an unfocused beam of 0.6×10^{-6} sterad. (In practice only a gain in intensity of about 250 is observed due to image broadening.)

A larger angle of acceptance for the focused beam is possible by increasing the internal radius of the six-pole and/or by decreasing the distance between source and six-pole. Such changes, however, cause a broadening of the image spot by an increase of magnification and by aberration. Broad images must be avoided in scattering experiments, where a reasonable angular resolution is required.

Details about the focusing properties and associated aberrations of the six-pole are described in (STO 70). In Section 3.7 we discuss another source of aberration, introduced by the velocity selector.

3.5. THE SECONDARY BEAM

Between six-pole and velocity selector the secondary beam is formed by a fused glass capillary array (Fig. 3.2). The manufacturer's specifications (Mosaic Inc.) give 5μ for the diameter of the capillaries and a 50% transparency. The length of the capillaries is 1 mm. The surface of the array has the dimensions of 38 mm in the direction of the primary beam and 10 mm perpendicular to it. The distance from the axis of the focussed beam is 13 mm, the angle of incidence is 90° (Fig. 3.2).

The advantage of the use of a directed secondary beam is twofold: first, the primary beam can be broad in the interaction region (finite angular acceptance of the six-pole); second, the velocity of the secondary beam molecules shows little spread in direction ($\approx \pm 20^\circ$). This facilitates the interpretation of the measurements.

The very brittle capillary array is clamped to the effuser holder with a thin teflon seal. We could lower the effuser temperature to 90°K without any damage. The effuser is connected to a reservoir filled with liquid nitrogen by means of a copper ribbon. The actual working temperature is regulated by a heating filament mounted inside the copper effuser holder. The temperature was measured by a Pt resistor mounted in the effuser holder. It was chosen such that the vapour pressure of the investigated condensable secondary beam molecules at this temperature was about 1 torr.; in all cases

the capillaries are driven by a pressure of about 0.1 torr. The mean free path of the molecules is then about 0.3 mm, if a total collision cross of 10^{-14} cm² is assumed. At this pressure the intensity of the primary beam is attenuated to roughly one half of its original value.

The effusing molecules are pumped by a cryopump. This pump is mounted to the bottom of a Leybold 500 l/sec Klippeling-Verdampferkryostat (VMK 500). The cryostat can be cooled with liquid nitrogen as well as with liquid helium. For the easily condensed compounds like N₂O, CO₂, CCl₄ etc., liquid nitrogen cooling is sufficient. About 2 liters of liquid He were necessary for cooling down to 20 °K. The cryopump was kept at this temperature with a consumption of 0.5 liter liquid He/hour. Except for the gold plating of the cryopump no special precautions against influx of radiation heat were taken. No effect of background scattering could be observed (STO 70a). When the secondary beam was switched on, a pressure rise of only about 2×10^{-7} torr. was measured in the secondary beam chamber. This means that the cryopump achieved a pumping speed of 10⁵ l/s (the flux of the secondary beam was about 10¹⁸ mol/s = 3×10^{-2} torr l/s). When the cryopump was working at liquid nitrogen temperature such good pumping results were only possible if the secondary beam gas had previously been distilled under vacuum.

To have a well defined scattering region, the primary beam entered and left the secondary beam intersection (50 mm long) through two tubes (ø 12 mm, 15 mm long). These tubes were at the same temperature as the cryopump so that no scattering could occur inside them. Although the pressure rise in the neighbouring chambers was small (about 10⁻⁸ torr.) with the secondary beam switched on, it turned out to be unfavourable to connect the UHV section (buffer and detector chamber) directly to the scattering chamber. Especially with N₂O and Ar, the gasload to the UHV caused a considerable rise in background current, which reduced signal to noise ratio and introduced drift effects. During the measurements of Section 7.3, the scattering chamber was still placed between the UHV and the velocity selector in contrast to the situation shown in Fig. 2.1. In the final geometry the gasload effect was much less disturbing.

In the total collision cross section experiments use was made of the variable slit s_2 as a collimating device. Such a slit consists of a circular hole in which two slit-plates can be moved independently in or out the beam by a

micrometer from outside. By means of this arrangement a slit of arbitrary width and position can be formed. The variable slits (s_3) and (s_4) were used to minimize the gasload from the scattering chamber into the detector chamber.

Fig.3.2. The configuration of the scattering region.

3.6. THE HELMHOLTZ COILS

In order to decouple the nuclear spin of the NO molecules in the selected

state from the molecular frame, a magnetic-field strength of 150 G is necessary (Sect. 6.1). Two pairs of coils in near Helmholtz configuration are used to produce a field of this strength with desired orientation in the collision plane. The coils are placed at the outside of the scattering chamber (Fig. 3.2). They can produce a field up to 200 G with reasonable homogeneity. A good filling factor (73%) of the coils has been achieved with copper wire of rectangular cross section (Duroflex, $1 \times 2.6 \text{ mm}^2$, copper cross section 2.46 mm^2). The coils are provided with water cooling for use at currents up to 10 A. The inhomogeneity of the B-field was investigated experimentally. The scattering region is positioned in a symmetry plane of the coils. The variation of the field strength along the primary beam axis causes the only important inhomogeneity. Experimental results are presented in Fig. 3.3. These results were compared with theoretical calculations (STO 70a). No discrepancies, except a small shift of the symmetry center of the experimental B-field for coil-pair I, was found. Apparently there is a small influence of the iron parts (pumps, machine support etc.) in the neighbourhood of the scattering region.

Fig.3.3. The inhomogeneity of the magnetic field produced by the Helmholtz coils. The quantity B_0 stands for the magnetic field strength in the scattering center. The abscissa x gives the distance along the beam axis between the scattering center and the point where B is measured.

3.7. THE VELOCITY SELECTOR

The design parameters of the slotted disc velocity selector are given in Table 3 2 The slits are arranged in such a way that the selector has two different resolutions, $\frac{\Delta v}{v}$, for clockwise and counter-clockwise rotation The $\frac{\Delta v}{v}$ differ by a factor of 3. This feature makes it possible to precisely align the selector axis and to work with the lower resolution if intensity considerations require this However, the higher resolution is needed in order to avoid overlap

TABLE 3 2

Design parameters of the velocity selector

The angle between the selector axis and the open channels with discs at rest is indicated by ψ , γ represents the ratio of the slit width of the i^{th} disc divided by the length of arc subtended by ψ The displacement of a slit center of the i^{th} disc with respect to the first disc, p_i , is measured at a radial distance of 85.84 mm from the selector axis The molecular velocity v_i is given in m/s at a rotational frequency of the selector of ν , measured in Hz, $\pm$ indicates one of the two possible directions of rotation for the discs

total length	121 mm
number of discs	7
radius of a disc (r)	100 mm
thickness of a disc (d)	1 mm
length of radial slit (s)	14 mm
number of slits	127
distance between discs i and j	59 (1,2), 20 (2,3), 5 (3,4), 8 (4,5), 11 (5,6), 11 (6,7) mm
slit width of disc i (w_i)	3 mm, $i = 3$ and 4 2 mm, $i = 1, 2, 5, 6$ and 7
tooth width of disc i	1 mm, $i = 3$ and 4 2 mm, $i = 1, 2, 5, 6$ and 7
p_i	0 mm ($i=1$), 3 mm ($i=2$), 0.7 mm ($i=3$), 1.1 mm ($i=4$), 0 mm ($i=5$), 3 mm ($i=6$), 2 mm ($i=7$)
ψ	$\psi_+ = \frac{1}{12}$ rad and $\psi_- = -\frac{3}{12}$ rad
transparency (T)	$T_+ = 45\%$ and $T_- = 40\%$
$\frac{\Delta v}{v}$, f.w.h.m	$(\frac{\Delta v}{v})_+ = 21\%$ and $(\frac{\Delta v}{v})_- = 6.7\%$
$\gamma = \frac{w_i}{(r-s)\psi}$	$\gamma_+ = 1/5$ and $\gamma_- = 1/15$
molecular velocity (v_i)	$v_+ = 6.472 \nu \frac{\text{m}}{\text{s}}$ and $v_- = 2.157 \nu \frac{\text{m}}{\text{s}}$

between the different states focussed by the six-pole.

In comparison to the similar selector of Grosser (GRO 67) the transparency of this selector has been increased considerably by the use of two discs with 50% wider slits (see Table 3.2). The total number of slits is the same for all seven discs. The discs have rectangular slits.

The finite resolution $\frac{\Delta v}{v}$ of the selector influences the width of the image formed by the molecules in the selected state. With our geometry, and with an ideally thin source slit, 70% of the focussed molecules are found within an image spot of 1 mm width if $\frac{\Delta v}{v} = 6.7\%$ is assumed.

Slightly different velocities are transmitted through the velocity selector under different angles. Because of the finite angular acceptance of the six-pole (lin. angle 1.2×10^{-2} rad.) this results in a shift (0.46 mm) and an extra broadening of the image spot in the detector plane. The molecules transmitted through the velocity selector have a higher velocity at one side of the acceptance cone than on the other side, and the velocity-dependent trajectories in the six-pole become asymmetrical. Large values of ψ , the angle between the selector axis and the open channels with the discs at rest, are favourable for keeping this effect small.

3.8. THE DETECTOR

To detect the NO beam a universal detector was developed. It consists of a Fricke type ionizer (FRI 55) and a magnetic mass spectrometer. The detector is mounted in a separate UHV chamber pumped by a 200 l/s ion getter pump (1×10^{-9} torr. under operating conditions). A schematic diagram of the detector is given in Fig. 3.4.

The ionizer consists of an equipotential box (volume $14 \times 10 \times 20$ mm³) where two ribbon shaped electron beams intersect the ribbon shaped molecular beam over a length of 10 mm. The electrons are emitted by two spiral filaments (CEC diatron, type 14888) which burn continuously. This prevents thermal shock and keeps the detector under optimum conditions. The lifetime of the filaments is almost unlimited (operation during half a year with a current of 3.0 A/filament). The electron acceleration slits (width 0.5 mm) and repeller electrodes were chosen to give, as close as possible, Pierce geometry (PIE 49, STO 67a). To have a minimum of background ions a narrow

Fig 3 4 Schematic diagram of the detector

electron beam (1.5 mm f.w.h.m.) is produced, as could be concluded by measuring the ionization efficiency of a sharply collimated beam as a function of horizontal displacement.

The ionizer entrance consists of a grid instead of the usual slit in order to enhance the pumping efficiency of the ionization volume. Ions are extracted in the direction of the primary neutral beam. The ionizer is able to detect a molecular beam with a height of up to 8 mm.

The potential of the six electrodes forming the ionization box can be independently adjusted for optimum performance. Two of them, the side plates, are also made of grids. The ions leave the ionization box through a 1 mm wide slit and form an approximately parallel beam. An immersion and an Einzel lens are used to achieve this condition in a horizontal plane.

For mass selection we made use of a rather unconventional half-90° magnetic sector field (BAK 60). Compared to a standard sector field the length of the ion path between the pole faces is reduced by a factor of 2 and the gap is kept very small (4 mm). This permits use of a sector field with a 10 cm ion trajectory radius, equipped with a simple and light magnetic yoke which is mounted outside the vacuum. A disadvantage of our sector field is a first order aberration related to non-parallelity of the incoming ion beam in the vertical plane (STO 68). This aberration limits the mass resolution. With auxiliary electrodes in front of the sector field a resolution of $M/\Delta M=20$ (half width at 10%) had been achieved.

The position of the mass spectrometer (m.s.) slit (2 mm width) is adjustable. Selected ions pass through this slit and are focussed and accelerated by an immersion lens onto the first dynode of a BeCu particle multiplier.

Characteristic parameters of the detection system can be found in Table 3.3. A full NO beam (without velocity selection) of 5×10^{11} mol/s is estimated to pass through the detector slit at 1 torr. source pressure, 3×0.05 mm² source slit, 300 °K source temperature, and 1×8 mm² detector slit. This figure has to be compared to 5×10^6 mol/s, the minimum detectable beam at the time constant of 1 s. The actual noise limitation during a scattering experiment comes from statistical fluctuations and instabilities in the molecular beam itself. The chopped beam signal (30 Hz) is fed into an electrometer, followed by a lock-in amplifier. Its dc-output is digitalized by a voltage-to-frequency converter and counted.

TABLE 3.3
Detector characteristics

ionization efficiency	1 500
filament current through 2 filaments (CEC-dia-tron, type 14888)	5.9 A
total emission	6 mA
dimension of ionisation volume	$1.5 \times 8 \times 10 \text{ mm}^3$
background pressure	10^{-9} torr
electron acceleration potential	150 V
sensitivity to background pressure (ion-current measured in front of m s magnet)	0.1 A/torr
type of mass spectrometer	half 90° magnetic sector field, parallel ion beam at entrance
radius of ion trajectory	100 mm
magnet gap	4 mm
B-field (mass 30)	1.4 kG
ion energy (mass 30)	550 eV
m.s. slit width	2 mm
$M/\Delta M$ (half width at 10%)	20
transmission through m s magnet	15%
minimum detectable NO beam (1 sec. measuring time)	$5 \cdot 10^6$ molecules/s
particle multiplier	BeCu, 17 dynodes, ETH Zurich normal operation 1300 V amplification 10^4

RESULTS ON STATE SELECTION OF NO

4.1. THE FOCUSING SPECTRUM

In Fig. 4.1, the measured beam intensity is shown as a function of the six-pole voltage for two different situations: the upper (lower) curve corresponds to Rabi field off (on). The difference between the two signals is also shown. The two peaks in the difference signal are found at the correct voltage, if we attribute them to the $^2\Pi_{3/2}, j=m_j=3/2$ state and the $^2\Pi_{3/2}, j=m_j=5/2$ state, respectively. The curves are measured with a molecular velocity of $v = 536$ m/s. (At lower NO velocities we were able to see four higher states clearly separated, at the cost of signal-to-noise ratio.) The maximum peak height of the $j=m_j=3/2$ state (the selected state) is 28% of the total zero-field beam. The peak width (f.w.h.m.) is $\Delta V/V = 20\%$.

The results of Fig. 4.1 and 4.2 were obtained with the following machine geometry: source slit 0.5×3 mm², detector slit 1×8 mm² and $L_D = 1065$ mm. In the final geometry of Fig. 2.1 the maximum signal of the selected state amounts to 79% of the total zero-field beam. The resolution of the spectrum stays the same.

A gratifying fact is that although the ratio of the effective electric dipole moments of the states attributed to the two peaks in Fig. 4.1 equals only 1/4, the difference signal drops almost to zero between the maxima.

In Fig. 4.1 the $^2\Pi_{3/2}, j=m_j=5/2$ peak is about 0.5 times the peak of the selected state. Theoretically, one expects a peak height of about 95% (see Table A2). Using small ceramic permanent magnets along the beam path we were able to provide a guiding field to prevent disorientation of molecules between Rabi magnet and six-pole. As a consequence, we observed no change in peak height of the selected state, whereas the $^2\Pi_{3/2}, j=m_j=5/2$ state now showed a peak height of about 90%. This was the first indication that the molecules in the selected state do not undergo transitions (flops).

Fig 4.1 The focusing spectrum. Above, the total beam signal is shown, with Rabi field on and off, as a function of six pole voltage. Below, the difference signal which falls close to zero between the focused states. The molecules have a velocity of about 540 m/s.

along the beam path. Moreover, when the beam signal at the voltage of the $^2\Pi_{3/2}, J=m_J=3/2$ peak was measured as a function of the Rabi field strength, no indication was found that the state selected beam consists of states other than those with $J=m_J=3/2$ (STO 70).

In order to be more certain about flops, a second Rabi field was installed at the position of the secondary beam. It served to cancel the deflection by the first Rabi field when the six-pole was set at the focusing voltage for the selected state. The crucial point is that molecules originally in the selected state, which change their state (and thus their magnetic moment) while passing through the machine, can not be re-deflected onto the detector slit by the second Rabi magnet. We recovered about 80% of the molecules in the selected state. If one considers the extra image broadening which is introduced by the variation of the magnetic field gradient in the second Rabi magnet this result appears quite satisfactory.

In view of angular resolution it is important, for total cross section measurements, that the image spot of the selected state is small and well defined. In our apparatus, a measurement of the spot shape is difficult because we are unable to move the whole detector (detector slit together with ionizer and mass-spectrometer magnet) across the beam. However, the ionizer detects molecules over a width of about 6 mm perpendicular to the plane of the molecular beam. This is possible, because of the grid at the entrance of the ionizer. At ± 3 mm the detection efficiency was about 20% of its value at the center during these measurements. This was measured with an uncollimated and unfocused beam and a 1 mm detector slit which was moved across the beam.

Given the detection efficiency, the beam signal of the focused beam as a

Fig 4.2 The spot size of the focused beam as a function of the position of the 1 mm wide detector slit. The results have been corrected for the variation of detector efficiency with different detector slit positions (see text). The broad background signal is due to the increase in the number of molecules, from states other than the selected state, effected by the six-pole field. Note that the shift of the sharply focused spot by the Rabi field ($D \approx 1$ mm) is only to one side.

function of detector slit position yields the spot size of the image formed by the molecules in the selected state (Fig. 4.2). The f.w.h.m. was found to be 1.4 mm. In Fig. 4.2 the spot size for a magnetically deflected beam is also shown; its f.w.h.m. is 1.65 mm. Here the extra broadening due to the inhomogeneous magnetic deflection is evident.

We also have calculated the focused beam intensity and spot width. The observations and calculations are in satisfying agreement (STO 70).

A remarkable feature of Fig. 4.2 is that all molecules which are sharply focused by the six-pole are deflected to *one* side in the detector plane by about the same distance. As we already remarked in Section 4.1, no indication was found that there is more than one Zeeman state when the beam signal was measured as a function of the Rabi field strength. A careful analysis of the deflection results makes it clear that all the selected molecules are transferred into the state with the strongest positive Zeeman effect: $j = |\Omega| = 3/2$, $m_j = 3/2$.

At first thought one would expect that the molecules in the selected state ($j = |\Omega| = |m_j| = 3/2$, $\Omega \cdot m_j < 0$) would show a positive or negative Zeeman effect depending on the sign of m_j . When hyperfine structure is taken into account, however, the situation is much more complicated (Sect. 6.1). A qualitative explanation of the experimental observations is given in A3.

The experimental finding has an important implication for our scattering experiment: all molecules in the selected state are modulated by switching the Rabi magnet on-off. Hereby, the maximum possible signal is obtained for the molecules in the selected state.

THEORY

5.1. THE INTERMOLECULAR POTENTIAL

Before the problem of two colliding molecules can be approached from the theoretical side, the intermolecular potential must be known. We first investigate, therefore, which types of potential terms play a role in the scattering process. For each molecule at least axial symmetry is assumed.

The interaction between two molecules is usually divided into a long range and a short range part. The long range interaction has recently been discussed by Buckingham (BUC 67) and Margenau and Kestner (MAR 69, Chap. 2). The relevant potential terms come from three different origins: electrostatic multipole-, induction- and dispersion-forces. The contribution of the dispersion forces normally overshadows the other two contributions. The expressions for the potential terms given in the literature are not in a form which is convenient for direct use in the Schrödinger Equation of the scattering problem. They are expressed in angles which are taken with respect to the axis which connects the centers of the two molecules. We transform all these expressions into elegant products of spherical harmonics, $C_m^l(\vartheta, \phi)$, referred to an arbitrary coordinate system. Both expressions are given for each potential term in the following collection of formulae.

The long-range intermolecular potential is written as a sum $V_{\text{long range}} = V_{\text{elec}} + V_{\text{ind}} + V_{\text{disp}}$. The electrostatic part V_{elec} has the form:

$$V_{\text{elec}} = V_{D_1 D_2} + V_{D_1 Q_2} + V_{D_2 Q_1} + V_{Q_1 Q_2} + V_{D_1 O_2} + V_{D_2 O_1} + \dots, \quad (5.1)$$

where:

$$\begin{aligned} V_{D_1 D_2} &= \frac{\mu_1 \mu_2}{r^3} [-2 \cos \vartheta_1 \cos \vartheta_2 + \sin \vartheta_1 \sin \vartheta_2 \cos(\varphi_1 - \varphi_2)] \\ &= -\frac{\mu_1 \mu_2}{r^3} \sum_{\beta, \gamma, \delta} C_{\beta}^1(\hat{r}_1) C_{\gamma}^1(\hat{r}_2) C_{\delta}^2(\hat{r}) \begin{pmatrix} 1 & 1 & 2 \\ \beta & \gamma & \delta \end{pmatrix}, \end{aligned} \quad (5.2)$$

$$V_{D_1 Q_j} = \frac{3/2 \mu_1 Q_j}{r^4} (-)^j \left[\cos \vartheta_1 (3 \cos^2 \vartheta_j - 1) - 2 \sin \vartheta_1 \sin \vartheta_j \cos \vartheta_j \cos(\varphi_1 - \varphi_2) \right] \\ = \frac{3/2 \mu_1 Q_j}{r^4} (-)^j 2 \sqrt{\frac{35}{3}} \sum_{\beta, \gamma, \delta} C_{\beta}^1(\hat{r}_1) C_{\gamma}^2(\hat{r}_j) C_{\delta}^3(\hat{r}) \begin{pmatrix} 1 & 2 & 3 \\ \beta & \gamma & \delta \end{pmatrix} \quad (5.3)$$

for $i=1, j=2$ and $i=2, j=1$,

$$V_{Q_1 Q_2} = \frac{3/4 Q_1 Q_2}{r^5} \left[1 - 5 \cos^2 \vartheta_1 - 5 \cos^2 \vartheta_2 + 17 \cos^2 \vartheta_1 \cos^2 \vartheta_2 + \right. \\ \left. + 2 \sin^2 \vartheta_1 \sin^2 \vartheta_2 \cos^2(\varphi_1 - \varphi_2) - 16 \sin \vartheta_1 \cos \vartheta_1 \sin \vartheta_2 \cos \vartheta_2 \cos(\varphi_1 - \varphi_2) \right] \\ = \frac{3/4 Q_1 Q_2}{r^5} 4 \sqrt{70} \sum_{\beta, \gamma, \delta} C_{\beta}^2(\hat{r}_1) C_{\gamma}^2(\hat{r}_2) C_{\delta}^4(\hat{r}) \begin{pmatrix} 2 & 2 & 4 \\ \beta & \gamma & \delta \end{pmatrix} ; \quad (5.4) \\ V_{D_1 O_j} = \frac{1/2 \mu_1 O_j}{r^5} \left[\cos \vartheta_1 \cos \vartheta_j (12 - 20 \cos^2 \vartheta_j) + \right. \\ \left. + \sin \vartheta_1 \sin \vartheta_j (15 \cos^2 \vartheta_j - 3) \cos(\varphi_1 - \varphi_2) \right] \\ = \frac{-1/2 \mu_1 O_j}{r^5} 12 \sqrt{7} \sum_{\beta, \gamma, \delta} C_{\beta}^1(\hat{r}_1) C_{\gamma}^3(\hat{r}_j) C_{\delta}^4(\hat{r}) \begin{pmatrix} 1 & 3 & 4 \\ \beta & \gamma & \delta \end{pmatrix} \quad (5.5)$$

for $i=1, j=2$ and $i=2, j=1$.

The contribution of the induction potential V_{ind} to $V_{long range}$ consists of two terms:

$$V_{ind} = V_{1-2} + V_{2-1}, \quad (5.6)$$

with

$$V_{1-j} = \frac{1/2 \mu_1^2 \alpha_j}{r^6} (3 \cos^2 \vartheta_1 + 1) + \frac{6 \mu_1 Q_1 \alpha_j}{r^7} (-)^j \cos^3 \vartheta + \dots \\ = \frac{1/2 \mu_1^2 \alpha_j}{r^6} 2 \left[1 + \sum_{\beta} C_{\beta}^2(\hat{r}_1) C_{\beta}^{2*}(\hat{r}) \right] + \frac{6 \mu_1 Q_1 \alpha_j}{r^7} (-)^j \left[2/5 \sum_{\beta} C_{\beta}^3(\hat{r}_1) \right. \\ \left. C_{\beta}^{3*}(\hat{r}) + 3/5 \sum_{\beta} C_{\beta}^1(\hat{r}_1) C_{\beta}^{1*}(\hat{r}) \right] + \dots \quad (5.7)$$

Finally, the dispersion potential (in Unsöld approximation) yields:

$$V_{disp} = \frac{-3/2 \frac{U_1}{U_1 + U_2}}{r^6} \left[\alpha_1 \alpha_2 - 1/9 \Delta \alpha_1 \Delta \alpha_2 + 1/3 \Delta \alpha_1 (\alpha_2 - 1/3 \Delta \alpha_2) \right. \\ \left. + (3/2 \cos^2 \vartheta_1 - 1/2) + 1/3 (\alpha_1 - 1/3 \Delta \alpha_1) \Delta \alpha_2 (3/2 \cos^2 \vartheta_2 - 1/2) + \right.$$

$$\begin{aligned}
& + 1/6 \Delta\alpha_1 \Delta\alpha_2 (\sin\vartheta_1 \sin\vartheta_2 \cos(\varphi_1 - \varphi_2) - 2\cos\vartheta_1 \cos\vartheta_2)^2 \Big] \\
& = \frac{-3/2 \frac{U_1 \cdot U_2}{U_1 + U_2}}{r^6} \alpha_1 \alpha_2 \left[1 + \frac{\Delta\alpha_1}{3\alpha_1} \sum_{\beta} C_{\beta}^2(\hat{r}_1) C_{\beta}^{2*}(\hat{r}) + \frac{\Delta\alpha_2}{3\alpha_2} \sum_{\beta} C_{\beta}^2(\hat{r}_2) \cdot \right. \\
& \cdot C_{\beta}^{2*}(\hat{r}) + \frac{\Delta\alpha_1}{3\alpha_1} \frac{\Delta\alpha_2}{3\alpha_2} \left\{ \frac{1}{5} \sum_{\beta} C_{\beta}^2(\hat{r}_1) C_{\beta}^{2*}(\hat{r}_2) + 5\sqrt{\frac{2}{35}} \sum_{\beta, \gamma, \delta} C_{\beta}^2(\hat{r}_1) C_{\gamma}^2(\hat{r}_2) \cdot \right. \\
& \cdot C_{\delta}^2(\hat{r}) \begin{pmatrix} 2 & 2 & 2 \\ \beta & \gamma & \delta \end{pmatrix} + 54\sqrt{\frac{2}{35}} \sum_{\beta, \gamma, \delta} C_{\beta}^2(\hat{r}_1) C_{\gamma}^2(\hat{r}_2) C_{\delta}^4(\hat{r}) \begin{pmatrix} 2 & 2 & 4 \\ \beta & \gamma & \delta \end{pmatrix} \Big\} \Big] \quad (5.8)
\end{aligned}$$

In these expressions we used the following definitions: the polar angles ϑ_1 and φ_1 (ϑ_2 and φ_2) define the orientation of the axis $\hat{r}_1$ ($\hat{r}_2$) of molecule 1 (molecule 2) with respect to the $\hat{r}$ -axis, pointing from the center of molecule 2 towards the center of molecule 1. This is the same convention as that used by Margenau and Kestner (MAR 69, Chapt. 2). The quantity μ_i stands for the electric dipole moment, $Q_i = \frac{1}{2} \int \rho_i(3z^2 - r^2) dV$ for the molecular quadrupole moment, $O_i = \frac{1}{2} \int \rho_i(5z^3 - 3zr^2) dV$ for the molecular octupole moment, α_i for the average polarizability, $\Delta\alpha_i = \alpha_{\parallel i} - \alpha_{\perp i}$ for the difference of the polarizability along and perpendicular to the molecular symmetry axis and U_i , for the average excitation energy in the Unsöld approximation; $\hat{r}$ indicates unit vectors. The subscript i refers to the i^{th} molecule.

The expressions for V_{elec} and V_{ind} in Eqs. (5.1) and (5.2) are exact, whereas V_{disp} is derived using the Unsöld approximation. An equivalent expression for V_{disp} was derived with the oscillator model (MAR 69). In expressions (5.1) – (5.8) we have restricted our attention to the (non-vanishing) lowest order terms. Higher order terms can be found in BUC 67 and MAR 69. These terms were omitted in our expressions because the force constants are either very small or unknown.

The short range part of the I.P. is in general poorly known and has to be treated empirically. Empirical values for the isotropic part of the I.P. can be calculated from the parameters of a Lennard-Jones 12-6 potential. These parameters are obtained from low temperature viscosity measurements (HIR 65) and combination rules $\sigma = \frac{(\sigma_1 + \sigma_2)}{2}$ and $\epsilon = (\epsilon_1 \epsilon_2)^{1/2}$, where ϵ_i and σ_i are the depth and the core, respectively, of the Lennard-Jones potential for a pure system. The short-range part of the isotropic I.P. is then described by a

repulsive term, $\frac{C_{12,emp}}{r^{12}} = \frac{4\epsilon\sigma^{12}}{r^{12}}$, and the long-range part by the attractive term, $\frac{C_{6,emp}}{r^6} = \frac{4\epsilon\sigma^6}{r^6}$

TABLE 5 1

Molecular Quantities Required for Calculation of the Intermolecular Potential

In this Table the following definitions were used U is the ionisation potential to be used as an average excitation energy in the Unsold approximation ϵ and σ are the depth and the core, respectively, of the 12 6 Lennard Jones potential obtained from low temperature viscosity measurements, k is the Boltzmann constant

	μ^a [10^{-18} esu cm]	Q^a [10^{-26} esu cm ²]	α^b [Å ³]	$\alpha_{\parallel} - \alpha_{\perp}^b$ [Å ³]	$\frac{\Delta\alpha^b}{3\alpha}$	U^c [eV]	ϵ/k^d [°K]	σ^d [Å]
NO	0 158	-1 8	1 74	0 84	0 162	9 5	119	3 47
N ₂ O	0 166	-3 0	3 00	2 96	0 329	12 9	220	3 879
CS ₂	—	1 8	8 74 ^d	9 60 ^d	0 33 ^d	10 03	488	4 438
CO ₂	—	-4 3	2 63	2 10	0 266	13 73	190	3 996
CCl ₄	—	—	10 24 ^d	—	—	11 0	327	5 881
Ar	—	—	1 64 ^d	—	—	15 7 ^e	124	3 418
N ₂	—	-1 52	1 77	0 69	0 131	15 51	91 5	3 681
H ₂	—	0 662	0 819	0 314	0 128	15 43	33 3	2 968

a) Reference STO 66 (recommended values)

b) Reference BRI 66 unless otherwise noted

c) Reference LAN 51, Vol 1, Part 3, Chap 14204 unless otherwise noted

d) Reference HIR 65, page 950 and 1110

e) Reference REE 62, page 61

The values of the different potential constants for the molecular systems which we have investigated are calculated from Table 5 1 and given in Table 5 2 For the purpose of comparison, values for the system NO-H₂ are also included The entries in Table 5 2 multiplied by the indicated 'multiplier' give the value of the potential terms for $r=10$ Å This is the internuclear distance which is characteristic of our total collision cross section measurements, the anisotropy of the IP was most sensitively probed here (Ect. 5 3) We note that CCl₄ is a special case in this set Because of its tetrahedral

symmetry the lowest order anisotropic potential terms are due to its octupole moment and dipole-quadrupole polarizability tensor, A, (BUC 67), the values of which are not known.

TABLE 5 2

The Values of the Various Potential Constants and the Strength of the Potential at $r=10 \text{ \AA}$
The values of the interaction strength are in ergs if the given value is multiplied by its appropriate 'multiplier'

The Interaction of NO with		N ₂ O	CS ₂	CO ₂	CCl ₄	Ar	N ₂	H ₂
		electrostatic potential (multiplier 10^{-16})						
CD ₁ D ₂	[10^{-37} erg cm ³]	0.26	—	—	—	—	—	—
CD ₁ Q ₂	[10^{-44} erg cm ⁴]	-0.71	0.43	1.02	—	—	-0.36	0.16
CD ₂ Q ₁	[10^{-44} erg cm ⁴]	-0.30	—	—	—	—	—	—
CQ ₁ Q ₂	[10^{-51} erg cm ⁵]	0.54	-0.32	0.77	—	—	0.27	-0.12
		induction potential (multiplier 10^{-18})						
CD ₁ D ₁ α ₂	[10^{-60} erg cm ⁶]	0.075	0.22	0.066	0.256	0.040	0.044	0.020
CD ₂ D ₂ α ₁	[10^{-60} erg cm ⁶]	0.047	—	—	—	—	—	—
CD ₁ Q ₁ α ₂	[10^{-67} erg cm ⁶]	0.26	0.75	0.23	0.88	0.14	0.15	0.07
CD ₂ Q ₂ α ₁	[10^{-67} erg cm ⁶]	0.26	—	—	—	—	—	—
		dispersion potential (multiplier 10^{-16})						
C ₆ ,disp	[10^{-58} erg cm ⁶]	0.686	1.783	0.617	2.183	0.406	0.406	0.201
$\frac{\Delta\alpha_1}{3\alpha_1}$ C ₆ ,disp	[10^{-58} erg cm ⁶]	0.111	0.289	0.099	0.354	0.066	0.066	0.033
$\frac{\Delta\alpha_2}{3\alpha_2}$ C ₆ ,disp	[10^{-58} erg cm ⁶]	0.226	0.588	0.164	—	—	0.053	0.026
$\frac{\Delta\alpha_1}{3\alpha_1} \frac{\Delta\alpha_2}{3\alpha_2}$ C ₆ ,disp	[10^{-58} erg cm ⁶]	0.037	0.095	0.027	—	—	0.009	0.004
		empirical potential (multiplier 10^{-16})						
C ₆ ,emp	[10^{-58} erg cm ⁶]	2.20	5.08	2.25	11.38	1.12	1.20	0.39
C ₁₂ ,emp	[10^{-58} erg cm ⁶]	0.0054	0.019	0.0061	0.012	0.0018	0.0025	0.0004

The various interaction constants are defined in the usual way:

$$\text{dipole-dipole interaction } \frac{C_{D_1 D_2}}{r^3} \equiv \frac{\mu_1 \mu_2}{r^3}$$

$$\text{dipole-quadrupole interaction } \frac{C_{D_1 Q_1}}{r^4} \equiv \frac{3/2 \mu_1 Q_1}{r^4}$$

$$\text{quadrupole-quadrupole interaction } \frac{C_{Q_1 Q_2}}{r^5} \equiv \frac{3/4 Q_1 Q_2}{r^5}$$

$$\text{dipole-induction interaction } \frac{C_{D_1 D_1 \alpha_j}}{r^6} \equiv \frac{\mu_1^2 \alpha_j}{r^6}$$

$$\text{dipole-quadrupole induction interaction } \frac{C_{D_1 Q_1 \alpha_j}}{r^7} \equiv \frac{6 \mu_1 Q_1 \alpha_j}{r^7}$$

$$\text{dispersion interaction in Unsöld approximation } \frac{C_{6, \text{disp}}}{r^6} \equiv 3/2 \cdot \frac{U_1 \cdot U_2}{U_1 + U_2} \cdot \frac{\alpha_1 \alpha_2}{r^6}$$

Octupole terms are not included in Table 5.2 because they are unknown.

The induction and dispersion terms are the only ones which contribute to the angular independent part of the long range I.P.. From Table 5.2 it follows that induction forces give only a very small contribution to the isotropic dispersion r^{-6} term. We will neglect these isotropic long range induction forces from here on. The empirical potential also possesses an r^{-6} long range dependence, and one should expect that $C_{6, \text{disp}} \approx C_{6, \text{emp}}$. For the systems in Table 5.2 the $C_{6, \text{emp}}$ is always much larger. This discrepancy is due to several factors. The Unsöld approximation, with its uncertain excitation energy, is a rather crude approximation. The same holds for the combination rules. It is not uncommon that $C_{6, \text{disp}}$ and $C_{6, \text{emp}}$ differ by a factor of two.

The velocity dependence of the total collision cross section has been determined experimentally for the system NO-D₂ (FEL 70). If one calculates the parameter $C_6 = 4\epsilon\sigma^6$ from the experimental values $\epsilon = 0.94 \times 10^{-14}$ erg and $\sigma = 3.25$ Å, one finds $C_6 = 0.44 \times 10^{-58}$ erg cm⁶ in fair agreement with $C_{6, \text{emp}}$ in Table 5.2 for NO-H₂. The same holds for C₁₂. Therefore, although on weak grounds, we prefer to use empirical potential parameters for the calculations of the angular independent part of the I.P. instead of $C_{6, \text{disp}}$.

As can be seen from the entries in Table 5.2 the influence of the $\frac{C_{12,emp}}{r^{12}}$ potential term at $r=10 \text{ \AA}$ is very small for all systems. We conclude, from Table 5.2 with aid of the multipliers, that the isotropic r^{-6} part of the I P is much larger than all the other isotropic and anisotropic terms.

The anisotropic r^{-6} contribution is of the same order as the electrostatic (angle-dependent) terms. Thus, we are in difficulties, because so many angle-dependent terms seem to determine the angle-dependent part of the total collision cross section. However, it will be shown in Sect. 5.2 that only the $C_0^2(r_1) C_0^2(r)$ term of the long range r^{-6} potential normally contributes to the measured effect. With the formulae (5.1)-(5.8) we define the anisotropy term with the relation

$$\frac{C_6}{r^6} \left[1 + q_{2,6} P_2(r_1, \hat{r}) \right] = \frac{C_{6,disp}}{r^6} \left[1 + \left(\frac{\Delta\alpha_1}{3\alpha_1} + \frac{\mu_1^2 \alpha_2}{C_{6,disp}} \right) P_2(r_1, \hat{r}) \right] \quad (5.9)$$

It is seen from Table 5.2, that $\frac{\mu_1^2 \alpha_2}{C_{6,disp}} \ll \frac{\Delta\alpha_1}{3\alpha_1}$ so the induction contribution may again be neglected and we have $q_{2,6} = \frac{\Delta\alpha}{3\alpha}$. As noted above we prefer to use Formula (5.9) with $C_{6,emp}$ instead of $C_{6,disp}$. Nevertheless, we keep the value of $q_{2,6}$ as given by the Unsold approximation, because $\frac{\Delta\alpha_1}{3\alpha_1}$ is independent of the uncertain value of the excitation energy U_1 .

We neglect the fact that NO is not completely centro-symmetric, its center of mass is displaced about $0.02 \text{ \AA}$ from the point from which the I P is calculated. This eccentricity gives extra angle-dependent terms (MAR 69 and REE 71). At a distance of $10 \text{ \AA}$, however, these effects play a negligible role. Moreover, these terms have an angle-dependence such that there is no contribution in first order.

In general, the I P for two cylindrically symmetric molecules can be written in the following form

$$V(r_1, \hat{r}_2, r) = \sum_{\{v\}} V_s^{n_1, n_2, n}(r) C_{\nu_1}^{n_1}(\hat{r}_1) C_{\nu_2}^{n_2}(\hat{r}_2) C_{\nu}^n(\hat{r}) \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix}, \quad (5.10)$$

where $\{v\}$ stands for $\{s, n_1, \nu_1, n_2, \nu_2, n, \nu\}$. The number s allows different r -dependent terms to exist for one particular set of $\{n_1, \nu_1, n_2, \nu_2, n, \nu\}$. This

occurs, for example, if use is made of a long range multipole expansion (Eq (5 1)-(5 8)) With the general form of Eq (5 10) we will begin the calculation of the scattering problem

5 2 DISTORTED WAVE APPROXIMATION

All scattering properties can be derived with the help of T-matrix elements (e g MES 64, Eq XIX 74), which can be defined as

$$T_{\mathbf{a} \rightarrow \mathbf{a}'} = T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)} + \langle \chi_{\mathbf{a}'}^- | \lambda V' | \psi_{\mathbf{a}}^+ \rangle \quad (5 11)$$

Here $\mathbf{a}$ ($\mathbf{a}'$) stands for the quantum numbers describing the initial (final) state, including the direction of the incoming (outgoing) particle $T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)}$ is the transition matrix if V' is zero The intermolecular potential V is arbitrarily split into two parts $V = V_0 + \lambda V'$, where λ is regarded as a parameter of perturbation strength $\psi_{\mathbf{a}}^+(\chi_{\mathbf{a}'}^-)$ is the wave function describing the particle as a superposition of a plane waves along $\mathbf{k}(\mathbf{k}')$, and an outgoing (incoming) spherical wave, for large r -values The wave function $\psi_{\mathbf{a}}^{\pm}$ is a solution of the Schrodinger equation with $V = V_0 + \lambda V'$, whereas $\chi_{\mathbf{a}}^{\pm}$ is the solution for $V = V_0$ From Eq (5 11) follows

$$T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)} = \langle e^{i \mathbf{k}' \cdot \mathbf{r}} | V_0 | \chi_{\mathbf{a}}^+ \rangle \quad (5 12)$$

Generally, the scattering cross section in the direction Ω is given by

$$\frac{d\sigma_{\mathbf{a} \rightarrow \mathbf{a}'}}{d\Omega} = -\frac{\mu^2}{2\pi^2 \hbar^4} |T_{\mathbf{a} \rightarrow \mathbf{a}'}|^2 \frac{k'}{k}, \quad (5 13)$$

where μ is the reduced mass of the system and $\mathbf{k}'$ is taken in the direction of Ω The total collision cross section of the initial state, summed over all possible final channels is obtained from the optical theorem

$$\sigma_{\mathbf{a}} = \frac{-2\mu}{\hbar^2 k} \text{Im } T_{\mathbf{a} \rightarrow \mathbf{a}} \quad (5 14)$$

Here (a) includes all quantum numbers of $\mathbf{a}$ except the specification of direction

In the distorted wave approximation (D W A), $\lambda V'$ is chosen such that ψ_a^+ differs only negligibly from χ_a^+ in Eq (5 11) In our case we select for V_0 the isotropic part of the I P and for $\lambda V'$ the angle-dependent part (REU 65) The first order D W A consists of replacing ψ_a^+ by χ_a^+ in Eq (5 11) This choice allows us to calculate $T_{a \rightarrow a'}^{(0)}$ with the partial wave method (e g MES 64, Eq XIX 51)

$$T_{a \rightarrow a'}^{(0)} = - \frac{2\pi\hbar^2}{\mu k} \sum_l (2l+1) P_l(\cos\vartheta) \sin\eta_l e^{i\eta_l} \delta_{k,k'} \delta_{m_1, m_1'} \quad (5 15)$$

The $\hat{k}$ -direction is chosen along the z -axis, ϑ is the angle between $\mathbf{k}'$ and $\hat{z}$, $\delta_{k,k'}$ indicates that inelastic processes are forbidden in $T_{a \rightarrow a'}^{(0)}$

To evaluate $\langle \chi_{a'}^- | \lambda V' | \psi_a^+ \rangle \approx \langle \chi_{a'}^- | \lambda V' | \chi_a^+ \rangle$ we use the fact that V' can be written as a sum over terms like

$$V_s^{n_1, n_2, n}(\mathbf{r}) C_{\nu_1}^{n_1}(\hat{\mathbf{r}}_1) C_{\nu_2}^{n_2}(\hat{\mathbf{r}}_2) C_{\nu}^n(\hat{\mathbf{r}}) \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix}$$

Consequently, the matrix elements which have to be evaluated are of the form

$$\langle \chi_{a'}^- | V_s^{n_1, n_2, n}(\mathbf{r}) C_{\nu_1}^{n_1}(\hat{\mathbf{r}}_1) C_{\nu_2}^{n_2}(\hat{\mathbf{r}}_2) C_{\nu}^n(\hat{\mathbf{r}}) \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix} | \chi_a^+ \rangle$$

We write $\chi_{a'}^\pm$ as a product

$$\chi_{a'}^\pm = u_{\text{rot}}(1) u_{\text{rot}}(2) \left(\frac{4\pi}{k'r} \right) \sum_{l,m} i^l e^{\pm i\eta_l} F_l(k', r) Y_{lm}(\hat{\mathbf{r}}) Y_{lm}^*(\mathbf{k}'),$$

$$\text{where } u_{\text{rot}}(1) = (-)^{m_1} \Omega_1 \sqrt{\frac{2J_1+1}{8\pi^2}} \mathcal{D}_{m_1 \Omega_1}^{J_1}(\alpha_1, \beta_1, \gamma_1) \quad (5 16)$$

is the rotational wave function of the i -th molecule, and $F_l(k', r)$ is a solution of the radial Schrodinger equation

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{2\mu}{\hbar^2} V_0 + k'^2 \right] F_l(k', r) = 0,$$

with $F_l(k', r) \xrightarrow{r \rightarrow \infty} \sin(k'r - \frac{1}{2}l\pi + \eta_l)$

$$\text{and } k'^2 = k^2 + \frac{2\mu}{\hbar^2} (E_{\text{rot}} - E'_{\text{rot}}), \quad (5 17)$$

The quantity $E_{\text{rot}}(E'_{\text{rot}})$ is the total rotational energy of the two molecules in the initial (final) state. We have made allowance only for rotational excitation of the colliding molecules. Vibrational transitions normally are energetically forbidden for thermal collisions. Chemical reactions were also excluded in the present treatment, consequently the internal wave functions $u_{\text{rot}}(1)$ and $u_{\text{rot}}(2)$ are simply the angular momentum eigen-functions expressed in matrix elements $\mathcal{D}_{m_1 \Omega_1}^{J_1}(\alpha_1, \beta_1, \gamma_1)$ of 3-dimensional rotations (EDM 60, Sect. 4.7 and 4.8). The factor $\sqrt{\frac{2J_1+1}{8\pi^2}}(-)^{m_1-\Omega_1}$ is introduced in

Eq. (5.16) to yield normalized eigen-functions which obey the Condon-Shortley phase convention. The functions $u_{\text{rot}}(i)$ can be used for: atoms in a 1S state ($j_1=m_1=\Omega_1=0$), $u_{\text{rot}}(i) = (8\pi)^{-\frac{1}{2}}$; linear molecules in a $^1\Sigma$ state ($\Omega_1=0$), $u_{\text{rot}}(i) = (2\pi)^{-\frac{1}{2}} Y_{j_1 m_1}(\alpha_1, \beta_1) = (2\pi)^{-\frac{1}{2}} Y_{j_1 m_1}(f_1)$; spherical and symmetric top molecules ($\Omega_1=K_1$); and diatomic molecules which possess a component of electronic angular momentum Ω_1 along their axis (half numbered j_1 and Ω_1 are included).

The NO molecule is an example of the last case if we assume Hund's case a) -wave functions and neglect hyperfine structure. The admixture of $^2\Pi_{\frac{1}{2}, j=\frac{3}{2}}$ to the $^2\Pi_{\frac{3}{2}, j=\frac{3}{2}}$ state is only 0.6%. Collisions take place in a magnetic field of 150 G, which is sufficient to decouple the nuclear spin.

We define:

$$t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\nu)} \equiv \langle \chi_{\mathbf{a}'}^- | V_s^{n_1, n_2, n}(\mathbf{r}) C_{\nu_1}^{n_1}(\hat{\mathbf{r}}_1) C_{\nu_2}^{n_2}(\hat{\mathbf{r}}_2) C_{\nu}^n(\hat{\mathbf{r}}) \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix} | \chi_{\mathbf{a}} \rangle \quad (5.18)$$

where (ν) stands for all the indices characterizing a specific potential term.

We can write $t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\nu)}$ as a triple product:

$$t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\nu)} = t_{\mathbf{a} \rightarrow \mathbf{a}'}(n_1, n_2, n, \nu, s) t'_{\mathbf{a} \rightarrow \mathbf{a}'}(n_1, \nu_1) t'_{\mathbf{a} \rightarrow \mathbf{a}'}(n_2, \nu_2) \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix}$$

with $t_{\mathbf{a} \rightarrow \mathbf{a}'}(n_1, n_2, n, \nu, s) =$

$$= \frac{4\pi}{kk'} \sum_{l, l'} (2l'+1)(2l+1) i^{l-l'} e^{i(\eta_{l'} + \eta_l)} \int_0^\infty F_{l'}(k', r) V_s^{n_1, n_2, n}(\mathbf{r}) F_l(k, r) dr \cdot$$

$$\cdot \begin{pmatrix} l' & n & l \\ -m' & \nu & 0 \end{pmatrix} \begin{pmatrix} l' & n & l \\ 0 & 0 & 0 \end{pmatrix} (-)^{m'} C_{m'}^{l'}(\hat{\mathbf{k}}');$$

and ($l=1,2$)

$$t'_{a \rightarrow a'}(n_1, \nu_1) = (-)^{m_1 - \Omega_1 + \nu_1} \begin{pmatrix} j_1' & n_1 & j_1 \\ -m_1' & \nu_1 & m_1 \end{pmatrix} \begin{pmatrix} j_1' & n_1 & j_1 \\ -\Omega_1' & 0 & \Omega_1 \end{pmatrix} ((2j_1' + 1)(2j_1 + 1))^{\frac{1}{2}} \quad (5.19)$$

The matrix element $t_{a \rightarrow a'}^{(\nu)}$ is proportional to a product of seven 3j-symbols

$$t_{a \rightarrow a'}^{(\nu)} \sim \begin{pmatrix} l' & n & l \\ m' & \nu & 0 \end{pmatrix} \begin{pmatrix} l' & n & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_1' & n_1 & j_1 \\ -m_1' & \nu_1 & m_1 \end{pmatrix} \begin{pmatrix} j_1' & n_1 & j_1 \\ -\Omega_1' & 0 & \Omega_1 \end{pmatrix} \begin{pmatrix} j_2' & n_2 & j_2 \\ -m_2' & \nu_2 & m_2 \end{pmatrix} \cdot \begin{pmatrix} j_2' & n_2 & j_2 \\ -\Omega_2' & 0 & \Omega_2 \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n \\ \nu_1 & \nu_2 & \nu \end{pmatrix} \quad (5.20)$$

From this expression follows the selection rule $\Delta\Omega_1=0$, which agrees with what physically might have been expected since no torque can be exerted on a molecule around the symmetry axis. Furthermore, from Eq (5.20) follows $\Delta(m_1 + m_2 + m) = 0$ which means that the component of the total angular momentum along the z-axis is conserved (Here $\hbar m$ is the component of the orbital angular momentum of the colliding particles along the z-axis). Inelastic transitions (for example $j_1 \rightarrow j_1' \neq j_1$) are only possible through lP terms with $n_1 \neq 0$, the maximum value $|j_1 - j_1'|$ equals n_1 . First order dipole-dipole interaction ($n_1 = n_2 = 1, n = 2$) in the elastic channel is possible only for 'symmetric top' molecules (with Ω_1 or $K_1 \neq 0$).

Because of the property $\begin{pmatrix} j_1 & 1 & j_1 \\ \Omega_1 & 0 & \Omega_1 \end{pmatrix} = 0$ for $\Omega_1 = 0$ this interaction vanishes for linear molecules in a $^1\Sigma$ state and for symmetric top molecules with $K_1 = 0$.

An important observation, at this point, is that in first order DWA ladder processes in which, for instance, a final state is reached by collaboration of two or more different potential terms are disregarded. This type of ladder processes could be included in higher order DWA. In that case, ψ_a^+ in Eq (5.11) is replaced by a wave function which is already distorted by angle-dependent terms (DAV 64). The perturbation of ψ_a^+ can be written as

$$\psi_a^+ = \chi_a^+ + \lambda \cdot \chi_a^{+,(1)} + \text{higher order terms (h.o.t.)} \quad (5.21)$$

The result for the T-matrix is then

$$T_{\mathbf{a} \rightarrow \mathbf{a}'} = T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)} + \lambda \sum_{(\nu)} t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\nu)} + \lambda^2 T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(2)} + \text{h.o.t.} \quad (5.22)$$

The replacement of $\psi_{\mathbf{a}}^+$ by $\chi_{\mathbf{a}}^+$ in formula (5.11) gives the first two terms of the expansion of $T_{\mathbf{a} \rightarrow \mathbf{a}'}$ (first order D.W.A.). The T-matrix $T_{\mathbf{a} \rightarrow \mathbf{a}'}$ is connected to the S-matrix by the relation: $S = \mathbb{1} - 2\pi i T$ (see MES 64 Eq. XIX.184). The exact S-matrix has to be unitary. Using the expansion for $T_{\mathbf{a} \rightarrow \mathbf{a}'}$ up to the terms linear in λ , violations of unitarity of the order λ^2 are tolerated; consequently within the order of approximation the unitarity is conserved.

From Eq. (5.14) and Eq. (5.22) we obtain:

$$\sigma_{\mathbf{a}} = \frac{2\mu}{\hbar^2 k} \left\{ \text{Im } T_{\mathbf{a} \rightarrow \mathbf{a}}^{(0)} + \lambda \sum_{(\nu)} \text{Im } t_{\mathbf{a} \rightarrow \mathbf{a}}^{(\nu)} + \lambda^2 \text{Im } T_{\mathbf{a} \rightarrow \mathbf{a}}^{(2)} + \text{h.o.t.} \right\} \quad (5.23)$$

Thus, first order D.W.A. yields the total collision cross section up to terms linear in λ . The same holds for the differential cross section, if the final state $\mathbf{a}'$ is not specified.

$$\frac{d\sigma_{\mathbf{a}}}{d\Omega} \equiv \sum_{\mathbf{a}'} \frac{d\sigma_{\mathbf{a} \rightarrow \mathbf{a}'}}{d\Omega} \quad (5.24)$$

On the other hand, for an inelastic transition $\mathbf{a}' \neq \mathbf{a}$, one has (Eq. (5.13) and Eq. (5.22)):

$$\frac{d\sigma_{\mathbf{a} \rightarrow \mathbf{a}'}}{d\Omega} = \frac{\mu^2}{4\pi^2 \hbar^4} \left| \lambda \sum_{(\nu)} t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\nu)} + \lambda^2 T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(2)} + \text{h.o.t.} \right|^2 \quad (5.25)$$

Thus, first order D.W.A. gives here terms in λ^2 . The same holds of course for the total inelastic cross section. Therefore, to calculate the influence of the inelastic channels on the total collision cross section $\sigma_{\mathbf{a}}$ one must use at least second order D.W.A. (LAW 67). In first order D.W.A. we have ($\lambda=1$)

$$\sigma_{\mathbf{a}} = \sigma^{(0)} + \sum_{\nu} \sigma_{\nu}$$

$$\text{with } \sigma^{(0)} = - \frac{2\mu}{\hbar^2 k} \text{Im } T_{\mathbf{a} \rightarrow \mathbf{a}}^{(0)} = \frac{4\pi}{k^2} \sum_l (2l+1) \sin^2 \eta_l$$

$$\text{and } \sigma_{\nu} = \frac{2\mu}{\hbar^2 k} \text{Im } t_{\mathbf{a} \rightarrow \mathbf{a}}^{(\nu)} \quad (5.26)$$

In our experiment, the molecules of the secondary beam are not state selected. besides summation over all j_2 -values, an average has to be taken over all spatial orientations of molecule (2).

$$\sigma(\Omega_1, j_1, m_1) \equiv \sigma^{(0)} - \frac{1}{2j_2+1} \sum_{m_2} \sum_{(v)} \frac{2\mu}{\hbar^2 k} \text{Im } t'_{a \rightarrow a}^{(v)} \quad (5.27)$$

Equation (5.19) shows that only $t'_{a \rightarrow a}(n_2, \nu_2)$ depends on j_2 and m_2 . Fortunately, this j_2 and Ω_2 dependence disappears as follows.

$$\begin{aligned} \frac{1}{2j_2+1} \sum_{m_2} t'_{a \rightarrow a}(n_2, \nu_2) &= \\ &= \begin{pmatrix} j_2 & n_2 & j_2 \\ -\Omega_2 & 0 & \Omega_2 \end{pmatrix} \sum_{m_2} (-)^{m_2 - \Omega_2 + \nu_2} \begin{pmatrix} j_2 & n_2 & j_2 \\ -m_2 & \nu_2 & m_2 \end{pmatrix} \\ &= \delta_{\nu_2, 0} \begin{pmatrix} j_2 & n_2 & j_2 \\ -\Omega_2 & 0 & \Omega_2 \end{pmatrix} (-)^{\Omega_2 + j_2} (2j_2+1) \cdot \\ &\quad \cdot \sum_{m_2} \begin{pmatrix} j_2 & 0 & j_2 \\ -m_2 & 0 & m_2 \end{pmatrix} \begin{pmatrix} j_2 & n_2 & j_2 \\ -m_2 & 0 & m_2 \end{pmatrix} \\ &= \delta_{\nu_2, 0} \delta_{n_2, 0} \end{aligned} \quad (5.28)$$

The total collision cross section with a non state-selected molecule (2) is equal to $\sigma(\Omega_1, j_1, m_1)$, and is independent^{*}) of potential terms with $n_2 \neq 0$. From Eqs (5.27) and (5.28) we get.

$$\sigma(\Omega_1, j_1, m_1) = \sigma^{(0)} - \frac{2\mu}{\hbar^2 k} \sum_{(v)} \frac{(-)^{n-\nu}}{\sqrt{2n+1}} \text{Im } t_{a \rightarrow a}(n_1, 0, n, \nu, s) t'_{a \rightarrow a}(n_1, \nu_1) \delta_{n_2, 0} \delta_{\nu, \nu_1} \delta_{n, n_1} \quad (5.29)$$

^{*}) This conclusion is not limited to the case that molecule (2) possesses cylindrical symmetry. Also for asymmetric-rotor molecules (e.g. H₂O) only those potential terms influence $\sigma(\Omega_1, j_1, m_1)$ which depend solely on the orientation of molecule (1).

Further evaluation of this expression yields:

$$\begin{aligned} \sigma(\Omega_1, j_1, m_1) = & \sigma^{(0)} - \sum_{(v)} \frac{8\pi\mu}{\hbar^2 k^3} \begin{pmatrix} j_1 & n & j_1 \\ m_1 & 0 & m_1 \end{pmatrix} \begin{pmatrix} j_1 & n & j_1 \\ -\Omega_1 & 0 & \Omega_1 \end{pmatrix} \cdot \\ & \cdot \frac{(-1)^{m_1 - \Omega_1 + n}}{\sqrt{2n+1}} (2j_1+1) \left[\sum_{l, l'} \begin{pmatrix} l' & n & l \\ 0 & 0 & 0 \end{pmatrix}^2 \operatorname{Im} \left\{ i^{(l-l')} e^{i(\eta_l + \eta_{l'})} \right\} \right. \\ & (2l+1)(2l'+1) \int_0^\infty F_{l'}(k, r) \lambda V_s^{(n_1, n_2, n)}(r) F_l(k, r) dr \\ & \left. \delta_{\nu, 0} \delta_{\nu_1, 0} \delta_{n, n_1} \delta_{n_2, 0} \right] \quad (5.30) \end{aligned}$$

The total collision cross section $\sigma(\Omega_1, j_1, m_1)$ reduces to $\sigma^{(0)}$, if one averages over m_1 .

The two 3-j symbols in Eq. (5.30) cause vanishing of all contributions with $n > 2j_1$. In our experiment ($j_1 = \frac{3}{2}$), we can leave out all terms of the I.P. with $n > 3$, in first order D.W.A.. Furthermore, it follows directly from substitution of odd n in Eq. (5.30) that their contribution equals zero. The only non vanishing terms come from $n_1 = n = 2$. This shows the advantage of our method; using NO molecules in a $j_1 = \frac{3}{2}$ -state as primary beam molecules, we are left with only the P_2 -term of the I.P. to be determined by the measurement of the anisotropy. (On the other hand, no information can be obtained about other anisotropy terms. Selecting NO molecules in successively higher states would allow determination of terms with $n > 2$.)

The dipole-dipole dispersion term $-\frac{C_6}{r^6} q_{2,6} P_2(\hat{r} \cdot \hat{r}_1)$ remains as the only contribution of the well understood long range part of the potential. In addition, the analogous short-range term $\frac{C_{12}}{r^{12}} q_{2,12} P_2(\hat{r} \cdot \hat{r}_1)$ must be considered, where $q_{2,12}$ acts as an adjustable parameter and the r^{-12} dependence forms an empirical Ansatz. Now we calculate the final expression for $\sigma(\Omega_1, j_1, m_1)$ using only the $P_2(\hat{r} \cdot \hat{r}_1)$ -terms:

$$\sigma(\Omega_1, j_1, m_1) = \sigma^{(0)} + \frac{8\pi\mu}{\hbar^2 k^3} \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1-1)} \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \cdot \sum_l \frac{l+1}{2l+3} \left\{ \frac{(2l+1)l}{2l-1} \sin 2\eta_l V_2^{l,l} - 3(l+2) V_2^{l,l+2} \sin(\eta_l + \eta_{l+2}) \right\}$$

$$\text{with } V_2^{l,l'} = \int_0^\infty F_l(k, r) F_{l'}(k, r) \left(\frac{q_{2,12} C_{12}}{r^{12}} - \frac{q_{2,6} C_6}{r^6} \right) dr \quad (5.31)$$

From Eq. (5.31) we conclude that $\sigma(\Omega_1, j_1, m_1)$ depends only on $|m_1|$. This property holds also in higher order for $\sigma(\Omega_1, j_1, m_1)$ (STO 67, page 34).

5.3 THE LANDAU-LIFSHITZ-APPROXIMATION

Before further approximations in the expression for $\sigma(\Omega_1, j_1, m_1)$ in Eq. (5.31) are introduced, we discuss briefly the general behaviour of the phase shift η_l as function of l at a fixed energy. Repulsive (attractive) potentials produce negative (positive) phase shift. For small l (i.e. for small impact parameters) η_l is large and negative. On the other hand, for large l the repulsive potential is screened off by the centrifugal barrier so that η_l is small and positive. In the intermediate region η_l has a maximum. Its values around the maximum may approach $N \frac{\pi}{2}$ thereby producing the well known glory structure of the total collision cross section.

The first conclusion, important for the introduction of the Landau-Lifshitz-Approximation (L.L.A.), is that η_l strongly depends on l except for large l where η_l goes to zero, and for l -values near the point where the maximum occurs in η_l . Many l -values (usually more than a hundred) contribute to the total collision cross section. Consideration of Eqs. (5.31) and (5.26) leads to the conclusion that strongly varying η_l 's give an average contribution of the l th partial wave to $\sigma^{(0)}$ of $\frac{2\pi}{k^2} (2l+1)$ and no contribution to the m_1 -dependent part of $\sigma(\Omega_1, j_1, m_1)$. The partial waves with η_l near the maximum influence the total collision cross section only if sufficiently high energy-resolution of the colliding molecules is obtained. In the

literature, normally glory undulations of a few percent at most have been reported. The systems investigated by us do not have a very favourable I P or kinematics to measure glory structures. In the present results (Sect. 7.2) on the total collision cross section measurements without state selection we show that no glories were observed at the velocity at which the anisotropy effect was measured. Consequently, we omit the contribution to Eq. (5.31) from l -values in the intermediate range. For large l -values η_l can be calculated in Born-approximation (LAN 59, § 1.11)

$$\eta_l^{\text{Born}} = \frac{3}{16} \frac{\pi \mu C_6 k^4}{\hbar^2 l^5} - \frac{63}{512} \frac{\pi \mu C_{12} k^{10}}{\hbar^2 l^{11}} \quad (5.32)$$

assuming the potential $V_0(r) = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6}$

For large l -values the influence of the repulsive part of the I P on η_l is very small, normally. We drop the second term of Eq. (5.32). At the end of this section we will justify this omission.

The application of the Landau-Lifshitz-approximation implies the following replacements in Eq. (5.31): the phase shift η_l is replaced by η_l^{Born} , the function $F_l(k, r)$ by $F_l^{\text{Born}}(k, r) = kr J_l(kr)$ (MES 64, Eq. X.73), and the summation over l -values by integration.

The effect of these replacements is that only the partial wave contributions for the large l 's with small η_l 's are taken properly into account. With decreasing l -values, however, η_l^{Born} in Eq. (5.32) varies also strongly. This feature is common to both η_l and η_l^{Born} , although their actual values may differ significantly (BER 63). The contributions from small l in Eq. (5.31) do not depend on the precise values of η_l if the average is taken over neighbouring l 's.

The L L A yields $\sigma_{LL}^{(0)} = 8.083 \left(\frac{C_6}{\hbar v_{\text{rel}}} \right)^{\frac{2}{5}}$

$$\text{and } \sigma_{LL}(\Omega_1, J_1, m_1) = \sigma_{LL}^{(0)} \left[1 + \frac{1}{10} q_{2,6} \frac{3m_1^2 - J_1(J_1+1)}{(2J_1+3)(2J_1-1)} - \frac{J_1(J_1+1) - 3\Omega_1^2}{J_1(J_1+1)} \right] \quad (5.33)$$

This result is obtained by using (RFU 64)

$$\eta_l^{\text{Born}} = \frac{3}{16} \frac{\pi \mu C_6 k^4}{\hbar^2 l^5},$$

$$V_2^{l/\text{Born}} = -\frac{3\pi}{32} \frac{C_6 k^4}{l^5} \text{ and } V_2^{l+2/\text{Born}} = -\frac{2\pi}{32} \frac{C_6 k^4}{l^5}. \quad (5.34)$$

With Eq. (5.33) we can immediately calculate the expected anisotropy effect:

$$\frac{\Delta\sigma}{\sigma^{(0)}} \equiv \frac{\sigma_{LL}(\frac{3}{2}, \frac{3}{2}, \frac{3}{2}) - \sigma(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})}{\sigma_{LL}^{(0)}} = \frac{-q_{2,6}}{25}. \quad (5.35)$$

With $q_{2,6} = 0.16$ for NO, the expected anisotropy effect is 0.64%.

To characterize the intermolecular distance at which the anisotropy of the I.P. is probed by measuring $\frac{\Delta\sigma}{\sigma^{(0)}}$ an impact parameter b_0 is introduced. We define $b_0 \equiv \frac{l_0}{k}$ where l_0 is the partial wave number for which η_l^{Born} has the value $\frac{1}{2}$. From Eq. (5.34) follows $b_0 = \left(\frac{3}{8} \frac{\pi \mu}{\hbar^2 k} C_6\right)^{\frac{1}{5}}$. (Thus b_0 has only a very weak dependence on the relative velocity.) The quantities b_0 , l_0 are given in Table 5.3 together with the values of $k = \frac{\mu}{v_{\text{rel}}}$ and the reduced mass μ for the collision partners used in the present investigation. The value of b_0 is about 10 Å for all the systems except for NO-H₂.

The influence of the repulsive part of the I.P. on the anisotropy in the total collision cross section is very small. The ratio of the repulsive term $\frac{C_{12}}{r^{12}}$ to the attractive term $\frac{C_6}{r^6}$ for $r = b_0$ equals $\left(\frac{C_{12}}{C_6 b_0^6}\right) = \left(\frac{\sigma}{b_0}\right)^6$ and is of the order of 1% (see column 6 of Table 5.3). Neglecting the correction to the Born phase shift (Less than 1% of η_{l_0} see Eq. (5.32)) the influence of r^{-12} potential term on the anisotropy effect can be taken into account if we calculate $V_2^{l,l'}$ including the $\frac{C_{12}}{r^{12}}$ term (Eq. (5.31) and SCH 70).

$$\sigma_{LL}(\Omega_1 j_1, m_1) = \sigma_{LL}^{(0)} \left[1 + \frac{1}{10} \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1-1)} \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \cdot \left(q_{2,6} - 0.235 q_{2,12} \left(\frac{\sigma}{b_0} \right)^6 \right) \right] \quad (5.36)$$

The actual value of $q_{2,12}$ is unknown for the investigated systems, but the

theoretical value for H₂-He (ROB 63) would indicate $q_{2,12} \approx 0.3$. The influence of the $q_{2,12}$ is therefore estimated to be smaller than 1% for all the systems of Table 5.3.

TABLE 5.3

Collision Parameters of the Investigated Systems

The quantities l_0 , b_0 and $\left(\frac{q}{b_0}\right)^6$ defined in the text, were calculated with the empirical potential parameters of Table 5.2. The relative velocity, v_{rel} , is assumed to be 600 m/s close to the experimental value.

Collision partner of NO	Reduced mass μ [AMU]	Wave number k [10 ⁸ cm ⁻¹]	Characteristic partial wave l_0	Characteristic impact-parameter b_0 [10 ⁻⁸ cm]	Relative strength of repulsive potential $\left(\frac{q}{b_0}\right)^6$ [%]
CCl ₄	25.11	23.7	276	11.6	0.42
CS ₂	21.25	20.3	201	9.9	0.41
N ₂ O	17.84	16.9	141	8.4	0.72
CO ₂	17.84	16.9	142	8.4	0.77
Ar	17.17	16.2	118	7.3	1.12
N ₂	14.48	13.7	101	7.4	1.26
H ₂	1.87	1.76	10.4	5.9	2.6

To investigate how sensitive the anisotropy effect is to the exact value of the inverse power of the long range part of the I.P. an expression for $\sigma(\Omega_1 j_1, m_1)$ was derived for a potential with arbitrary r^{-s} , $s \geq 3$. In agreement with Miller (MIL 69) we find:

$$\sigma_{LL,s}(\Omega_1 j_1, m_1) =$$

$$\sigma_{LL,s}^{(0)} \left[1 + \frac{s-3}{s(s-1)} q_{2,6} \cdot \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1+1)} \cdot \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \right] \quad (5.37)$$

The factor of interest, $\frac{s-3}{s(s-1)}$ has the value 0 for $s = 3$, $\frac{1}{12}$ for $s = 4$, $\frac{1}{10}$ for

$s = 5$, $\frac{1}{10}$ for $s = 6$, $\frac{2}{21}$ for $s = 7$, $\frac{5}{56}$ for $s = 8$ and $\frac{1}{12}$ for $s = 9$. So the anisotropy effect has a broad maximum for $s \approx 6$.

5.4 DISCUSSION OF THE APPROXIMATIONS

A general discussion of the total collision cross section including inelastic channels was given by Bernstein *et al* (BER 63) for molecule-molecule scattering without state selection. The range of impact parameters was divided in three regions, collisions at large, intermediate and small impact parameters were treated separately.

For the collisions with *large* impact parameters only the long range part of the I P is important (see Table 5.3). Born approximation may be used and inelastic transitions may be neglected. This is not the case if the angle-dependent part of the I P becomes larger than the isotropic part of the long range part of the potential. This occurs, for example, if dipole-dipole forces govern the long range interaction (e.g. TIF-NH₃, TOE 66, see also CRO 66 and MCD 70). In this situation, even for large impact parameters mainly inelastic processes may occur.

For *intermediate* impact parameters weak coupling between the different channels is assumed, i.e. direct transitions from the entrance to an exit channel occur much more frequently than ladder processes, where the exit channel is reached by many intermediate steps. Bernstein *et al* assume a phase shift η_l strongly varying with l , in the same way as is assumed in Sect 5.3. Accordingly, the contribution of the l^{th} partial wave to the total collision cross section reduces to an average value of $\frac{2\pi}{k^2} (2l+1)$. Again, a predominance of isotropic forces is assumed. This is the region where D W A. could be applied. The assumption of strongly varying η_l (random phase) is correct only for cases where no glory-structure is observed.

For *small* impact parameters a dominant coupling scheme is defined in which all energetically accessible exit channels become equally populated. Unitarity of the S-matrix gives an average value for the partial wave contribution to the total collision cross section of $\frac{2\pi}{k^2} (2l+1)$. Here l is defined in the entrance channel. The average is taken over an (experimental) energy spread.

In conclusion the contributions to $\sigma^{(0)}$ from the short and intermediate

impact parameters are randomized to an average partial wave contribution equal to $\frac{2\pi}{k^2} (2l+1)$. Only the long range shift is not randomized (This is exactly what the L L A does, as we discussed in Sect 5 3)

To extend this discussion to the anisotropy of the total collision cross section the impact parameters are again divided in the three regions

For the anisotropy effect are mainly responsible the collisions with large impact parameters. We have for $\sigma_l(\Omega_1, J_1, m_1)$ the contribution to the total collision cross section of a single partial wave l in Born Approximation from Eqs (5 34) and (5 31)

$$\frac{\sigma_l(\Omega_1, J_1, m_1)}{\sigma_l^{(0)}} = 1 + \frac{1}{2} q_{2,6} \frac{3m_1^2 - J_1(J_1+1)}{(2J_1+3)(2J_1-1)} \cdot \frac{J_1(J_1+1) - 3\Omega_1^2}{J_1(J_1+1)} \quad (5 38)$$

$$\text{with } \sigma_l^{(0)} = \frac{4\pi}{k^2} (2l+1) \left(\eta_l^{\text{Born}} \right)^2$$

This anisotropy is 5 times stronger than the anisotropy in the total collision cross section, about 20% of $\sigma(\Omega_1, J_1, m_1)$ (Eq 5 33) is due to collisions with large impact parameters. We call this 20% contribution the 'Born tail'

In the *intermediate* range of impact parameters (where D W A is applicable), Eq (5 31) shows that the random phase argument kills the anisotropic contribution from first order D W A because of the $\sin(\eta_l + \eta_{l+2})$ factors. But as we are now considering intermediate impact parameters, we must be alert for possible higher order effects (ladder processes). Those ladder processes are neglected in our first order D W A. There is no really satisfying procedure to treat higher order effect.

The high energy approximation (H E A) has the advantage, at least that it is simple (BEN 64). In H E A many restrictive assumptions are introduced (PAU 65, BEN 69b), notably, straight line trajectories and vanishing spacing of rotational levels. The last assumption in particular leads to an overestimation of inelastic processes. In favor of the H E A, we note that no restrictions are placed on the strength of the anisotropy parameter, $q_{2,6}$. (Thus higher order effects are taken into account.)

The total collision cross section in H E A, $\sigma_{\text{HE}}(\Omega_1, J_1, m_1)$ may be written as

$$\sigma_{\text{HE}}(\Omega_1, j_1, m_1) = \sigma_{\text{LL}}^{(0)} \left\langle \Omega_1, j_1, m_1 \left| g(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{z}}) \right| \Omega_1, j_1, m_1 \right\rangle$$

$$\text{where } g(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{z}}) = 1 - \frac{1}{10} q_{2,6} P_2(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{z}})$$

$$\frac{1}{100} q_{2,6}^2 \left(\frac{129}{140} P_4(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{z}}) - \frac{11}{7} P_2(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{z}}) + \frac{7}{5} \right) + \text{h.o.t.} \quad (5.39)$$

is obtained by expanding Eq. 5.1.6 of BEN 64 in powers of $q_{2,6}$.

For molecules which are averaged over spatial orientation (this means averaging over m_1) Eq. (5.39) yields: *)

$$\sigma_{\text{HE}}^{(0)} = \sigma_{\text{LL}}^{(0)} \left(1 - \frac{7}{500} q_{2,6}^2 + \text{h.o.t.} \right) \quad (5.40)$$

For state selected molecules up to terms in $q_{2,6}^2$ we obtained in accordance with MIL 69:

$$\sigma_{\text{HE}}(\Omega_1, j_1, m_1) = \sigma_{\text{LL}}^{(0)} \left\{ 1 - \frac{7}{100} q_{2,6}^2 + \frac{1}{10} \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1-1)} \cdot \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \left(q_{2,6} - \frac{11}{70} q_{2,6}^2 \right) - q_{2,6}^2 \begin{pmatrix} j_1 & 4 & j_1 \\ \Omega_1 & 0 & -\Omega_1 \end{pmatrix} \begin{pmatrix} j_1 & 4 & j_1 \\ m_1 & 0 & -m_1 \end{pmatrix} \right\} \quad (5.41)$$

The term with $\begin{pmatrix} j_1 & 4 & j_1 \\ m_1 & 0 & -m_1 \end{pmatrix}$ vanishes if one has $j_1 < 2$ and the same Ω_1, j_1, m_1 dependence is obtained as in the D.W.A. (Eq. (5.33)). For small $q_{2,6}$ -values, the H.E.A. and our L.L.A. are equivalent. When $q_{2,6} = 0.16$, only a 2.5% correction on $\frac{\Delta\sigma}{\sigma^{(0)}}$ due to second order terms is present in H.E.A..

Another support for our conclusion that higher order D.W.A. contributions do not introduce sizeable anisotropy effects in the total collision cross section, comes from the excellent agreement between the exact strong coupling calculations and the first order D.W.A. calculations of Reuss and Stolte (REU 69) for $\text{H}_2\text{-Ar}$.

*) Lawley (LAW 67) derived an expression for $\sigma_{\text{HE}}^{(0)}$. His result $\sigma_{\text{HE}}^{(0)} = \sigma_{\text{LL}}^{(0)} (1 + \frac{7}{300} q_{2,6}^2)$ is incorrect, both, in sign and in magnitude in our opinion

Small impact parameter collisions can not be treated, in practice, with D W A. Strong coupling calculations can only be done in exceptional cases, where the number of energetically allowed channels is small. The only way to discuss these collisions is to make use of the dominant coupling scheme (BER 63). It turns out that 50% of the total cross section in this region is due to inelastic events, fine features of the angle-dependent part of the I P are irrelevant. Therefore, entrance channels, with different orientations (given by $j_1 m_1$), have the same total cross section when summed over all accessible elastic and inelastic exit channels. This discussion shows, that for small impact parameters the precise form of repulsive forces does not show up in the total collision cross sections.

The numerical accuracy of the L L A for $\sigma_L^{(0)}$ was investigated by Bernstein and Kramer (BER 63a). They found agreement to within 0.5%, with an exact calculation. In the approximations of Sect. 5.4, the small anisotropy effect we measure originates only from the collisions with large impact parameters. We expect

$$\frac{\sigma(\frac{3}{2}, \frac{3}{2}, \frac{3}{2}) - \sigma(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})}{\sigma^{(0)}} \equiv \frac{\Delta\sigma}{\sigma^{(0)}} = -6 \cdot 10^{-3}$$

The most pessimistic estimate could then be that our measured effect equals the uncertainty of the used theory. On the other hand, we may argue that the maximum error of 0.5% is roughly the same for different orientations, i.e. the estimated $\frac{\Delta\sigma}{\sigma^{(0)}}$ is rather insensitive to the 0.5%-error of the L L A. The relative error will, in our opinion, be little larger than 0.5% of the contribution from the Born-'tail' (which is about 20%), i.e. 25%.

The basic assumptions underlying the present calculation of anisotropy in the total collision cross section are: use of D W A for large and intermediate impact parameters, and presence of many accessible channels for small impact parameters. The first assumption fails if the secondary collision partner undergoes an inelastic collision with high probability at intermediate or large impact parameters. The second assumption fails if only a few exit channels are accessible. If glory structure is observed, an extra contribution to the anisotropy appears (MIL 69 and SCH 70). This contribution arises from intermediate impact parameters as consequence of an imperfect randomizing of the phase shifts. We have refrained from discussion of these effects.

because our experiment was not expected to show glory effects (perhaps with the exception of NO-Ar), as a result of the rather large glory numbers at the experimental velocities (Sect 7 2) and expected strong quenching, at least for systems like NO-CO₂ (BUT 71)

5 5 SMALL ANGLE SCATTERING

Small angle scattering affects our experimental results due to the finite angular resolution of our apparatus. It is expected that the effect upon anisotropy is larger than upon the average total collision cross section. The reason is that only collisions with large impact parameters contribute to $\Delta\sigma$ (Sect 5 4), these collisions are mainly affected by finite angular resolution. Angular resolution corrections were recently discussed in BUS 66 and CRO 66. For not too large corrections the 'quantum mechanical' contribution of the differential scattering is important. In this section we shall derive an expression for the small angle scattering, where angle-dependent terms of the long range potential are taken into account in first order D W A. Starting from Eq (5 13) and Eq (5 24) we have

$$\frac{d\sigma_{\mathbf{a}}}{d\Omega} = \frac{\mu^2}{4\pi^2 \hbar^4} \left[\left| T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)} \right|^2 + 2 \operatorname{Re} \left\{ T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)*} \sum_{(\mathbf{v})} t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\mathbf{v})} \right\} \right] \delta_{\mathbf{a}, \mathbf{a}'} \quad (5 42)$$

Higher order D W A contributions are neglected because only first order D W A terms do appear in the elastic channel, and higher order D W A contributions are unimportant in comparison with small angle scattering at large impact parameters. For $T_{\mathbf{a} \rightarrow \mathbf{a}'}^{(0)}$ we use Eq (5 15) and for $t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\mathbf{v})}$, Eq (5 19). Due to the averaging over all m_2 -quantum numbers (see Eq (5 28)), all $t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\mathbf{v})}$ disappear except those with $n_2 = \nu_2 = 0$. Because of Eq (5 15) we get $m_1 = m_1'$, and $\nu_1 = \nu = 0$, in first order D W A. The remaining terms are the same as for the total collision cross section

$$t_{\mathbf{a} \rightarrow \mathbf{a}'}^{(\mathbf{v})} = t_{\mathbf{a} \rightarrow \mathbf{a}'}(n_1, n_2, n, 0, s) t'_{\mathbf{a} \rightarrow \mathbf{a}'}(n, 0) \delta_{\nu_2, 0} \delta_{\nu, 0} \delta_{\nu_1, 0} \delta_{n, n_1} \delta_{n, 2} \delta_{n_2, 0} \quad (5 42)$$

with $t_{a \rightarrow a'}(n_1, n_2, n, 0, s)$ and $t_{a \rightarrow a'}(n, 0)$ explicitly given by Eq (5.19). The potential $V_0(r)$ is assumed to be proportional to r^{-6} . The term with $n = 2$ is the only angle-dependent term remaining when $n_2 = 0$. Thus one has similarly to Eq (5.31)

$$\sum_{(v)} t_{a \rightarrow a'}^{(v)} = - \frac{3m_1^2 - J_1(J_1 + 1)}{(2J_1 + 3)(2J_1 - 1)} \cdot \frac{J_1(J_1 + 1)}{J_1(J_1 + 1)} \cdot \frac{3\Omega_1^2}{k^2} \cdot \frac{4\pi}{k^2} \sum_l \frac{l+1}{2l+3} \left[\frac{l(2l+1)}{2l-1} V_2^{l,l} \right. \\ \left. \cdot e^{2i\eta_l} P_l(\cos\vartheta) - \frac{3}{2} (l+2) V_2^{l,l+2} e^{i(\eta_l + \eta_{l+2})} [P_l(\cos\vartheta) + P_{l+2}(\cos\vartheta)] \right] \quad (5.43)$$

This expression can be simplified with the approximations of Eq (5.34)

$$\eta_l = \frac{1}{2} \left(\frac{l_0}{l} \right)^5 \text{ with } l_0 = \left(\frac{3\pi}{8} \frac{\mu C_6 k^4}{\hbar^2} \right)^{\frac{1}{5}}$$

$$V_2^{l,l'} = V_2^{l,l'}{}^{\text{Born}} \text{ and } \sum_l \rightarrow \int dl$$

As further approximation we introduce $P_l(\cos\vartheta) = 1 - \frac{l^2 \vartheta^2}{4} + \dots$ for $l\vartheta \ll 1$. The final result is

$$\sum_{(v)} t_{a \rightarrow a'}^{(v)} = - \frac{3m_1^2 - J_1(J_1 + 1)}{(2J_1 + 3)(2J_1 + 1)} \cdot \frac{J_1(J_1 + 1)}{J_1(J_1 + 1)} \cdot \frac{3\Omega_1^2}{2\mu k} \cdot q_{2,6} \left[I_2 - \vartheta^2 I_4 \right] \quad (5.44a)$$

Similarly, we use (HEL 64, BER 66, MAS 64)

$$T_{a \rightarrow a'}^{(0)} = \frac{\pi \hbar^2}{\mu k} \left[I_1 - \vartheta^2 I_3 \right] \quad (5.44b)$$

The function I_i with $i = 1, 2, 3$ and 4 , stands for

$$I_1 = \int_0^\infty \sin \eta_l^{\text{Born}} e^{i\eta_l^{\text{Born}}} 4l dl = l_0^2 \Gamma\left(\frac{3}{5}\right) e^{i \frac{3}{10} \pi} \\ I_2 = \int_0^\infty e^{i 2 \eta_l^{\text{Born}}} \left(\frac{l_0}{l} \right)^5 l dl = \frac{1}{5} l_0^2 \Gamma\left(\frac{3}{5}\right) e^{i \frac{3}{10} \pi}$$

$$\begin{aligned}
I_3 &= \int_0^{\infty} \sin \eta_l^{\text{Born}} e^{i \eta_l^{\text{Born}}} l^3 dl = \frac{1}{8} l_0^4 \Gamma\left(\frac{1}{5}\right) e^{i \frac{1}{10} \pi} \\
I_4 &= \int_0^{\infty} e^{i \cdot 2 \eta_l^{\text{Born}}} \left(\frac{l_0}{l}\right)^5 \cdot \frac{1}{4} l dl = \frac{1}{10} l_0^4 \Gamma\left(\frac{1}{5}\right) e^{i \frac{1}{10} \pi} \quad (5.45)
\end{aligned}$$

The integrals were calculated using GROB 61 (Eq. 333.10a and 10b). Combining these results with Eq. (5.42) we get for the differential cross section, $\frac{d\sigma(\Omega_1, j_1, m_1)}{d\Omega}$, of a state selected beam up to second order in ϑ :

$$\begin{aligned}
\frac{d\sigma(\Omega_1, j_1, m_1)}{d\Omega} &= \frac{l_0^4}{4k^2} \left\{ \Gamma\left(\frac{3}{5}\right) \cdot \frac{1}{4} (\vartheta l_0)^2 \cdot \Gamma\left(\frac{3}{5}\right) \cdot \Gamma\left(\frac{1}{5}\right) \cdot \cos\left(\frac{1}{5}\pi\right) \right\} + \\
&+ \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1-1)} \cdot \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \cdot \\
&\cdot \frac{1}{5} q_{2,6} \left\{ \Gamma\left(\frac{3}{5}\right)^2 - \frac{3}{8} (\vartheta l_0)^2 \cdot \Gamma\left(\frac{3}{5}\right) \cdot \Gamma\left(\frac{1}{5}\right) \cdot \cos\left(\frac{1}{5}\pi\right) \right\} \quad (5.46)
\end{aligned}$$

If the Γ -functions are replaced for numerical values and the quantity ϑ^* is introduced (HEL 64):

$$\vartheta^* \equiv \frac{1}{l_0} \sqrt{\frac{4\Gamma\left(\frac{3}{5}\right)}{\Gamma\left(\frac{1}{5}\right) \cos\left(\frac{\pi}{5}\right)}} = \frac{1.965}{k} \sqrt{\frac{\pi}{\sigma_{LL}^{(0)}}} \quad (5.47)$$

we obtain:

$$\begin{aligned}
\frac{d\sigma(\Omega_1, j_1, m_1)}{d\Omega} &= \frac{d\sigma^{(0)}}{d\Omega} \bigg|_{\vartheta=0} \cdot \\
&\cdot \left[1 - \left(\frac{\vartheta}{\vartheta^*}\right)^2 + \frac{1}{5} q_{2,6} \frac{3m_1^2 - j_1(j_1+1)}{(2j_1+3)(2j_1-1)} \cdot \frac{j_1(j_1+1) - 3\Omega_1^2}{j_1(j_1+1)} \left\{ 1 - \left(\frac{\vartheta}{\frac{1}{\sqrt{2}}\vartheta^*}\right)^2 \right\} \right] \\
\text{and } \frac{d\sigma^{(0)}}{d\Omega} \bigg|_{\vartheta=0} &= 1.528 \left(\frac{k\sigma_{LL}^{(0)}}{4\pi} \right)^2 \quad (5.48)
\end{aligned}$$

Comparison of Eq. (5.33) with Eq. (5.47) shows that the anisotropy term in the forward part of the differential cross section is twice as strong (factor $\frac{1}{\frac{1}{6}}$) as the corresponding term in the total collision cross section (factor $\frac{1}{10}$). For increasing ϑ we see a sharper fall off for the m_1 -dependent term $(1 - (\frac{\vartheta}{\frac{2}{3}\vartheta^*})^2)$ than for the term independent of m_1 $(1 - (\frac{\vartheta}{\vartheta^*})^2)$.

FORMAL TRANSFORMATION OF EXPERIMENTAL DATA INTO PHYSICAL QUANTITIES

6.1 THE TOTAL COLLISION CROSS SECTION IN A MAGNETIC FIELD

In this Section we will provide the formalism needed for the discussion of the influence of the direction and the strength of a magnetic field in the scattering region on the total collision cross section. The rotational behaviour of an NO molecule is actually more complicated than was assumed in Chapter 5. Hyperfine structure and Λ -doubling produce eigenstates which are a mixture of several $|\Omega, J, m_J\rangle$ states (KUIJ 69, NEU 70, MFL 72). A particular rotational state of NO in an arbitrary B-field is characterized by the set of quantum numbers $\{|\Omega|^\pm, J, I, \tilde{F}, m_F\}$. The quantum number I stands for the spin of the ^{14}N nucleus, and $\tilde{F}$ for the total angular momentum of the molecule in the case $B \rightarrow 0$ ($F = I + J$). Each $\tilde{F}$ -state consists of a Λ -doublet; the superscript $+$ ($-$) of $|\Omega|^\pm$ indicates the higher (lower) level. The projections of the total angular momentum and the nuclear spin along the B field direction are $\hbar m_F$ and $\hbar m_I$ with $m_F = m_J + m_I$. We make the expansion

$$| |\Omega|^\pm, J, I, \tilde{F}, m_F \rangle = \sum_{m_I, m_J} \alpha_{m_I, m_J}^{|\Omega|^\pm, J, I, \tilde{F}}(B) | |\Omega|^\pm, I, m_I \rangle | J, m_J \rangle \delta_{m_I + m_J, m_F} \quad (6.1)$$

The coefficients $\alpha_{m_I, m_J}^{|\Omega|^\pm, J, I, \tilde{F}}(B)$ depend on the magnetic field strength B and are different for each $| |\Omega|^\pm, J, I, \tilde{F}, m_I \rangle$ state.

Let the relative velocity of a particular scattering event make an angle β with respect to the direction of the B-field. If $| J, m_J \rangle$ describes the state with m_J' specified along the direction of the relative velocity we get

$$| |\Omega|^\pm, J, I, \tilde{F}, m_F \rangle = \sum_{m_I, m_J, m_J'} \alpha_{m_I, m_J}^{|\Omega|^\pm, J, I, \tilde{F}}(B) d_{m_J', m_I}^J(\beta) | |\Omega|^\pm, I, m_I \rangle | J, m_J' \rangle \delta_{m_I + m_J, m_F} \quad (6.2)$$

The rotation matrix elements, $d_{m_j' m_j}^j(\beta)$, are defined in Edmonds [FDM 60 Eq (4 1 15)] The quantum number m_I remains defined along the direction of the B-field We assume for the total collision cross section of a molecule in a $|\Omega|^{\pm}, J, I, \tilde{F}, m_F\rangle$ state

$$\sigma(B, |\Omega|^{\pm}, J, I, \tilde{F}, m_F) = \sum_{m_j, m_j'} \left| \alpha_{m_I, m_j}^{|\Omega|^{\pm}, I, J, \tilde{F}}(B) \right|^2 \left| d_{m_j' m_j}^j(\beta) \right|^2 \delta_{m_I + m_j, m_I} \sigma(\Omega, J, m_j') \quad (6.3)$$

Using explicit expressions for $d_{m_j' m_j}^j(\beta)$ given in BRI 62, and Eq (5.31), we get for $J=3/2$

$$\sigma(B, \tilde{F}, m_F) = \sigma^{(0)} + (2W_{\tilde{F}, m_F} - 1) \left(\frac{3}{4} \cos 2\beta + \frac{1}{4} \right) \frac{\Delta\sigma}{2}$$

where $\sigma(B, \tilde{F}, m_I) \equiv \sigma(B, |\Omega|^{\pm}, J, I, \tilde{F}, m_F)$,

$$\text{and } W_{\tilde{F}, m_F} \equiv \left| \alpha_{m_F - 3/2, 3/2}^{|\Omega|^{\pm}, I, J, \tilde{F}}(B) \right|^2 + \left| \alpha_{m_F + 3/2, -3/2}^{|\Omega|^{\pm}, I, J, \tilde{F}}(B) \right|^2$$

$$\text{with } |\Omega|^{\pm} = \frac{3}{2}^{\pm}, I = 1, J = \frac{3}{2} \quad (6.4)$$

The definition of $\Delta\sigma$ was given in Eq (5.31)

The quantity $W_{\tilde{F}, m_F}$ is the probability of finding the NO molecule in a state with $|m_j| = 3/2$ (In $W_{\tilde{F}, m_F}$ we dropped the $(\pm)$ superscript since the Zeeman effect is practically identical for states differing only in $(\pm)$ symmetry (KUIJ 69))

As is discussed in Appendix (A2), NO molecules with $J=3/2$, $\tilde{F}=5/2$, $|\Omega|^{\pm}=3/2^+$ and $m_I = 5/2, 3/2, 1/2$, are in the selected state In Table 6.1 $W_{5/2, m_F}$ is given as a function of the magnetic field for $m_F > 0$ between 0 and 500G In strong magnetic fields, the nuclear spin is completely decoupled and $W_{5/2, m_F} = 1$ for $m_F = 5/2, 3/2, 1/2$

Molecules in zero field states with $|\Omega|^{\pm}=3/2^+$, $m_F=-5/2, -3/2, -1/2$ are also focused by the action of the state selector During their passage from the six-pole to the scattering region, molecules in such states adiabatically change to a single state with $|\Omega|^{\pm}=3/2^+$, $\tilde{F}=5/2$, $m_F > 0$ This is discussed in the Sections 4.2 and Appendix (A3) Consequently, the $W_{5/2, m_F}$ with $m_I > 0$ of Table 6.1 are also used here

TABLE 6.1

Numerical values of $W_{5/2,m_F}$, W and P at various B-fields

These quantities were calculated with a computer program of Meerts (MEE 70). The molecular constants used in this program are taken from new M.B.R. measurements (MEE 72).

B[G]	$W_{5/2,5/2}$	$W_{5/2,3/2}$	$W_{5/2,1/2}$	W	$P \equiv 2W - 1$
0	1.000	0.400	0.100	0.500	0.000
10	1.000	0.470	0.139	0.537	0.073
25	1.000	0.578	0.221	0.600	0.199
50	1.000	0.730	0.419	0.717	0.433
75	1.000	0.831	0.632	0.821	0.642
100	1.000	0.889	0.781	0.890	0.780
125	1.000	0.924	0.865	0.930	0.859
150	1.000	0.946	0.911	0.952	0.905
175	1.000	0.959	0.938	0.966	0.932
200	1.000	0.969	0.955	0.974	0.949
250	1.000	0.980	0.973	0.984	0.969
500	1.000	0.995	0.994	0.996	0.993
∞	1.000	1.000	1.000	1.000	1.000

The attenuation of the primary beam for a particular hyperfine level is given by:

$$i_{m_F} = i_{m_F}^{(0)} \exp \left[-nl \frac{v_{rel}}{v_1} \left(\sigma^{(0)} + \frac{\Delta\sigma}{2} (2W_{F,m_F} - 1) \left(\frac{3}{4} \cos 2\beta + \frac{1}{4} \right) \right) \right], \quad (6.5)$$

with n = density of the secondary beam,

l = length of the scattering region,

v_1 = velocity of the primary beam in the laboratory system ,

v_{rel} = relative velocity of the colliding molecules.

The exponent is approximately -1 in our experiment. With $i = \sum_{m_F} i_{m_F}$ and $i^{(0)} = \sum_{m_F} i_{m_F}^{(0)}$ it follows from Eq. (6.5) for the intensity i of the state selected beam to good approximation:

$$i = i^{(0)} \exp \left[-nl \frac{v_{rel}}{v_1} \left(\sigma^{(0)} + P \frac{\Delta\sigma}{2} \left(\frac{3}{4} \cos 2\beta + \frac{1}{4} \right) \right) \right]. \quad (6.6)$$

The polarization P is defined as $P=2W-1$, with $W=\sum_{m_F > 0} W_{\tilde{F}, m_F} i_{m_F}^{(0)}$. (6.7)

A sufficient condition for the approximation leading to Eq. (6.6) is $\Delta\sigma \ll \sigma^{(0)}$, which is of course very well satisfied. In Table 6.1, values of P and W are shown for different field strengths. They were calculated using $i_{m_F}^{(0)} = \frac{1}{3}$. Possible small differences in $i_{m_F}^{(0)}$ for different m_F values do not effect the values of P and W needed for the experiment because $W_{\tilde{F}, m_F}$ is nearly independent of m_F in fields of about 150 G used for the anisotropy measurements.

6.2. EXPERIMENTAL CORRECTION FACTORS

In the experiment we compare the beam intensities for two situations, $\beta=0^\circ$ and 90° . To these two situations correspond the two experimental (effective) total cross sections σ_H^e and $\sigma_\perp^e$. We form the quantity $\frac{\sigma_H^e \sigma_\perp^e}{\sigma_0^e}$ which is related to the theoretical anisotropy $\frac{\sigma_H - \sigma_\perp}{\sigma_H} = \frac{3}{4} \frac{\Delta\sigma}{\sigma_H} \approx \frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}}$. The last approximation is allowed because $|\frac{\Delta\sigma}{\sigma^{(0)}}| \ll 1$. From now on we will always use this approximation without further mention.

The relation between $\frac{\sigma_H^e \sigma_\perp^e}{\sigma_0^e}$ and $\frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}}$ is complicated by the unavoidable inhomogeneity of the magnetic field both in strength and in direction over the scattering region, by the incomplete decoupling of the nuclear spin, by the velocity distribution of the secondary beam, and by finite angular resolution. We write this relation in the form:

$$\frac{\sigma_H^e \sigma_\perp^e}{\sigma_0^e} = C \frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}}$$

$$\text{with } C = C_{\gamma, \Delta} C_{v_2} C_{\tilde{B}} C_{\Delta B} C_{B_0} \quad (6.8)$$

The quantity C is a product of a number of correction factors, each associated with a deviation of experimental conditions from the ideal situation assumed in the theoretical derivation of $\frac{\Delta\sigma}{\sigma^{(0)}}$. $C_{B_0}=P$ comes from the incomplete decoupling of the nuclear spin. $C_{\Delta B}$ arises from variation in strength of the B-field in the scattering region. $C_{\tilde{B}}$ takes into account a variation in the direction of the B-field. $C_{\gamma, \Delta}$ is determined by the finite angular resolution of the machine, and finally, C_{v_2} comes from the velocity distribution of the

secondary beam molecules effusing from the multichannel array. In the next Sections of this Chapter we will discuss these C-factors.

6.3 EVALUATION OF C_{AB} AND C_B

The Helmholtz coils produce a magnetic field with considerable inhomogeneity in the scattering region (Sect. 3.6). Its influence on $\frac{\sigma_H - \sigma_V}{\sigma_H^0}$ will be investigated and shown to be very small. The correction will be performed in lowest order assuming a unidirectional and monochromatic secondary beam with velocity v_2 . The choice of $\mathbf{B}$ in the experiment is sensitive to the direction of the relative velocity $\mathbf{v}_{rel}$ with respect to the direction of the primary beam molecules $\mathbf{v}_1$. This direction is defined by the angle θ , with $\tan \theta = \frac{v_2}{v_1}$. The direction of $\mathbf{B}$ with respect to $\mathbf{v}_1$ is described by the angle τ , with $\tau = \theta + \beta$. From Eq. (6.6) the collision cross section in a uniform field is

$$\sigma(\beta, v_{rel}) = \frac{v_{rel}}{v_1} \left[\sigma^{(0)}(v_{rel}) + P \frac{\Delta\sigma(v_{rel})}{2} \left(\frac{3}{4} \cos 2(\tau - \theta) + \frac{1}{4} \right) \right] \quad (6.9)$$

For a given θ we choose, in the center of the scattering region, the magnetic field $|\mathbf{B}| = B_0$. To this field strength corresponds a definite value of P ($\equiv P_0$), which is independent of τ . The direction of the field is made parallel or perpendicular to $\mathbf{v}_{rel}$. These two choices of $\mathbf{B}$ define, in the center of the scattering region, two values of τ ($\tau_{\parallel}$ and $\tau_{\perp} = \tau_{\parallel} + 90^\circ$). We then have

$$\frac{\sigma_H^0 - \sigma_V^0}{\sigma_H^0} = \frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}} P_0 \cos 2(\tau_{\parallel} - \theta) \quad (6.9a)$$

However, at a distance from the scattering center along the primary beam axis we have two different values for τ and for P : $\tau = \tau_{\parallel} + \Delta\tau_{\parallel}$ or $\tau_{\perp} + \Delta\tau_{\perp}$ and $P = P_{\parallel}$ or $P_{\perp}$. This comes from the fact that the strength of the field at a point outside the scattering center changes slightly when the field orientation is changed by 90° . Moreover, this strength is different from B_0 as a result of imperfect homogeneity of the Helmholtz field.

The averaging of $\sigma(\beta, v_{rel})$ (of Eq. (6.9)) over the scattering region for the appropriate field orientations yields, under the assumption of a uniform secondary beam density

$$\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e} = \frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}} P_0 \cos 2(\tau_H - \theta) \quad (6.10)$$

$$\left\langle \frac{\frac{1}{6}(P_H - P_\perp) + \frac{1}{2}P_H \cos 2(\tau_H - \theta + \Delta\tau_H) + \frac{1}{2}P_\perp \cos 2(\tau_H - \theta + \Delta\tau_\perp)}{P_0 \cos(\tau_H - \theta)} \right\rangle_{\text{scattering region}}$$

We neglect higher order corrections and find for $\tau_H - \theta = 0$

$$\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e} = \frac{3}{4} \frac{\Delta\sigma}{\sigma^{(0)}} C_{B_0} C_{\Delta B} C_{\hat{B}} \quad (6.11)$$

where we identify

$$C_{B_0} = P_0 \quad (6.12)$$

$$C_{\Delta B} = \left\langle \frac{2P_H + P_\perp}{3P_0} \right\rangle_{\text{scattering region}} \quad (6.13)$$

and

$$C_{\hat{B}} = 1 - \left\langle \Delta\tau_H^2 + \Delta\tau_\perp^2 \right\rangle_{\text{scattering region}} \quad (6.14)$$

For the magnetic field at position x along the primary beam axis we write

$$\mathbf{B} = B_H \hat{x} + B_V \hat{z} \quad (6.15)$$

where $B_H(B_V)$ is the magnetic field strength of the Helmholtz coil pair I (II) which is pointed along the $v_1(v_2)$ direction defining the $\hat{x}(\hat{z})$ axis respectively (Sect. 3.6). Furthermore, we use the quadratic approximations

$$B_H = B_H^{(0)} \left[1 + \frac{\Delta B_H}{B_H^{(0)}} \left(\frac{x}{x_0} \right)^2 \right]$$

$$B_V = B_V^{(0)} \left[1 + \frac{\Delta B_V}{B_V^{(0)}} \left(\frac{x}{x_0} \right)^2 \right] \quad (6.16)$$

where x_0 is the maximum distance from the scattering center, along the primary beam axis, at which scattering takes place. For our experiments $x_0 = 2.5$ cm. From an empirical fit to the measured B-fields of Fig. 3.3 we

have $\frac{\Delta B_h}{B_h^{(0)}} = 0.24$ and $\frac{\Delta B_v}{B_v^{(0)}} = -0.06$ Here, $B_h^{(0)}$ and $B_v^{(0)}$ are the components

of B at $x=0$ along the $\hat{x}$ and $\hat{z}$ -axis, respectively

As $\frac{\Delta B_v}{B_v^{(0)}} \ll 1$ and $\frac{\Delta B_h}{B_h^{(0)}} \ll 1$, simple geometric considerations yield

$$\Delta\tau_{\parallel} = \Delta\tau_{\perp} = \frac{1}{2} \left(\frac{B_v}{B_v^{(0)}} - \frac{B_h}{B_h^{(0)}} \right) \sin 2\theta \quad (6.17)$$

Also, at x , with $B_0 \parallel v_{rel}$

$$B_{\parallel} = B_0 \left[1 + \cos^2 \tau_{\parallel} \left(\frac{B_h - B_h^{(0)}}{B_h^{(0)}} \right) + \sin^2 \tau_{\parallel} \left(\frac{B_v - B_v^{(0)}}{B_v^{(0)}} \right) \right], \quad (6.18)$$

and with $B_0 \perp v_{rel}$

$$B_{\perp} = B_0 \left[1 + \cos^2 \tau_{\perp} \left(\frac{B_h - B_h^{(0)}}{B_h^{(0)}} \right) + \sin^2 \tau_{\perp} \left(\frac{B_v - B_v^{(0)}}{B_v^{(0)}} \right) \right] \quad (6.18a)$$

Using the Taylor expansions, $P_{\parallel} = P_0 + \frac{dP_0}{dB_0} (B_{\parallel} - B_0)$ and $P_{\perp} = P_0 + \frac{dP_0}{dB_0} (B_{\perp} - B_0)$, and substituting the explicit expressions (6.18), (6.18a) and (6.16) into Eq (6.13), we find

$$C_{\Delta B} = 1 + \frac{1}{9} \frac{B_0}{P_0} \frac{dP_0}{dB_0} \left[(\cos^2 \theta + 1) \frac{\Delta B_h}{B_h^{(0)}} + (\sin^2 \theta + 1) \frac{\Delta B_v}{B_v^{(0)}} \right] \quad (6.19)$$

At $B_0 = 150$ G it follows from Table 6.1 that

$$\frac{B_0}{P_0} \frac{dP_0}{dB_0} = 0.23$$

Substitution of Eqs (6.17) and (6.16) into Eq (6.13) yields

$$C_{\mathbf{B}} = 1 - \frac{1}{10} \left[\left(\frac{\Delta B_v}{B_v^{(0)}} - \frac{\Delta B_h}{B_h^{(0)}} \right) \sin 2\theta \right]^2 \quad (6.20)$$

In Table 6.2, the values of $C_{\mathbf{B}}$ and $C_{\Delta B}$ appropriate to our experiment are shown. For all θ , the C-values are notably close to one

TABLE 6.2

The values of the correction factors C_B and $C_{\Delta B}$ for $B_0=150^\circ$, and different θ values

	$\tan \theta=1$	$\tan \theta=1.2$	$\tan \theta=1.3$	$\tan \theta=1.4$	$\tan \theta=\infty$
C_B	0.991	0.994	0.997	0.998	1.000
$C_{\Delta B}$	1.007	1.009	1.010	1.010	1.011

6.4 THE INFLUENCE OF THE TARGET MOTION

In this Section, the influence of the velocity distribution of the secondary beam on $\frac{\sigma_H^e - \sigma_e^e}{\sigma_H^e}$ is investigated. We assume that the secondary beam is sharply directed perpendicular to the primary beam and has a Maxwellian velocity distribution. Buck *et al.* (BUC 71) have shown experimentally with a Hg-beam, that the assumption of a Maxwellian distribution is valid in the forward direction for a single channel with length and diameter of 4 and 1 mm, respectively. The Hg-effusive beam ($P \approx 0.1$ torr) was found to be Maxwellian to within 2%.

We use a multi channel effuser, under conditions of the mean free path of the molecules much larger than the channel diameter (Permeonics, channel diameter 5μ , driven by a pressure of about 0.2 torr). With the assumption of a Maxwellian velocity distribution the effect on the anisotropy $\frac{\sigma_H^e - \sigma_e^e}{\sigma_H^e}$ can readily be estimated in a way similar to the procedure of Berkling *et al.* (BLR 62). Using Eq. (6.9), we have

$$\frac{\sigma_H^e - \sigma_e^e}{\sigma_H^e} = \frac{\int_0^\infty n l [\sigma(\beta, v_{rel}) - \sigma(\beta+90^\circ, v_{rel})] \frac{v_{rel}}{v_1} f(v_2) dv_2}{\int_0^\infty n l \sigma^{(0)}(v_{rel}) \frac{v_{rel}}{v_2} f(v_2) dv_2} \quad (6.21)$$

$$\text{with } f(v_2) = \frac{4}{\sqrt{\pi}} (v_{2,p})^{-\frac{3}{2}} e^{-\left(\frac{v_2}{v_{2,p}}\right)^2} v_2^2, \quad (v_{2,p})^2 = \frac{2 kT}{m_2}$$

$$\text{and } \sigma(\beta, v_{rel}) \equiv \sigma^{(0)}(v_{rel}) C_{B_0} \frac{\Delta \sigma(v_{rel})}{2} \left(\frac{3}{4} \cos 2\beta + \frac{1}{4} \right)$$

In Eq (6 21) we have assumed that $C_B=1$ and $C_{\Delta B}=1$ For a pure r^{-6} dependent attractive potential, Eqs (5 33) and (6 21) yield

$$\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e} = \frac{\sigma_H - \sigma_L}{\sigma(0)} \left[[1 - 2 \text{Sb}_2(6, X)] \cos 2 \tau_H - 2 \frac{\text{Fn}(6, X)}{\text{Fb}_0(6, X)} \sin 2 \tau_H \right] \quad (6 22)$$

$$\begin{aligned} \text{Here (BER 62)} \quad \text{Fb}_0(6, X) &= \frac{4}{\sqrt{\pi}} X^{-3/5} \int_0^\infty [X^2 + u^2]^{-7/10} u^2 e^{-u^2} du, \\ \text{Sb}_2(6, X) &= \frac{4}{\sqrt{\pi}} X^{-3/5} \int_0^\infty [X^2 + u^2]^{-7/5} u^4 e^{-u^2} du \end{aligned}$$

$$\text{and } X = \frac{v_1}{v_{2,p}}$$

In addition, we define

$$\text{Fn}(6, X) \equiv \frac{4}{\sqrt{\pi}} X^{2/5} \int_0^\infty [X^2 + u^2]^{-7/10} u^3 e^{-u^2} du \quad (6 23)$$

(Numerical values of $\text{Fn}(6, X)$ are collected in RAG 72)

Equation (6 22) can also be written as

$$\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e} = \frac{\sigma_H - \sigma_L}{\sigma(0)} C_{v_2} \quad \text{with } C_{v_2} = C_X \cos 2(\tau_H - \theta_X) \quad (6 24)$$

where

$$C_X = \sqrt{[1 - 2 \text{Sb}_2(6, X)]^2 + [2 \text{Fn}(6, X) / \text{Fb}_0(6, X)]^2}$$

and

$$\tan 2 \theta_X = \frac{\text{Fn}(6, X)}{\text{Fb}_0(6, X)} \frac{2}{1 - 2 \text{Sb}_2(6, X)}$$

Comparison of Eq (6 24) with Eq (6 9a) shows that the behaviour of a monochromatic and of a Maxwellian secondary beam are similar. If all the molecules of the secondary beam are assumed to have the velocity $v_{2,p}$ the effect would be maximum at $\tau = \theta = \arctan \frac{1}{X}$. Table 6 3 shows that the difference between θ_X and θ is very small over the entire X -range ($\leq 2.6^\circ$). Also, the correction factor C_X remains close to unity, the deviation is the largest around $X=1$.

TABLE 6.3

Influence of target motion on the anisotropy effect

A unidirectional secondary beam with a Maxwellian velocity distribution is assumed. The quantities X , C_X , θ_X and θ are defined in the text

X	C_X	θ_X	$\theta \equiv \arctan \frac{1}{X}$
0	1.000	90.0°	90.0°
1/4	0.990	76.9°	75.0°
1	0.911	47.6°	45.0°
2	0.940	29.0°	26.6°
3	0.964	20.4°	18.4°
4	0.976	15.7°	14.0°
5	0.984	12.7°	11.3°
6	0.988	10.6°	9.5°
∞	1.000	0.0°	0.0°

These corrections are much smaller than in the earlier experiments with state selected CsF and TIF beams (BFN 64 and BFN 69a)

In the above discussion we assumed a unidirectional secondary beam. However, multichannel effusers have a peculiar and broad angular distribution (approximately 20° effective angular spread). A discussion of the angular spread and its influence on glory undulations is given by Feltgen (FFL 70). In our situation, corrections are more difficult to calculate, but less severe. More difficult, because the direction of the relative velocity also enters, less severe, because the absolute value of v_{rel} is of little importance. For r^{-6} potentials $\frac{\sigma_{\parallel}}{\sigma_{\perp}}$ is independent of v_{rel} in contrast to the case of glory undulations.

If $\frac{v_1}{v_2} = 2$, a variation of the secondary beam direction of +20° and -20° only produces a variation in the direction of the relative velocity of +3° and -5°, respectively. A strong change in C_X and θ_X is not to be expected from this angular spread. The combined effect of angular and velocity spread has been calculated in more detail by Ragas (RAG 72), using a Zugenmaier profile (ZUG 66) for the angular distribution. His results confirm our assumptions that these corrections are small.

The angular resolution of our molecular beam machine influences the experimental *total* collision cross section (BUS 66)

$$\begin{aligned}\sigma^e|_\gamma &= \sigma^e - \int_{\Omega_a} \frac{d\sigma^e}{d\Omega} d\Omega \\ &= C_\gamma \sigma^e\end{aligned}\quad (6.25)$$

In this formula σ^e is the effective collision cross section of an m_j -averaged primary beam and Ω_a is the laboratory (lab) acceptance angle of the detector as seen from the scattering center. In the case of slit geometry, as discussed by Von Busch (BUS 66), C_γ is given by

$$\begin{aligned}C_\gamma &= 1 - 0.2314 \frac{\gamma}{\theta^*} \left[1 - 0.0983 \frac{\gamma}{\theta^*} + 0 \left(\frac{\gamma}{\theta^*} \right)^3 \right] \\ \text{with } \theta^* &= \frac{1.965}{k_1} \left[\frac{\pi}{\sigma^{(0)}(v_1) \left(1 + \frac{0.4}{X^2} \right)} \right]^{1/2}\end{aligned}\quad (6.26)$$

where γ is the lab angle under which, in the plane of the detector slit, the full width at half maximum of the primary beam profile is seen from the scattering center. The wave number $k_1 = m_1 v_1 / \hbar$, the angle θ^* in the lab system corresponds to ϑ^* in the c.m. system (Sect. 5.5). If terms of order $\left(\frac{\gamma}{\theta^*} \right)^2$ and higher are neglected Eq. (6.26) simplifies to

$$C_\gamma = 1 - 0.06646 \left[\sigma^{(0)}(v_1) \right]^{1/2} k_1 \gamma \left(1 + \frac{0.374}{X^2} \right) \quad (6.27)$$

Equations (6.26) and (6.27) were derived by Von Busch under the assumptions 1) pure r^{-6} attraction, 2) height of the detector slit much larger than its width, 3) use of scattering chamber instead of secondary beam, 4) $X \geq 2$, and finally 5) $C_\gamma \approx 1$. The assumption 1) is in agreement with our general treatment (see Chap. 5). Assumption 2) applies because for the measurements of Sect. 7.3 the detector has a slit height of 8 mm and a width of 1 mm. Assumption 3) is not valid in our experiment. However, Beck and Loesch (BEC 66) have shown that, for a secondary beam, only the correction term $\frac{0.374}{X^2}$ in Eq. (6.27) should be replaced by $\frac{0.225}{X^2}$. We neglect this

TABLE 6 4

(correction factors due to finite angular resolution)

The cross section $\sigma^{(0)}(v_1)$ is calculated with aid of empirical potential parameters (see Table 5 2) The primary beam velocity (corresponding to the experimental situation) is $v_1=525$ m/sec Different γ 's correspond to slightly different machine geometries The correction factors C_γ and $C_{\gamma \Delta}$ were calculated with Eqs (6 27) and (6 32) respectively The influence of X was neglected in θ^* , C_γ and $C_{\gamma \Delta}$

Collision partners of NO	$\sigma^{(0)}(v_1)$ [10^{-16} cm ²]	γ [10^{-3} rad]	θ^* [10^{-3} rad]	λ	C_γ	$C_{\gamma \Delta}$
Cl ₂	1078	2.79	4.28	3.14	0.849	0.888
S ₂	781	2.79	5.03	2.53	0.872	0.907
N ₂ O	559	2.79	5.94	2.34	0.891	0.923
O ₂	563	3.41	5.92	2.34	0.867	0.903
Ar	426	2.79	6.80	2.57	0.905	0.934
N ₂	439	3.41	6.70	1.86	0.882	0.916
H ₂	279		8.41			

correction term since it contributes less than 0.6% to the total collision cross section (Table 6 4) Assumption 4) and 5) also apply in our case Von Busch strictly required $\frac{\gamma}{\theta^*} \leq 0.2$, but Formula (6 26) may be used as long as $\frac{\gamma}{\theta^*} \leq 1$ (MUL 71)

In the anisotropy experiment, not σ^e_γ but $\frac{\sigma^e_\parallel}{\sigma^e_\perp}$ is measured Therefore we have

$$\left. \frac{\sigma^e_\parallel}{\sigma^e_\perp} \right|_\gamma = \frac{(\sigma^e_\parallel - \sigma^e_\perp) \int_{\Omega_a} \left(\frac{d\sigma^e_\parallel}{d\Omega} - \frac{d\sigma^e_\perp}{d\Omega} \right) d\Omega}{\sigma^e - \int_{\Omega_a} \frac{d\sigma^e}{d\Omega} d\Omega} \quad (6 28)$$

and we define

$$\left. \frac{\sigma^e_\parallel}{\sigma^e_\perp} \right|_\gamma = C_{\gamma \Delta} \frac{\sigma^e_\parallel}{\sigma^e} \quad (6 29)$$

With Eq (5.47) we have for small ϑ

$$\frac{d\sigma_{\parallel}}{d\Omega} - \frac{d\sigma_{\perp}}{d\Omega} = (\sigma_{\parallel} - \sigma_{\perp}) \frac{\left. \frac{d\sigma^{(0)}}{d\Omega} \right|_{\vartheta=0}}{\sigma^{(0)}} 2 \left\{ 1 - \left(\frac{\vartheta}{\sqrt{\frac{2}{3}} \vartheta^*} \right)^2 \right\} \quad (6.30)$$

and

$$\frac{d\sigma^{(0)}}{d\Omega} = \sigma^{(0)} \frac{\left. \frac{d\sigma^{(0)}}{d\Omega} \right|_{\vartheta=0}}{\sigma^{(0)}} \left\{ 1 - \left(\frac{\vartheta}{\vartheta^*} \right)^2 \right\} \quad (6.31)$$

The integrand of the numerator and of the denominator of Eq (6.28) have a similar small angle dependence. This needs not to be the case for larger angles ($\vartheta \geq \vartheta^*$), but the value of the differential cross section has then become so small, that its precise value is no longer of importance. With Eqs (6.31) and (6.28) we obtain

$$C_{\gamma,\Delta} = \frac{1 - 2 \sqrt{\frac{2}{3}} 0.06646 k_1 (\sigma^{(0)}(v_1))^{1/2} \gamma}{1 - 0.06646 k_1 (\sigma^{(0)}(v_1))^{1/2} \gamma} \quad (6.32)$$

Values of C_{γ} and $C_{\gamma,\Delta}$ are shown in Table 6.4, a correction of approximately 10% has to be applied to $\frac{\sigma_{\parallel}^E - \sigma_{\perp}^E}{\sigma_{\parallel}^E} \Big|_{\gamma}$

Some comment should be made concerning this result. First, we have not taken into account the part of the state selected primary beam which, deflected by the Rabi field, is scattered back into the detector slit by the molecules of the secondary beam. During the scattering measurements a deflection in the detector plane of about 2 mm or a deflection angle of 3.8×10^{-3} rad seen from the scattering center, was obtained. This has to be compared to $\sqrt{\frac{2}{3}} \vartheta^* = 2.7 \times 10^{-3}$ rad in the case of NO-Cl₄. Although more accurate calculations have not yet been performed, we estimate a decrease in $(1 - C_{\gamma})$ of about 30%.

Second, Von Busch *et al* (BUS 67) claim to have given a slightly better formula instead of Eq (6.27). The new formula was obtained using a numerical fit for the differential collision cross section (see Sect. 7.1). The factor 0.06646 in our Eq (6.27) then becomes 0.0761. A similar correction should be made in Eq (6.32), but there are no calculations available for $\frac{d\sigma_{\parallel}}{d\Omega}$ and $\frac{d\sigma_{\perp}}{d\Omega}$.

Therefore we use Eq. (6.32) for correcting $\frac{\sigma_H^2}{\sigma_E^2} \Big|_{\gamma}$. The extra error caused hereby in $\frac{\sigma_H^2}{\sigma_E^2}$ is 3%. This should be compared with the statistical error, which is never smaller than 10%.

The corrections derived in this Chapter are applied to the experimental data in Chapter 7, and the final results are presented in Table 8.1.

SCATTERING RESULTS

7.1. DETERMINATION OF THE TOTAL COLLISION CROSS SECTION

The systems, for which the anisotropy effect in the total collision cross section is measured, were never before investigated in molecular beam scattering experiments. Consequently, the interesting and, for the present experiments, important quantity, the total collision cross section $\sigma^{(0)}$, was not known. The importance of $\sigma^{(0)}$ stems from the fact that it is directly connected to the intermolecular distance at which we probe the anisotropy of the I.P. (Sect. 5.3).

Normally, the difficult point in measuring the absolute value of $\sigma^{(0)}$ is the determination of the absolute particle density in the scattering region (BEN 65, SCH 71). With secondary beams such a determination looks hopeless. An alternative way to find $\sigma^{(0)}$ is the measurement of $\sigma^e|_\gamma$ as a function of the angular resolution (HEL 64). Moreover, such a measurement provides information about the angular resolution correction C_γ (Sect. 6.4).

In our apparatus we can continuously vary the width of the collimating slit s_2 (Fig. 2.1), thereby changing the angular resolution in a known way. The cross section for small γ (see Eq. (6.27) and the remarks following that equation) is given by:

$$\sigma^e|_\gamma = \left[1 - 0.0761 k_1 \sqrt{\sigma^{(0)}(v_1)} \gamma \left(1 + \frac{0.225}{X^2} \right) \right] \sigma^e,$$

$$\text{with } \sigma^e = \sigma^e|_{\gamma=0}. \quad (7.1)$$

The nice feature of Eq. (7.1) is that $(\sigma^e - \sigma^e|_\gamma)/\sigma^e$ is proportional to γ for small γ and contains, in the proportionality factor, the square root of the absolute value of $\sigma^{(0)}(v_1)$. During the experiment the slit s_4 was used as detector slit and its width was fixed at 0.2 mm. This width is chosen so small that the value of γ is only determined by the width w_{s_2} of the collimator slit

s_2 which is then varied between 0.15 and 3.00 mm. From the definition of γ (Sect. 6.5) follows directly

$$\gamma = \frac{l_{s_4}}{l_{s_2}} \frac{w_{s_2}}{l_{s_4} l_{\text{scat}}} \quad (7.2)$$

All l -distances are measured from the source slit. l_{s_4} is the distance to s_4 ($l_{s_4} = 2095$ mm), l_{s_2} is the distance to s_2 ($l_{s_2} = 1090$ mm), and l_{scat} is the distance to the scattering center ($l_{\text{scat}} = 1215$ mm). The selected range of w_{s_2} gives $0.33 \times 10^{-3} \leq \gamma \leq 6.5 \times 10^{-3}$ rad.

Thus far we have measured $\sigma^e|_\gamma$ only for the system NO-CCl₄. With $v_1 = 525$ m/sec, $X = 2.96$ and $\frac{\Delta v_1}{v_1} = 6.7\%$, the value of $\frac{d}{d\gamma} \left(\frac{\sigma^e|_\gamma}{\sigma^e} \right) = (-52 \pm 2) \text{ rad}^{-1}$ was obtained for $\gamma \ll \theta^*$. (Using Eq. (6.26) we find $\theta^* = 5.1 \times 10^{-3}$ rad). With Equation (7.1) we obtain $\sigma^{(0)}(v_1) = (720 \pm 60) 10^{-16} \text{ cm}^2$.

The factor 0.076 in Eq. (7.1) was obtained by Von Busch *et al.* (BUS 67) with limited accuracy. The exactly calculated small angle distribution could be fitted within 10% to the function $I(\vartheta) = I(0)e^{-0.7(\vartheta/\vartheta^*)^2}$, $0 \leq \vartheta \leq 2\vartheta^*$. Von Busch *et al.* used this function, and not the exact small angle distribution, to calculate the coefficient 0.076. A maximum systematic error of 20% in $\sigma^{(0)}(v_1)$ can be introduced by this approximation.

We see that the experimental values of $\sigma^{(0)}(v_1)$ and θ^* are in fair agreement with the estimated values $1078 \times 10^{-16} \text{ cm}^2$ and 4.28×10^{-3} rad, respectively (Table 6.4).

The observed deviation from the linear behaviour (Eq. (7.1)) of $\sigma^e|_\gamma$ for NO-CCl₄ with increasing γ turns out to be small. The deviation amounts to 10% of the angular resolution correction.

It is of interest to extend these measurements to other molecules. Systems for which the absolute total cross section already is known would provide a test of the method, and relative measurements would overcome the difficulty of the limited accuracy of Eq. (7.1). Comparison of $\sigma^e|_\gamma$ for different systems over the entire range of γ would provide information about the r -dependence of the long range interaction and make it possible to drop the assumption of an exact r^{-6} -dependence in the evaluation of measurements of the total collision cross section.

An experimental investigation of the velocity dependence of the total collision cross section was prompted by the following two considerations

First, we wanted to verify the expected Landau-Lifshitz behaviour, $\sigma \sim v^{-2/5}$, for the investigated systems. Deviations from $v^{-2/5}$ dependence were observed for several molecule-atom systems (HES 65, BEN 69, RIC 70 and DAV 70). An observation for our systems of a $v^{-2/5}$ dependence would justify the proposed evaluation of $\frac{\sigma_{\parallel} \sigma_{\perp}}{\sigma_{\parallel}}$ in Chapter 5 and 6. Small deviations from the $v^{-2/5}$ dependence are unimportant because of the weak dependence of the anisotropy effect upon s , the exponent of the force law (Eq (5.37)).

Second, we wanted to investigate the possible presence of glory undulations in the total collision cross section. An observation of glory undulations in the total collision cross section would make their omission in the analysis of the anisotropy effect in Chapter 5 rather questionable.

The velocity dependence of the total collision cross section of a non state-selected beam was measured for the systems NO-CCl₄, NO-CS₂, NO-CO₂, NO-Ar and NO-N₂. The system NO-N₂O was left out because of its close resemblance to the system NO-CO₂. The measurements were done with two resolutions of the velocity selector ($\frac{\Delta v}{v} = 6.7\%$ and 21% f w h m). The attenuation of the NO beam was about 0.3. The directly observed experimental cross section, $\sigma^e|_{\gamma}$, needs correction for finite angular resolution and for the velocity distribution of the secondary beam.

The angular resolution correction C_{γ} is calculated with Eq (7.1) using for $\sigma^{(0)}(v_1)$ the value $8.083 \times \left(\frac{C_6 \text{ e.m.p.}}{\hbar v_1} \right)^{2/5}$. The slits s_2 and s_4 (used as collimator and detector slit, respectively) were set to such values that the angular resolution γ was determined only by the width of the collimator slit. In this geometry γ is given by Eq (7.2).

The measurements on the system NO-CCl₄ were performed with $\gamma = 0.651 \times 10^{-3}$ rad. In the investigated velocity range the angular resolution correction C_{γ} was $0.960 \leq C_{\gamma} \leq 0.975$. The measurements on CS₂, CO₂, Ar and N₂ showed a slightly worse angular resolution $\gamma = 1.35 \times 10^{-3}$ rad. The C_{γ} values lay between 0.89 and 0.96. The correction for the velocity distribution of the secondary beam is done with the factor $Fb_0(6.X)$ of Berkling *et al* (BER 62). The most probable secondary beam velocity, $v_{2,p}$, necessary

for calculating X, was determined by measuring the temperature of the effuser holder, and was about 200 m/s for all systems.

A standard way of evaluation is to make a plot of $\sigma^e(v_1) | \gamma \cdot \frac{v_1^{2/5}}{\text{Fb}_0(6,X) C \gamma}$ vs v_1 , a quantity expected to be independent of v_1 (Fig. 7.1). The measurements of NO-CCl₄ show a slight deviation from a $\bar{v}^{2/5}$ dependence. To estimate the actual velocity dependence of $\sigma^{(0)}$, we fit the plot graphically to a new s-value. As result we find $s = 6.4 \pm 0.1$. The accuracy of a single measured point is about 0.5%, and the small observable undulations are not significant.

The measurements on the other systems are less accurate (about 1% unless indicated otherwise in the Figure). They were done in an earlier arrangement of the machine where the positions of the scattering chamber and velocity selector were interchanged. For the different systems, the resulting s-values are: NO-CS₂, $s = 6 \pm 1$; NO-CO₂, $s = 7.0 \pm 0.5$; NO-Ar, $s = 6.0 \pm 1.0$ ($v_1 \lesssim 700$ m/s); NO-N₂, $s = 6.0 \pm 1$ ($v_1 \lesssim 700$ m/s). The accuracy was limited by the detector stability. So, for all systems, we verify an r^{-6} long range potential within an error of 10%.

Glory undulations, if present, should also show up in the plotted curves. The glory effect in $\sigma^{(0)}$ can be calculated easily for a Lennard-Jones 12-6 potential in the semi-classical approximation (BER 63b, OLS 68, FEL 70). Using the empirical potential parameters of Table 5.2 and following the procedure of Olson and Bernstein (OLS 68), the theoretical glory amplitudes and positions were calculated. In the investigated velocity range of Fig. 7.1 we obtained a theoretical glory amplitude of 4% for CCl₄ and CS₂, 6% for CO₂, 7% for Ar, and 8% for N₂. The glory positions are indicated with the number N_{glory} in Fig. 7.1. Maxima occur at $N_{\text{glory}} = 1, 2, 3, \dots$ and minima at $N_{\text{glory}} = \frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \dots$.

Experimentally, only for the systems NO-N₂ and NO-Ar at $v_1 \approx 1000$

Fig. 7.1. The velocity dependence of the total collision cross section.

$G(v_1) = \frac{\sigma^e(v_1) | \gamma v_1^{2/5}}{C \gamma \text{Fb}_0(6,X)}$ (in arbitrary units) is plotted against v_1 . Only if the accuracy is less than 1% is this indicated with an error bar. Measurements indicated with (●) correspond to $\frac{\Delta v}{v} = 6.7\%$ and $T_{\text{source}} = 180^\circ \text{K}$, measurements with $\frac{\Delta v}{v} = 21\%$ and $T_{\text{source}} = 180^\circ \text{K}$, 300°K are indicated by (x), (⊙). The lines drawn in the Figure give the estimated velocity dependence of the total collision cross section. The theoretical glory extrema N_{glory} , plotted in the Figure, are obtained by setting $v_{\text{rel}} = (v_1^2 + v_{2,p}^2)^{1/2}$.

m/s did we obtain an indication of a glory undulation. Nearly all these measurements were performed with the $\frac{\Delta v}{v} = 21\%$ resolution of the velocity selector. One can argue that the rise of the collision cross section at $v_1 \approx 1000$ m/s is caused by a shift of the average selected velocity to a lower value in comparison with the value of v_1 indicated in the Figure. At this velocity we are in the tail of the velocity-distribution of the molecules emerging from the source. The value of v_1 in the Figure stands for the primary beam velocity at maximum transmission. To investigate the influence of this effect, measurements on NO-N₂ were done with two source temperatures T=300 °K and T=180 °K. The Figure shows that the influence of the corresponding change in beam velocity upon the results is marginal. We believe that the glory undulations for the systems NO-Ar and NO-N₂ are realistic. Absence of glory undulations in the experimental results for other systems (NO-CCl₄, NO-CS₂, NO-CO₂) can be explained by (1) damping due to the velocity distribution of the secondary beam, and (2) quenching of the glory amplitude because of the anisotropy of the colliding molecules (OLS 68, OLS 69).

The velocity distribution of the secondary beam tends to damp glory undulations, especially when their spacing is small. This is the case for CCl₄, CS₂, and, at $v_1 \leq 700$ m/s, for N₂, Ar and CO₂ (relative low X and high N_{glory} values).

Normally, glory measurements are only done with v_1 velocities larger than 700 m/s. Systems like Na-Hg (BUC 71), K-SF₆ (GIS 67) and K-Ar, K-Kr (BEC 66, BUS 67) show no, or very small, glories in the low-velocity region. From this observation one concludes that velocity averaging is most probably sufficient to explain why glory amplitudes are smaller than 1% in our experimental results.

Quenching of the glory amplitude is induced by the averaging over the different rotational states of the molecule (OLS 68) and by inelastic transitions (OLS 69). These are second order processes. Quenching is important for collisions of molecules which possess a strong inelastic behaviour. This is the case for molecules with a large anisotropy and large moment of inertia like CO₂, CS₂ and N₂O.

The glory effect in the total collision cross section has the same periodicity as in its anisotropy (REU 69, MIL 69, SCH 70). The damping due to velocity distribution is the same for both. The glory amplitude of the total

collision cross section is strongly anisotropic. A rather crude estimate, based upon the calculation of the systems CsF-He (BEN 69b) and Ar-H₂ (REU 69), shows that the relative effect of the glories on the anisotropy $\frac{\sigma_{||} - \sigma_{\perp}}{\sigma_{||}}$ can be about 10 times larger than the relative glory amplitude in the total cross section. A weakness in this argument comes from the fact that both systems are considered in the N=1 region and involve a light collision partner. Unfortunately, there are no better calculations available. For our measurements, which show an isotropic glory amplitude of $\leq 1\%$ at $v_1 \approx 525$ m/s, the amplification factor of 10 implies that a glory effect of 10% in $\frac{\Delta\sigma}{\sigma} \approx 5 \times 10^{-3}$ is possible, corresponding to a 5×10^{-4} effect in $\sigma^{(0)}$. Such small effects can barely be detected within our experimental accuracy.

In conclusion, the results of this Section confirm our use of an r^{-6} potential for the evaluation of the anisotropy effect.

7.3. THE ANISOTROPY EFFECT

7.3.1. Data Collection

During the experiment eight different intensities are measured. The following relations hold for the eight intensities defined in Table 2.1:

$$(I_5 - I_6) = (I_1 - I_2) e^{-nI} \sigma_{||}^e, \text{ and } (I_7 - I_8) = (I_3 - I_4) e^{-nI} \sigma_{\perp}^e.$$

Extraction of $\frac{\sigma_{||}^e - \sigma_{\perp}^e}{\sigma_{||}^e}$ from these two expressions yields:

$$\frac{\sigma_{||}^e - \sigma_{\perp}^e}{\sigma_{||}^e} = \left[\ln \left(\frac{I_7 - I_8}{I_5 - I_6} \right) - \ln \left(\frac{I_3 - I_4}{I_1 - I_2} \right) \right] / \ln \left(\frac{I_1 - I_2}{I_5 - I_6} \right), \quad (7.3)$$

where $\sigma_{||}^e$ and $\sigma_{\perp}^e$ are the experimental cross sections for the two field orientations uncorrected for the velocity distribution of the secondary beam, for the finite and not entirely homogeneous B-field in the scattering region, etc.. The transformation of $\sigma_{||}^e$ and $\sigma_{\perp}^e$ into 'ideal' cross sections was discussed in the preceeding Chapter.

Typically we find $\frac{\sigma_{||}^e - \sigma_{\perp}^e}{\sigma_{||}^e} \approx 5 \times 10^{-3}$. To obtain this result with modest accuracy (10%), a very small fraction of the beam signal has to be detected. With an optimum beam attenuation ($\ln \left(\frac{I_1 - I_2}{I_5 - I_6} \right) \approx 1$), about 10% of the

I_5 -signal is due to molecules in the selected state. If one wants to know $\frac{\sigma_H^c - \sigma_L^c}{\sigma_F^c}$ within 10%, intensity measurements should be performed with an accuracy of 2×10^{-5} .

To determine $\frac{\sigma_H^c - \sigma_L^c}{\sigma_F^c}$, the necessary eight intensities are repeatably measured in an order which compensates for drift instabilities in the beam and averages out random fluctuations. In a measuring time of 20 seconds an I_5 -signal for example is measured with an accuracy of about 4×10^{-4} . In practice we achieve an absolute accuracy of about 1×10^{-3} in $\frac{\sigma_H^c - \sigma_L^c}{\sigma_F^c}$ after a measuring time of 10 hours.

During the measurements we convert the signal from the lock-in amplifier into pulse rates and count each intensity ($I_1, \dots, I_8$) for 20 seconds, before we switch to the next one. When the secondary beam is switched on or off, stable attenuation is obtained only after about 100 seconds because the detector shows a memory effect. As this may introduce serious errors we adopted the following procedure. We sample I_1, I_2, I_3, I_4 12 times in a fixed sequence (during a so called T_1 -period). In a second T-period (T_2) we sample with the sequence order I_5, I_6, I_7, I_8 . In the third T-period (T_3), we proceed with I_3, I_4, I_1, I_2 , followed by sampling I_7, I_8, I_5, I_6 , in the fourth T-period (T_4). From here we go back to the situation of the first T-period (T_1). One T-period lasts 27 minutes, containing 16 minutes actual measuring time. During these measurements a relay-system is used. This system is controlled by a punched program card which changes the settings (of valves etc.) appropriate to the different intensities. The length of the program card is equal to the length of a T-period. At the end of a T-period, the relay system is switched automatically to the sequence order of the new T-period and restarts the same program card.

The difference between the first and third (second and fourth) T-period is only that the orientation fields are changed between corresponding time intervals. All systematic errors due to erroneous timing differences or linear drift, change sign and cancel when the results are averaged.

7.3.2. Data Evaluation

The results of a day's measurements are punched on paper tape to be fed into an off-line computer (IBM 360/50). In this Section we discuss the averaging procedure applied to these raw data to produce the relevant $\frac{\sigma_H^c - \sigma_L^c}{\sigma_F^c}$ -values. The collection of data obtained in one day we call a 'tape',

consisting, normally, of about 25 T-periods.

The individual values for $D_1 = [I_1 - I_2 - I_3 + I_4] / [I_1 - I_2]$ are calculated from successive intensity-measurements of the first ($i=1$) or third ($i=3$) T-periods. The average over a tape, $\langle D_i \rangle$, with $i=1$ and $i=3$, is expected to be zero, as it measures an anisotropy in the unscattered beam. However, the field from the Helmholtz coils around the scattering region slightly influences the detector performance, resulting in $\langle D_i \rangle$ -values of about 2×10^{-3} . The same magnetic effect is observed with unselected beam molecules (Rabi field and six-pole switched off). While $\langle D_1 \rangle = \langle D_3 \rangle$ is expected and normally found (see NO-CCl₄ in Table 7.4, for example), for NO-Ar (Table 7.8) and also for NO-N₂O (Table 7.6) differences $\langle D_1 \rangle - \langle D_3 \rangle$ are observed of about 3×10^{-3} . An explanation comes from the fact that for these systems a considerable pressure increase (3×10^{-9} torr) is observed in the detector chamber when the secondary beam is switched on. The measurements reported in this Section were performed in the early arrangement of the machine, where the positions of the scattering chamber and velocity selector were interchanged. In this arrangement the pressure builds up very slowly during the T₂- and T₄-periods and also drops back to the original value in the T₁- and T₃-periods with time constants of 10 minutes or more. These background variations interfere with the detector performance and produce what we call drift effect. Contribution of this effect to $\langle D_1 \rangle$ and $\langle D_3 \rangle$ during the T₁- and T₃-period, respectively, is of the same magnitude but of opposite sign.

Similarly, quantities $D_j = (I_5 - I_6 - I_7 + I_8) / (I_5 - I_6)$, ($j=2,4$) are formed from the intensity measurements during the T₂- and T₄-periods. Their average values $\langle D_2 \rangle$ and $\langle D_4 \rangle$ contain the anisotropy and the magnetic and drift effects just mentioned.

The next step is to collect all the D_j -values of the tape (twelve in a T_j-period) and to produce an average^{*} $\langle D_j \rangle$ and its standard deviation ΔD_j . We have verified that the $\langle D_j \rangle$ -values do have uncertainties obeying the $\frac{1}{\sqrt{n}}$ law, where n equals the total number of D_j -determinations.

The denominator of Eq. (7.3) contains the attenuation $N \equiv \frac{I_1 - I_2}{I_5 - I_6}$. The accuracy requirements for the intensities entering in N are of course much less severe than for the intensities of the numerator of Eq. (7.3). The inten-

*) The distribution of the D_j -values may be assumed normal because $I_1 - I_2 - I_3 + I_4 \ll I_1 - I_2$ and $I_5 - I_6 - I_7 + I_8 \ll I_5 - I_6$.

sity of the secondary beam (stability better than 1% over a tape) is chosen such that $\ln N \approx 1$. The intensities I_1 and I_2 were taken from all T_1 - or T_3 -periods, I_5 and I_6 from all T_2 - or T_4 -periods and averaged to give:

$$\langle N_{1j} \rangle = \frac{\langle I_1 \ I_2 \rangle_1}{\langle I_5 \ I_6 \rangle_j}, \quad (7.4)$$

with $i, j=1, 2$ or $3, 4$, respectively.

The next step is the rejection of intensity measurements which are seriously affected by pressure bursts, high voltage failures and other disturbing phenomena. We use $\sqrt{n} \Delta D_j$ to judge the quality of an individual measurement. If a D_j differs by more than three times $\sqrt{n} \Delta D_j$ from the calculated average $\langle D_j \rangle$, it is rejected from the sample. This procedure is repeated (two or three times normally), until all D_j 's lie within $3 \sqrt{n} \Delta D_j$. The total number of removals amounts to about 5% of all D_j -values*).

From $\langle D_1 \rangle, \langle D_2 \rangle$ and $\langle N_{1j} \rangle$ we obtain directly the value of $\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e}$ and its standard deviation**) S_1^{tape} . With the data of the T_1 - and T_2 -periods we form:

$$\left(\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e} \right)_{12} = \frac{\ln [1 + \langle D_1 \rangle - \langle D_2 \rangle]}{\ln \langle N_{12} \rangle}; \quad \left(S_1^{\text{tape}} \right)_{12} = \frac{\sqrt{(\Delta D_1)^2 + (\Delta D_2)^2}}{\ln \langle N_{12} \rangle} \quad (7.5)$$

and with the T_3 - and T_4 -periods:

$$\left(\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e} \right)_{34} = \frac{\ln [1 + \langle D_3 \rangle - \langle D_4 \rangle]}{\ln \langle N_{34} \rangle}; \quad \left(S_1^{\text{tape}} \right)_{34} = \frac{\sqrt{(\Delta D_3)^2 + (\Delta D_4)^2}}{\ln \langle N_{34} \rangle} \quad (7.6)$$

Only for NO-Ar and NO-N₂O did the values of $\left(\frac{\sigma_H^e - \sigma_L^e}{\sigma_H^e} \right)_{ij}$ change due

*) It is this fraction of rejected measurements which induced us to work with the sampling time as short as 20 seconds. Otherwise, for a minimum dead-time, the sampling time should be as long as possible.

**) For the calculation of the standard deviation we replaced $\ln [1 + \langle D_1 \rangle - \langle D_2 \rangle]$ by $\langle D_1 \rangle - \langle D_2 \rangle$. This approximation is justified because $\langle D_1 \rangle - \langle D_2 \rangle < 10^{-2}$. Moreover, the error in $\langle N_{ij} \rangle$ is always sufficiently small and may be neglected.

to pressure-drift. However, for $\left(\frac{\sigma_H^e \sigma_I^e}{\sigma_H^e}\right)_{1,2}$ the effect of the pressure drift is practically equal in magnitude and opposite in sign as for $\left(\frac{\sigma_H^e - \sigma_I^e}{\sigma_H^e}\right)_{3,4}$. To obtain a meaningful value for the anisotropy of the total collision cross section we form in these cases:

$$\frac{\sigma_H^e - \sigma_I^e}{\sigma_H^e} = \frac{1}{2} \left[\left(\frac{\sigma_H^e \sigma_I^e}{\sigma_H^e} \right)_{1,2} + \left(\frac{\sigma_H^e \sigma_I^e}{\sigma_H^e} \right)_{3,4} \right] \quad (7.7)$$

7.3.3. Results

The anisotropy measurements were performed with three different machine configurations (a, b and c), whose characteristics are summarized in Table 7.1. In configuration c) we used a beam stop consisting of a horizontal rod (diameter 1.5 mm) which was situated on the beam-axis at the position of the s_1 slit. This beam stop, which partially intercepts both background beam and selected beam, was intended to obtain a higher fraction of state-selected molecules in the total beam. The quality of the focusing spectrum remained the same as without beam stop. In the final geometry we removed the beam stop again, because no significant gain in accuracy of $\frac{\sigma_H^e - \sigma_I^e}{\sigma_H^e}$ was obtained and alignment was more difficult.

TABLE 7.1

Machine configurations used during the anisotropy measurements

During the measurements of this Section the scattering chamber and velocity selector positions were interchanged with respect to Figure 2.1. The angle γ is calculated with the width (f.w.h.m.) of the experimental focused spot of Fig. 4.2.

Configuration	Source slit	Detector slit	Central beam stop	γ
a	$3 \times 0.05 \text{ mm}^2$	$s_4: 8 \times 1 \text{ mm}^2$	no	$3.41 \times 10^{-3} \text{ rad}$
b	$3 \times 0.05 \text{ mm}^2$	$s_5: 8 \times 1 \text{ mm}^2$	no	$2.79 \times 10^{-3} \text{ rad}$
c	$1 \times 0.05 \text{ mm}^2$	$s_5: 8 \times 1 \text{ mm}^2$	yes	$2.79 \times 10^{-3} \text{ rad}$

TABLE 7.2

Results for NO-CCl₄ (very early measurements)Configuration a), v₁ = 505 m/s, X = 2.88, B₀ = 150 G

Orientation fields // and ⊥ v _{rel} (tan τ _{//} = 0.410)		Orientation fields 45° with respect to v _{rel} (tan τ _{//} = 2.40)	
N _{tape}	$\left(\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}} \right)_{12}$ [10 ⁻³]	N _{tape}	$\left(\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}} \right)_{12}$ [10 ⁻³]
24	-2.93±1.59	33	-1.39±0.93
26	-0.80±2.23	34	2.04±0.85
27	-2.73±2.50	36	0.41±1.23
37	-3.62±1.24	40	1.76±0.67
38	-3.72±1.58	41	2.04±0.62
39	-3.33±1.04	43	-0.30±0.76
$\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}} = (-3.18 \pm 0.61) \times 10^{-3}$ $(S_D = 0.33 \times 10^{-3})$ $\frac{\sigma_{//} - \sigma_{\perp}}{\sigma_{//}} = (-4.21 \pm 0.81) \times 10^{-3}$ (corrected value)		$\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}} = (1.05 \pm 0.56) \times 10^{-3}$ $(S_W = 0.32 \times 10^{-3})$	

The experimental data of the anisotropy measurements are collected in the Tables 7.2 through 7.9. The caption indicates the investigated system, the machine configuration, the primary NO beam velocity v₁, the ratio (X) of v₁ to the most probable velocity of the secondary beam, the magnetic field strength B₀, and the angle τ_{//}. Besides the values of ⟨D₁⟩ (⟨D₃⟩) and ⟨D₂⟩ (⟨D₄⟩), the number of individual D_i-values are indicated by N₁ (N₃) and N₂ (N₄) for each tape (numbered by N_{tape}). The values of ⟨D₁⟩ and ⟨D₂⟩ are always given in the upper row, ⟨D₂⟩ and ⟨D₄⟩ in the lower row.

As mentioned above, $\left(\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}} \right)_{jk}$ was formed with j, k=1, 2 or 3, 4. From all these values we took a final average of $\frac{\sigma_{//}^{\text{f}} - \sigma_{\perp}^{\text{f}}}{\sigma_{//}^{\text{f}}}$. To obtain this average we weighted all these values with the inverse square of their standard deviation, S_i^{tape}, which is also given in the Tables (using Eqs. (7.5) and (7.6) or, for Ar and N₂O, Eq. (7.7)). For this final average, the value of the standard deviation

TABLE 7.3

Results for NO-CCl₄ (early measurements)Configuration b), $v_1 = 518$ m/s, $X = 2.96$, $B_0 = 150$ G and $\tan \tau_H = 0.410$

Ntape	$\left(\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} \right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N_1, N_3	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N_2, N_4
58	-3.34±2.15	1.06±0.72	60	4.56±2.03	64
	-2.46±1.47	0.58±0.80	58	2.00±1.24	69
59	-4.39±2.27	2.68±0.82	37	7.46±2.11	46
	-4.42±4.45	-0.68±1.97	30	3.97±3.99	33
60	-4.62±3.30	1.30±2.10	30	6.14±2.54	28
	-7.21±2.81	-0.48±1.37	30	6.96±2.46	34
$\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} = (-3.74 \pm 0.93) \times 10^{-3} \quad (S_D = 0.66 \times 10^{-3})$ $\frac{\sigma_H - \sigma_L}{\sigma_H} = (-4.80 \pm 1.19) \times 10^{-3} \quad (\text{corrected value})$					

TABLE 7.4

Results for NO-CCl₄ (best measurements)Configuration c), $v_1 = 550$ m/s, $X = 3.14$, $B_0 = 150$ G and $\tan \tau_H = 0.336$

Ntape	$\left(\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} \right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N_1, N_3	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N_2, N_4
71	-4.49±1.13	2.20±0.35	48	6.57±1.07	44
	-2.80±1.24	2.17±0.31	47	4.88±1.20	33
72	-2.55±0.70	3.95±0.40	103	6.39±0.57	106
	-4.56±0.66	3.38±0.33	91	7.72±0.58	95
73	-2.94±0.63	3.34±0.27	81	6.20±0.56	93
	-4.16±0.73	2.86±0.32	79	6.91±0.65	80
74	-3.13±0.66	3.50±0.27	84	6.44±0.60	82
	-2.81±0.63	3.59±0.25	95	6.25±0.58	70
75	-0.74±1.43	3.93±0.68	47	4.64±1.25	57
	-2.76±0.87	3.30±0.45	44	5.95±0.75	59
$\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} = (-3.24 \pm 0.28) \times 10^{-3} \quad (S_W = 0.24 \times 10^{-3})$ $\frac{\sigma_H - \sigma_L}{\sigma_H} = (-4.15 \pm 0.36) \times 10^{-3} \quad (\text{corrected value})$					

TABLE 7 5

Results for NO-C S₂(configuration b) $v_1 = 524$ m/s, $X = 2.52$, $B_0 = 150$ G and $\tan \tau_H = 0.40$

N_{tape}	$\left(\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} \right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N_1, N_3	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N_2, N_4
61	-2.81 ± 2.21	1.92 ± 1.14	26	5.01 ± 1.89	28
	-3.30 ± 2.73	-1.06 ± 1.83	17	2.60 ± 2.01	28
62	-3.54 ± 1.62	0.49 ± 0.77	31	3.51 ± 1.43	36
	-6.61 ± 2.08	1.14 ± 0.83	23	8.51 ± 1.90	31
63	-0.22 ± 2.18	0.23 ± 0.63	33	0.48 ± 2.08	22
	-6.56 ± 1.90	0.72 ± 1.13	15	8.17 ± 1.52	18
64	-8.97 ± 2.61	1.06 ± 1.17	31	10.64 ± 2.33	42
	-6.71 ± 2.11	1.52 ± 0.70	26	9.70 ± 1.99	25
65	-4.33 ± 2.50	0.71 ± 0.89	31	4.13 ± 2.34	28
	-5.23 ± 1.82	0.71 ± 1.20	19	6.52 ± 1.37	19
$\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} = (4.78 \pm 0.74) \times 10^{-3}$ ($S_W = 0.66 \times 10^{-3}$)					
$\frac{\sigma_H - \sigma_L}{\sigma_H} = (6.09 \pm 0.94) \times 10^{-3}$ (corrected value)					

TABLE 7 6

Results for NO-N₂O(configuration a), b), $v_1 = 520$ m/s, $X = 2.34$, $B_0 = 150$ G and $\tan \tau_H = 0.460$

Ntape	(configuration)	$\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E}$ [10 ⁻³]	$\left(\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E}\right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N ₁ , N ₃	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N ₂ , N ₄
55	a	5.82±2.09	3.42±2.64	2.84±0.93	54	6.61±2.47	54
			8.28±2.90	0.02±1.12	51	8.86±2.68	44
56	b	5.31±1.92	5.06±2.16	2.08±1.11	57	6.48±1.86	61
			-5.55±2.71	-0.15±1.21	50	4.72±2.42	50
57	b	6.79±1.66	0.00±2.01	3.73±1.01	53	3.73±1.73	55
			-13.86±2.21	-3.09±1.02	61	8.12±1.96	59

$$\frac{\sigma_H^E - \sigma_L^E}{\sigma_H^E} = (6.07 \pm 1.07) \times 10^{-3} \quad (S_D = 0.46 \times 10^{-3})$$
$$\frac{\sigma_H - \sigma_L}{\sigma_H} = (-7.62 \pm 1.34) \times 10^{-3} \quad (\text{corrected value})$$

TABLE 7 7

Results for NO-CO₂Configuration a), $v_1 = 520$ m/s, $X = 2.34$, $B_0 = 150$ G and $\tan \tau_H = 0.460$

Ntape	$\left(\frac{\sigma_H^E - \sigma_{\perp}^E}{\sigma_H^E} \right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N ₁ , N ₃	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N ₂ , N ₄
49	-3.45±1.79	0.76±0.91	80	3.82±1.54	75
	-4.04±2.05	1.33±1.10	76	4.90±1.74	72
52	-8.36±1.50	-0.95±0.86	67	5.97±1.23	71
	-8.37±1.49	0.63±0.81	74	7.52±1.25	72
53	-5.69±1.94	0.49±0.99	69	5.74±1.67	61
	-5.64±1.99	-1.00±1.16	57	5.22±1.61	59
54	-3.96±1.76	1.52±1.14	49	4.55±1.34	51
	-4.04±1.67	1.14±1.49	47	4.49±0.76	55
$\frac{\sigma_H^E - \sigma_{\perp}^E}{\sigma_H^E} = (-5.74 \pm 0.76) \times 10^{-3} \quad (S_W = 0.61 \times 10^{-3})$ $\frac{\sigma_H - \sigma_{\perp}}{\sigma_H} = (-7.37 \pm 0.98) \times 10^{-3} \quad (\text{corrected value})$					

tion can be calculated in two different ways. First, a standard deviation S_D is calculated from the spread of the values of $\left(\frac{\sigma_H^E - \sigma_{\perp}^E}{\sigma_H^E} \right)_{jk}$. Second, we calculated a standard deviation S_W directly from the standard deviations $S_{i^{\text{tape}}}$:

$$S_W = \left[\sum_i^{\text{all tapes}} \left(\frac{1}{S_{i^{\text{tape}}}} \right)^2 \right]^{-1/2}. \quad (7.8)$$

For an infinite number of tapes, and a normal distribution of the individual values of $\frac{\sigma_H^E - \sigma_{\perp}^E}{\sigma_H^E}$, S_W should be equal to S_D . In practice, we have only a rather small number of tapes and are therefore unable to verify that the distribution really is normal. For this reason we took the larger value of S_W or S_D for the error in the final average of $\frac{\sigma_H^E - \sigma_{\perp}^E}{\sigma_H^E}$. In parenthesis, the smaller of S_W and S_D is also shown in the Tables. There is not much difference between these two values. For reasons of completeness, the corrected anisotropy, $\frac{\sigma_H - \sigma_{\perp}}{\sigma_H}$, is given as the last number. Here all corrections described in Chapter 6 are applied.

In the Tables 7.2, 7.3 and 7.4., the results for the system NO-CCl₄ are

TABLE 7.8

Results for NO-Ar

Configuration b), c), $v_1 = 525$ m/s, $X = 2.57$, $B_0 = 150$ G and $\tan \tau_H = 0.396$

N_{tape}	Configuration	$\frac{\sigma_H^f - \sigma_L^f}{\sigma_H^f}$ [10 ⁻³]	$\left(\frac{\sigma_H^f - \sigma_L^f}{\sigma_H^f}\right)_{j,k}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N_1, N_3	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N_2, N_4
66	b	-5.75±1.32	-2.91±1.98	0.91±0.51	38	3.30±1.92	26
			-8.66±1.73	-1.88±0.54	42	7.14±1.65	29
67	b	-6.40±0.80	-3.69±1.18	1.14±0.64	63	5.02±1.00	60
			-9.03±1.06	-0.26±0.65	56	9.19±0.85	61
68	c	-6.62±1.08	-2.37±1.51	-1.53±0.55	54	4.21±1.41	59
			-9.70±1.54	-2.86±0.48	50	8.02±1.47	46
69	c	-6.27±0.92	-1.56±1.38	2.59±0.43	87	4.36±1.31	78
			-10.97±1.21	-2.97±0.43	64	9.43±1.14	81
70	c	-3.80±0.93	-1.02±1.27	3.60±0.31	68	4.77±1.23	45
			-6.59±1.36	0.96±0.40	61	8.57±1.30	44

$$\frac{\sigma_H^f - \sigma_L^f}{\sigma_H^f} = (-5.78 \pm 0.52) \times 10^{-3} \quad (S_W = 0.24 \times 10^{-3})$$
$$\frac{\sigma_H - \sigma_L}{\sigma_H} = (-7.14 \pm 0.64) \times 10^{-3} \quad (\text{corrected value})$$

collected. All values, taken at different times (N_{tape}), configuration and velocities are in agreement with each other. There is no indication of systematic errors. At the time of Table 7.2 we did not have the possibility for automatically interchanging the Helmholtz field-orientations for different T-periods. In this Table some tapes (see tape numbers) were canceled because unstable operation of the machine had made the results doubtful.

As a check, measurements with the orientation field of the scattering chamber at 45° with respect to v_{rel} were also made. Table 7.2 shows, as was to be expected, that the anisotropy effect is zero, within its experimental error, in this case.

In the Tables 7.5–7.9 the results for NO-CS₂, NO-N₂O, NO-CO₂, NO-Ar and NO-N₂ are shown. All these measurements have a $\frac{\sigma_H^f - \sigma_L^f}{\sigma_H^f}$ of about -0.5% .

TABLE 79

Results for NO-N₂Configuration a), $v_1 = 517$ m/s, $X = 2.86$, $B_0 = 160$ G and $\tan \tau_{\parallel} = 0.55$

Ntape	$\left(\frac{\sigma_{\parallel}^c - \sigma_{\perp}^c}{\sigma_{\parallel}^c} \right)_{jk}$ [10 ⁻³]	$\langle D_1 \rangle, \langle D_3 \rangle$ [10 ⁻³]	N ₁ , N ₃	$\langle D_2 \rangle, \langle D_4 \rangle$ [10 ⁻³]	N ₂ , N ₄
44	-3.97±2.41	0.18±1.04	47	3.88±2.17	43
	-3.94±2.43	2.68±1.17	38	6.41±2.13	41
45	-5.61±3.06	0.64±0.96	59	6.64±2.90	43
	-4.44±2.74	0.60±1.10	39	6.06±2.50	38
46	-7.01±2.91	-0.25±1.12	60	7.79±2.68	47
	-7.18±3.05	1.66±1.42	53	6.17±2.70	49
47	6.12±2.26	0.15±1.52	52	5.55±1.67	54
	-5.89±2.35	0.13±1.40	40	5.62±1.89	44
$\frac{\sigma_{\parallel}^c - \sigma_{\perp}^c}{\sigma_{\parallel}^c} = (-5.41 \pm 0.91) \times 10^{-3} \quad (S_D = 0.44 \times 10^{-3})$ $\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_{\parallel}} = (-6.96 \pm 1.17) \times 10^{-3} \quad (\text{corrected value})$					

DISCUSSION OF THE RESULTS AND CONCLUDING REMARKS

8.1 GLORY UNDULATIONS

The results of Chapter 7 should be seen as a snapshot, taken at a fixed moment, in a longer course of experiments. Before we start to analyse the anisotropy measurements, we report^{*)} briefly some preliminary results obtained recently.

As pointed out in Sect. 7.2, the quantitative argument which led us to disregard glory undulations in the anisotropy of the total collision cross section was rather weak. In order to get a clearer picture one should actually investigate the velocity dependence of the anisotropy effect itself. Such an investigation is now in progress^{**)}. So far two systems, NO-CO₂ and NO-Kr, were investigated in the velocity range $423 \text{ m/s} \leq v_1 \leq 607 \text{ m/s}$.

For NO-CO₂, $\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e}$ was determined at five velocities (Fig. 8.1). No indication of a glory undulation could be observed. All values of $\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e}$ were lying within $\pm 1 \times 10^{-3}$ around a weighted average of $\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e} = (-7.2 \pm 0.2) \times 10^{-3}$. With the corrections of Chapter 6, we obtain $\frac{\sigma_H - \sigma_\perp}{\sigma_H} = (-8.6 \pm 0.2) \times 10^{-3}$, a value in satisfying agreement with the value of $(-7.37 \pm 0.98) \times 10^{-3}$ of Table 7.7.

The situation is quite different for the system NO-Kr for which glory effects in $\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e}$ are clearly observed. In Fig. 8.1, the results are shown. To our knowledge this is the first time that a glory undulation on the anisotropy of the total collision cross section is observed. From an estimated non-glory contribution to $\frac{\sigma_H^e - \sigma_\perp^e}{\sigma_H^e}$ of 7.2×10^{-3} , a glory amplitude of 3×10^{-3} is obtained. The investigated velocity range corresponds then to three

*) The glory undulations in the anisotropy of the total collision cross section were measured by Dr. Henry L. Schwartz.

**) These anisotropy measurements are performed in the final configuration of the machine (Fig. 2.1). This results in an improvement of the angular resolution ($\gamma = 1.69 \times 10^{-3} \text{ rad}$) by about a factor of 2 compared to the earlier measurements.

Fig. 8.1 Preliminary results for NO-CO₂ and NO-Kr

quarters of a glory period. The glory positions, as well as the glory period, are in satisfying agreement (within 5%) with calculated values obtained from the empirical potential derived from the combination rules (Sect. 5.1).

The glory amplitude of $\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_{\parallel}}$ is directly related to the anisotropy of the I.P. at the potential minimum. Here the anisotropy of the repulsive $\frac{C_{12}}{r^{12}}$ potential term, as well as the anisotropy of the $\frac{C_6}{r^6}$ attractive potential term is of importance (MIL 69, REU 69). Determination of the glory part and of the non-glory part (depending only on $q_{2,6}$) of $\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_{\parallel}}$ (by measuring, for example, a full glory period), will make it possible to extract both $q_{2,6}$ and $q_{2,12}$. The solution of this problem, however, lies beyond the scope of this thesis.

The observation of a glory for NO-Kr makes it necessary to consider again the estimate (Sect. 7.2) of the anisotropic glory undulations. The system NO-Kr differs from the systems of Sect. 7.3.3 by its excellent kinematics $v_{2,p} = 136$ m/s (or $X=3.9$ at $v_1=530$ m/s). Consequently, the damping of the glory undulations due to the velocity distribution of the secondary beam is less important for this system. The systems NO-Ar and NO-N₂ which are, of the systems discussed in this thesis, the next best to observe glory undulations, have only $X \approx 2$. Therefore, the glory effect in the anisotropy should be smaller than 37% of the non-glory effect as is the case for NO-Kr. For the systems NO-N₂O, NO-CS₂ and NO-CCl₄ the situation is rather clear. The molecules N₂O and CS₂ are similar in their I.P. ('glory quenching') and kinematics to CO₂ for which no glory undulation was observed in the recent experiments (Fig. 8.1). For the system NO-CCl₄ the values of $\frac{\sigma_{\parallel} - \sigma_{\perp}}{\sigma_{\parallel}}$ at $v_1 = 550$ m/s, 518 m/s and 505 m/s (Table 7.2-7.4) are the same. This result is in agreement with experimental findings of Gislason and Kwei (GIS 67) who did not observe glories in the total collision cross section for the system K-CCl₄. Their explanation was that CCl₄, a very slowly vibrating molecule, presents itself as a rather asymmetric collision partner. Therefore, in the case of NO-CCl₄, quenching due to dipole-dipole forces looks possible. (It is possible that the same forces cause the exceptionally small non-glory asymmetry value.)

The glory effects in $\frac{\sigma_{\parallel}^g - \sigma_{\perp}^g}{\sigma_{\parallel}^g}$ for NO-CO₂, NO-CS₂, NO-N₂O and NO-CCl₄ are expected to be smaller than 1×10^{-3} .

8.2. ANALYSIS OF THE EXPERIMENTAL RESULTS

In addition to glory undulations, several other mainly experimental factors can affect the observed anisotropy. These factors will be discussed in this Section. We begin by mentioning the effects we did not take into account and which may be neglected in our opinion.

Flops of NO molecules from the selected state, during their passage from the state selector to the scattering region, would decrease the polarization P of the state selected beams (Sect. 6.1), and hence $\frac{\sigma_{\parallel}^e}{\sigma_{\perp}^e}$ (which is proportional to P). Such flops would be serious for our accuracy if more than 10% of all molecules in the state selected beam undergo flops to other states. The results of the experiments with a second Rabi field (Sect. 4.1) exclude such a high percentage of flops.

Stray fields of the Helmholtz coils could cause a small deflection of the state selected beam, which possibly is different for the two settings of the field direction. This 'deflection' is also responsible for the fact that $\langle D_1 \rangle$ and $\langle D_3 \rangle$ are different from zero (Sect. 7.3.2). However, the same 'deflection' effect will also occur when the secondary beam is switched on. Therefore, the deflection effect in Eqs. (7.5) and (7.6) cancels in first order. Systematic errors in $\frac{\sigma_{\parallel}^e}{\sigma_{\perp}^e}$ may, however, occur in higher order because the angular resolution becomes slightly different for the two orientations. Fortunately, these errors are negligible; anisotropy measurements performed with the final configuration (Fig. 2.1) showed a first order effect in $\langle D_1 \rangle \langle D_3 \rangle$ of about 5×10^{-3} . Variation of the strength of the Rabi field and secondary beam intensity did not alter the measured anisotropy effect. Moreover, rather radical changes of configuration, and repeated alignment of the machine in the course of experiments (1½ years), did not affect the observed anisotropy values within the stated accuracy. As pointed out in Sect. 7.2, it was not necessary to take into account the small observed deviations from the $v^{-2/5}$ -dependence of the total collision cross section. In the analysis of the anisotropy results we always assumed $s=6$.

For all effects discussed in Chapter 6, corrections were applied. In Table 8.1 we give the values of the correction factors by which the theoretical anisotropy should be multiplied to yield the experimental result. Of main importance are only the corrections C_{B_0} for the incomplete decoupling of the nuclear spin (9.5%), $C_{\chi\Delta}$ for finite angular resolution (10%), and C_{v_2} ,

TABLE 8 1

Summary of the results of the anisotropy measurements with the applied corrections

Target mole- cule	$\frac{\sigma_{ }^c - \sigma_{\perp}^c}{\sigma_{ }^c}$ [10 ⁻³]	v_1 [m/s]	X	C_{B_0}	$C_{\Delta B}$	$C_{\hat{B}}$	C_{v_2}	$C_{\gamma, \Delta}$	C	$\frac{\sigma_{ } - \sigma_{\perp}}{\sigma(o)}$ [10 ⁻³]	$q_{2,6}$
CCl ₄	3.24±0.28	550	3.14	0.905	1.010	0.997	0.969	0.883	0.780	-4.15±0.36	0.138±0.012
CCl ₄	-3.74±0.93	518	2.96	„	„	„	0.961	0.889	0.779	4.80±1.19	0.160±0.040
CCl ₄	-3.18±0.61	505	2.88	„	„	„	0.961	0.862	0.755	4.21±0.81	0.140±0.027
CS ₂	-4.78±0.74	524	2.53	„	„	0.996	0.951	0.907	0.785	-6.09±0.94	0.203±0.031
N ₂ O	-6.07±1.07	518	2.34	„	1.009	0.995	0.949	0.924	0.797	7.62±1.34	0.254±0.045
CO ₂	5.74±0.76	520	2.34	„	„	„	0.949	0.903	0.779	7.37±0.98	0.246±0.033
Ar	5.78±0.52	525	2.57	„	1.010	0.996	0.953	0.934	0.810	7.14±0.64	0.238±0.021
N ₂	-5.41±0.91	517	1.86	„	1.009	0.994	0.933	0.917	0.777	-6.96±1.17	0.232±0.039

the Berkling-factor of the secondary beam velocity distribution ($6'$). The correction factor $C=C_{B_0}C_{\Delta B}C_{B_{v_2}}C_{\gamma,\Delta}$ is also shown in the Table. In the two last columns the values of $\frac{\sigma_{\parallel}-\sigma_{\perp}}{\sigma_{\parallel}}$ and of $q_{2,6}$ (using Eq. 5.35) are shown for the various systems. The error given for these quantities is the statistical error of 1 standard deviation.

8.3 THEORETICAL ASPECTS

In Chapter 5, the theoretical formulae which are needed for the discussion of the results were derived. For a r^{-6} -potential we obtained (Eqs. 5.35) and (6.8))

$$\frac{\sigma_{\parallel}-\sigma_{\perp}}{\sigma_{\parallel}} = \frac{3}{4} \frac{\sigma_{3/2}-\sigma_{1/2}}{\sigma(0)} = \frac{3}{100} q_{2,6} \quad \text{with} \quad q_{2,6} = \frac{\Delta\alpha}{3\alpha} \quad (8.1)$$

Using the experimental value of $q_{2,6}=0.16$ (BRI 66) one would expect $\frac{\sigma_{\parallel}-\sigma_{\perp}}{\sigma_{\parallel}} = 4.8 \times 10^{-3}$. The present results (Table 8.1) confirm this simple result of Eq. (8.1) in sign as well as order of magnitude.

Qualitatively, the sign is directly obvious from Fig. 2.1. For collisions with large impact parameters the axis of the NO molecule is preferentially directed perpendicular (parallel) to the intermolecular distance during the measurement of $\sigma_{\parallel}$ ($\sigma_{\perp}$). The interaction between the NO molecule and its collision partner is stronger when the molecular axis is pointed parallel to the intermolecular distance. Consequently, the collision cross section $\sigma_{\perp}$ will be larger than $\sigma_{\parallel}$.

As Eq. (8.1) shows (and has been made plausible in Chap. 5), $\frac{\sigma_{\parallel}-\sigma_{\perp}}{\sigma_{\parallel}}$ depends only on the anisotropy of the NO molecule and not on the anisotropy of its collision partner. Consequently, we expect that the anisotropy in the total collision cross section should be the same for all systems. Table 8.1 shows that for all the systems, with the exception of NO-CCl₄, the anisotropy in the total collision cross section does not differ significantly. It is difficult to assert with certainty why NO-CCl₄ behaves differently. Possibly transient dipole-dipole forces disturb the dispersion forces in such a way that their small orientational dependence is somewhat smeared out. Semi-empirical calculations of Victor and Dalgarno (VIC 70) have shown that $q_{2,6}$

is slightly dependent on the second collision partner. They found differences of about 10% between $\text{H}_2\text{-Xe}$, $\text{H}_2\text{-Kr}$, $\text{H}_2\text{-Ar}$ and $\text{H}_2\text{-He}$.

The inelasticity of the collision partner of NO does not seem to influence $\frac{\sigma_{\parallel}}{\sigma_{\perp}}$. The system K-CO_2 is known to have a very large inelastic cross section (BLC 70), there is no reason to assume that NO-CO_2 , $\text{NO-N}_2\text{O}$ and NO-CS_2 behave differently.

Leaving the system NO-CCl_4 out, we calculate for the systems of Table 8.1 an average $q_{2,6}=0.24$. A possible explanation for the discrepancy between this value and the theoretical $q_{2,6}=0.16$ is the following.

From precision collision experiments, Buck *et al.* (BUC 71a) have shown, for the systems Na-Hg , Cs-Hg and K-Hg , that molecular collisions at thermal energies do not sensitively depend on the I.P. at such large distances that perturbation theory is valid. The potential at 10 Å was twice as attractive as predicted by the theoretical C_6 -value (i.e. the semi-empirical value of Stwalley and Kramer (STW 68)). This may also be the case with the relative strength of the long-range anisotropy. When the I.P. is probed at about 10 Å (Table 5.2) the relative strength of the anisotropy should also be larger, than at much larger distances, because more of the structure of the NO molecule is 'felt'. This argument casts a serious doubt on the direct interpretation of our results, or those of Bennewitz (BLN 64), in terms of $\frac{\Delta\alpha}{3\alpha}$.

Olson and Bernstein (OLS 68, OLS 69) investigated the role of the anisotropy of the I.P. in quenching the glory extrema in $\sigma^{(0)}$. The system Li-NO was analysed using the data of Helbing and Rothe (HLL 68). Assuming $q_{2,6}=0.16$, a value of $q_{2,12}=0.45$ was estimated. With our value of $q_{2,6}=0.24$ we obtain $q_{2,12}=0.8$. However, the quenching theories are in such a bad state, in our opinion, that not too much weight should be attached to this value.

8.4 DISCUSSION OF THE BONN RESULTS

The system most extensively investigated by the Bonn group is CsF-Ar . There is no reason to expect an isotropic behaviour very different from the NO-Ar system. The main difference lies in the angle-dependent part of the I.P. CsF is a polar and excentric molecule (RFF 71) and rotates slowly in the selected $j=2, m_j=2$ state (BFN 69a). In Table 8.2 the characteristic para-

TABLE 8.2

Comparison of NO-Ar with CsF-Ar

In this Table are given the reduced mass μ , the isotropic potential parameters ϵ and σ , and the theoretical glory number N_{glory} and the relative glory amplitude. The values of N_{glory} and glory amplitude are obtained using the procedure of Olson and Bernstein (OLS 68). We used for NO-Ar the empirical potential parameters (Table 5.1), and for CsF-Ar the potential parameters of Van de Ree and Okel (REE 71). Although developed especially for TlF-Ar, these parameters are also suitable for CsF-Ar, as Van der Ree and Okel pointed out. In parenthesis the, in our opinion, unrealistic parameters of Bennewitz et al. (BEN 69) are indicated.

Collision partners	v_{rel} [m/s]	μ [AMU]	ϵ [10^{-14} erg]	σ [10^{-8} cm]	N_{glory}	Glory amplitude
NO-Ar	563	17.1	1.68	3.5	3.0	7%
CsF-Ar	446-717	31.7	2.77 [0.033]	3.8 [8.7]	6.8-4.5 [0.54-0.48]	3½%

meters for the two systems are compared.

From their experimental total collision cross sections for CsF-Ar, Bennewitz *et al.* deduced an unrealistically small ϵ -value. The Bonn group (BEN 69) concluded, from the absence of glory structure and an observed small curvature in the $\log \sigma^{(0)}$ versus $\log v_1$ -plot, that the attractive long range part of the I.P., already at thermal energies, was of minor importance in comparison to the repulsive part of the I.P.. However, in our opinion, absence of glories can be explained by quenching due to the anisotropic part of the I.P. and by damping due to the velocity averaging. At the expected $N=4.5-6.8$ nobody has yet been able to resolve glories for any molecule-atom system (RIC 70). Concerning the small curvature, one should remember that the potential may deviate from a pure r^{-6} long-range term at those distances at which it was probed. Once they had chosen such a small ϵ -value, Bennewitz and Haerten (BEN 69b) tried to explain the velocity dependence of the observed anisotropy parameter $q_{2,6}$ ($q_{2,6} = q_6$ in Table 2 of BEN 69a),

invoking the repulsive part of the I P We believe that our method of evaluation of $q_{2,6}$ with Eq (6 8) (using a pure r^{-6} -potential) should be applied to the CsF-Ar scattering

The angular resolution correction $C_{\gamma,\Delta}$ introduced by us for the anisotropy measurements is much more important for CsF than for NO ($m_{\text{CsF}}=5m_{\text{NO}}$) The angular resolution correction for CsF rises from 10% for $v_1=274$ m/s to 40% for $v_1=625$ m/s When this correction is applied, the velocity dependence of the anisotropy in Table 2 of BEN 69a disappears (We are aware that for corrections as large as 40% our Eq (6 32) giving $C_{\gamma,\Delta}$ can also be questioned!) From a weighted average for the anisotropy measurements we obtain $q_{2,6}=0.355\pm0.013$ The old value of Bennewitz *et al* (BEN 69a, BLN 69b) for CsF-Ar was $q_{2,6}=0.28\pm0.02$

8 5 CONCLUDING REMARKS AND FUTURE POSSIBILITIES

It has cost us a large effort to design and build the machine with which we have gathered the results reported in this thesis Although we regard the obtained results as preliminary in nature, we would like to summarize the most important conclusions and say a few words about future possibilities

Excluding the system NO-CCl₄, we have observed a rather constant long range anisotropy, $q_{2,6}=0.24$, for the system NO-CS₂, NO-CO₂, NO-N₂O, NO-Ar and NO-N₂ The number of investigated systems is still small, yet we believe that the independence of $q_{2,6}$ of the secondary beam molecule is shown The average value of $q_{2,6}$ is not equal to the result of the Unsold-approximation, $q_{2,6}^{(\text{U nsold})}=0.16$

The quoted errors of the results are of statistical origin, systematic errors can be neglected in comparison

A glory undulation has been clearly observed for the system NO-Kr, with the expected period The absence of glory structure has been shown for NO-CO₂, at $v_1\approx 550$ m/s

The next objective should be the performance of very precise measurements on many systems to further establish the independence of $q_{2,6}$ from the collision partner

To investigate for which systems deviations occur from the average value of the anisotropy, the following systems look interesting

- (1) Systems like NO-SnCl₄, NO-SnI₄ and NO-SF₆ for comparison with NO-CCl₄ and for checking the average value of the anisotropy.
- (2) Systems with drastically different long range behaviour like NO-CF₃H, NO-NH₃ and NO-TIF, where dipole-dipole forces and quadrupole-dipole forces govern the long range part of the I.P., rendering D.W.A. useless (TOE 66, CRO 66a).
- (3) Systems like NO-Ne (and perhaps NO-He) which can be observed with our machine in the transition region where short range forces and their anisotropy take over the dominating role (BEN 69b).
- (4) The systems NO-H₂ and NO-D₂ which have an I.P. similar to H₂-Ar. A strong anisotropy effect is expected at about $v_{rel} \approx 700$ m/s due to the orbiting effect (REU 69).

A careful analysis of anisotropic and isotropic glory effects should be undertaken. The ratio of the anisotropic and isotropic glory amplitude is free of the uncertainty arising from damping due to the velocity distribution of the collision partner.

On the instrumental side, there is the possibility of replacing the electrostatic six-pole by a magnetic six-pole. Such six-poles, with permanent magnets, are commercially available. We would prefer an electromagnetic six-pole which permits a continuous adjustment of the focal length. The advantage of this relatively costly device would be that one could work with an energy of the NO molecule about 5 times larger compared to the present possibilities (1 kG/cm produces the same force on an NO molecule in the selected state as 3×10^4 V/cm). This factor of 5 would allow us to observe several glory undulations and to come into a region where chemical reactions start to occur (with activation energies smaller than 2 kcal/molc). Another way to enter this region would be an increase of energy of the secondary beam molecules using nozzle techniques. This would also help to obtain better kinematics, because angular beam spread and velocity distribution are narrowed that way.

Naturally one can ask, what other molecules could be state selected in a way similar to NO. In our opinion, OH looks interesting and promising. An OH beam can be produced rather efficiently (MEU 71). Moreover, OH can be easily focused electrostatically (electric dipole moment 1.6D). Its ground state is $\Pi_{3/2}$. Due to the larger rotational spacing, the occupation of a single substate looks more favourable than for NO. Perhaps the intensity loss due to the more difficult production of OH can be compensated in this way.

APPENDIX

PROPERTIES OF NO

A1. NO WITHOUT FIELD

In the $^2\Pi$ -ground state, the projection of the electronic angular momentum on the molecular axis of NO is $|\Lambda| = 1$; the projection of the electronic spin momentum is $|\Sigma| = 1/2$. Furthermore, the ^{14}N nucleus has a nuclear spin $I = 1$. Consequently, the structure of energy levels is rather complicated.

TABLE A1

Approximate energy differences ΔE for various interactions,
hyperfine structure effects are due to the properties of the N nucleus,
 Λ -doubling is due to inertial effects in the rotating molecular frame

Transitions	Fine structure	Rotational structure	Hyperfine structure	Λ -doubling
levels involved	$^2\Pi_{3/2} \rightarrow ^2\Pi_{1/2}$	$^2\Pi_{3/2}$ $j=3/2 \rightarrow j=5/2$	$^2\Pi_{3/2}$ $j=3/2$ $F=3/2 \rightarrow F=5/2$	$^2\Pi_{3/2}$ $j=3/2$ $F=3/2$ $+ \rightarrow -$
ΔE [Hz]	3.6×10^{12}	2.6×10^{11}	0.75×10^8	0.61×10^6

In Table A1, the approximate energy splitting is shown for a given set of quantum numbers, in the order of decreasing strength of interaction. The $^2\Pi_{1/2}$ states are roughly $k \times 170^\circ\text{K}$ lower than the corresponding $^2\Pi_{3/2}$ states. The lower index stands for $|\Omega| = |\Lambda + \Sigma|$. If $F = j + I$ is the total angular momentum of electrons and rotating nuclear frame (J) and the ^{14}N nucleus

(1), then three F-states are possible, $F=5/2; 3/2; 1/2$, for $j=3/2$. Furthermore, each F-state consists of a Λ -doublet where + () indicates the higher (lower) level. Remarkably, the Λ -doubling is much smaller than the hyperfine structure (hfs) splitting in the $^2\Pi_{3/2}$ states with small rotational quantum numbers (see Table A1 or NEU 70).

TABLE A2
Approximate relative occupation of a single sublevel,
belonging to a fixed rotational quantum number j ,
for both electronic states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$,
at three different temperatures.

j	$^2\Pi_{3/2}$			$^2\Pi_{1/2}$		
	$T=90^\circ\text{K}$ [10^{-3}]	$T=200^\circ\text{K}$ [10^{-3}]	$T=300^\circ\text{K}$ [10^{-3}]	$T=90^\circ\text{K}$ [10^{-3}]	$T=200^\circ\text{K}$ [10^{-3}]	$T=300^\circ\text{K}$ [10^{-3}]
1/2	—		—	3.9	1.4	0.87
3/2	0.52	0.57	0.47	3.6	1.4	0.84
5/2	0.45	0.54	0.45	3.1	1.3	0.80
7/2	0.37	0.49	0.43	2.6	1.2	0.77
9/2	0.29	0.44	0.40	2.0	1.1	0.70

For thermal equilibrium, the occupation of a single sublevel is shown in Table A2. (A sublevel is assumed to be characterized by a complete set of quantum numbers including the nuclear spin.) In our experiment we are interested in a $^2\Pi_{3/2}$ state ($j=m_j=3/2$) which is roughly three times less populated than the low-lying $^2\Pi_{1/2}$ states, at $T=200^\circ\text{K}$. The six-pole is so adjusted that the state is focused on the detector slit.

A2. STARK EFFECT OF NO

In strong electric fields, the NO molecule shows a linear Stark effect due to the conserved projection of angular momentum onto the molecular axis during the rotational motion of the molecule. The dipole moment of the NO

molecule is $\mu_{\text{NO}} = 0.16 \times 10^{-18}$ esu. In strong electric fields, the effective dipole moment of a rotating molecule is unaffected by the hfs and the Λ -doubling $W_{\text{stark}} = -\mu_{\text{NO}} \mathcal{E} \frac{\Omega m_j}{j(j+1)}$, where $|\Omega| = 3/2$ for the $^2\Pi_{3/2}$ states. In total, six single sublevels with $j=3/2$ have $\Omega m_j = 9/4$ i.e. the strongest positive Stark-effect $(m_j \Omega m_j) = (\pm 3/2 \mp 3/2, +1, 1, 0)$. Because levels with equal m_j may not cross, when the electric field strength $\mathcal{E}$ is increased from zero to high values, all these six sublevels come from the highest hfs-state with $F=5/2, +$ (See, for example, Fig. 15 of STO 70).

In the center region of the six-pole, the strength of the $\mathcal{E}$ -field is not sufficient to decouple the nuclear and rotational angular momenta. In the present experiment, about 32 kV is applied across neighbouring rods of the six-pole. This leaves a center-region with a radius of about 1 mm where $\mathcal{E} \leq 2$ kV/cm, so that the simple Eq. (2.1) may not be used for the effective electric dipole moment of an NO molecule in the selected state. This means that about 2% of the cross-section of the six-pole does not participate in the sharp focusing of molecules in the selected state.

A3 ZEEMAN EFFECT OF NO

We are interested in the behaviour of molecules in the selected state (six sublevels $F=5/2, +$), if the Stark field is replaced in a Zeeman field. If the non-crossing rule for levels with equal m_j is observed, we find, in strong B-fields, three sublevels with an effective magnetic moment of $-1.17 \mu_B$, one sublevel with $-0.39 \mu_B$ (positive linear Zeeman effect), one sublevel with $+0.39 \mu_B$ and one sublevel with $+1.17 \mu_B$ (negative linear Zeeman effect).

However, due to the electric dipole moment of the NO molecule, small electric fields perpendicular to the B-field cause the extra non-crossing rule for levels with m_j -values differing by ± 1 . Those electric fields originate from the motion of the NO molecules in the B-field ($\mathcal{E} = \frac{\mathbf{v}}{c} \times \mathbf{B}$) and from stray fields of the six-pole. Taking into account this extra non-crossing rule one finds that the considered 6 sublevels all have a positive linear Zeeman effect with an effective magnetic moment of $-1.17 \mu_B$ in sufficiently strong fields.

In accordance with this picture we observe that the focus of the mole-

cules in the selected state is deflected to *one* side, when the molecules pass through a magnetic Rabi two-pole field in series with the six-pole. Deflection occurs to the side with decreasing B-field strength. No indication of splitting is observed. The average B-field strength between the Rabi pole-faces is about 5 kG in the actual experiment. This is more than sufficient to obtain total decoupling of the nuclear spin.

SAMENVATTING

In dit proefschrift wordt een experimenteel onderzoek van de hoekafhankelijkheid (het anisotrope gedeelte) van de intermoleculaire potentiaal (I P) van NO voor verschillende botsingspartners (CCl_4 , CS_2 , N_2O , CO_2 , Ar, N_2) beschreven

In tegenstelling tot het hoekonafhankelijke gedeelte is het anisotrope gedeelte van de I P tot op heden vrijwel niet experimenteel onderzocht. Onze methode om de hoekafhankelijkheid van de I P te bepalen, bestaat uit een meting van de invloed der orientatie van de moleculaire as op de totale botsingsdoorsnede. Hiertoe is nodig dat men de botsende moleculen in een gedefinieerde rotatie toestand brengt. De ruimtelijke orientatie wordt vastgelegd door de quantumgetallen j, m_j van een rotatie-toestand. Bundels van moleculen in een rotatie-toestand kunnen worden geproduceerd met behulp van inhomogene (electrische en magnetische) afbuigvelden. De krachten op de moleculen in zo een veld hangen af van het effectieve dipoolmoment, dat op zijn beurt weer afhangt van de rotatie-toestand. Onze keuze viel op het NO-molecuul o.a. omdat het qua intermoleculaire potentiaal lijkt op de veel voorkomende moleculen N_2 en O_2 . Bovendien kan voor NO de experimentele anisotropie vergeleken worden met de (in Unsold-approximatie berekende) waarde, $q_{2,6} = \frac{\Delta\alpha}{3\alpha}$. Een algemene beschrijving van de toestandsselectie is gegeven in Hoofdstuk 2. Het bleek dat moleculen met een lineair Stark-effect zoals NO, relatief gemakkelijk zijn af te buigen doch moeilijk te selecteren ten gevolge van de kleine verschillen tussen de effectieve dipoolmomenten van de diverse rotatie-toestanden. Een methode is ontwikkeld voor toestandsselectie bestaande uit de combinatie van focusatie- en deflectie-technieken. Na de toestandsselectie ($j=\frac{3}{2}, m_j=\frac{3}{2}$) blijft de orientatie van de NO-moleculen behouden dank zij het magnetisch geleide veld, dat de quantisatie-as ruimtelijk vasthoudt.

De toestandsgeselecteerde NO-bundel wordt gekruist en verzwakt door een niet toestandsgeselecteerde secundaire bundel. Een massa-spectrometer detector is zodanig opgesteld dat alleen die NO-moleculen die geen verstrooiing hebben ondergaan kunnen worden waargenomen. Door de secundaire

bundel aan en uit te schakelen kan de verzwakking worden bepaald. Met behulp van Helmholtz-spoelen wordt de quantisatie-as (en dus de moleculaire orientatie) evenwijdig en loodrecht op de relatieve snelheid van de botsende moleculen gekozen. Vergelijking van de verzwakking voor deze twee situaties maakt de bepaling van de slechte invloed van het anisotrope gedeelte van de I P mogelijk.

De technische details van de machine zijn beschreven in Hoofdstuk 3. De resultaten van de toestandsselectie worden behandeld in Hoofdstuk 4. Een sterke, scherp gefocusseerde en geselecteerde NO-bundel kon worden verkregen.

De theorie voor de evaluatie van de anisotropie der I P uit de anisotropie van de totale botsingsdoorsnede is behandeld in Hoofdstuk 5. Eerst laten wij zien dat de I P bij $10 \text{ \AA}$ overheerst wordt door de isotrope r^6 -dispersiekrachten. Deze $10 \text{ \AA}$ stellen ongeveer de afstand voor, bij welke de I P door meting van de totale botsingsdoorsnede afgetast wordt. Als men alleen naar de anisotrope termen kijkt, blijkt dat de hoekafhankelijke dispersiepotentiaal van dezelfde sterkte is als de multipooltermen. Al deze potentiaaltermen konden in een handige vorm gebracht worden. Na toepassing van de distorted wave approximatie (Sectie 5.2) blijkt dat de hoekafhankelijke dispersieterm reeds in eerste orde, de multipooltermen echter pas in hogere orde tot de anisotropie in de totale botsingsdoorsnede bijdragen. Wij meten dus, als hogere orde-effecten verwaarloosd mogen worden, de hoekafhankelijkheid in de dispersiepotentiaal. Na toepassing van de Landau-Lifshitz-approximatie wordt een simpele uitdrukking voor de anisotropie van de I P verkregen (Sectie 5.3). De toepasbaarheid van al deze benaderingen wordt onderzocht en voor onze systemen als gerechtvaardigd bevonden (Sectie 5.4).

In Hoofdstuk 6 is aangegeven hoe men de experimentele grootheden zuivert van alle instrumentele invloeden. Correcties werden uitgevoerd voor de invloed van de kernspin op de moleculaire orientatie, de veld-inhomogeniteiten van de Helmholtz-spoelen, de snelheidsverdeling van de secundaire bundel moleculen en het eindige hoek-oplossende vermogen.

In Hoofdstuk 7 zijn resultaten van de verstrooiingsmetingen verzameld. Een overzicht is gegeven van de data verwerking. Naast de anisotropie-metingen (Sectie 7.3) werd de snelheidsafhankelijkheid en de invloed van het eindig hoek-oplossend vermogen op de totale botsingsdoorsnede ook experi-

menteel onderzocht. De resultaten zijn beschreven in de Sectie 7.1 en 7.2.

In Hoofdstuk 8 worden de uitkomsten van de metingen besproken. Allereerst, zoals metingen aan het systeem NO-Kr laten zien, kan de anisotropie in de totale botsingsdoorsnede beïnvloed worden door glorie-undulaties. Dit maakt het ook mogelijk informatie over de anisotropie van de I.P. rond het potentiaal minimum te verkrijgen. Met uitzondering van NO-N₂ en NO-Ar, kan dit effect echter van weinig invloed zijn op de onderzochte systemen. Voor alle systemen met uitzondering van NO-CCl₄ vonden we een anisotropie-parameter $q_{2,6} \simeq 0.24$, een waarde die hoger ligt dan de waarde van de Unsold-approximatie $q_{2,6} = 0.16$. In Sectie 8.3 pogen wij een verklaring voor dit verschil te geven. Experimenten, waarmee dit onderzoek voortgezet zou kunnen worden, worden besproken in Sectie 8.5.

REFERENCES

- BAK 60 M R Baker, Thesis, Department of Physics, Harvard University, Boston (1960)
- BEK 66 D Beck and H J. Loesch, Z Physik **195** (1966), 444
- BEK 70 D Beck and H Forster, Z Physik **240** (1970), 136.
- BEN 64 H G Bennewitz, K H Kramer, W Paul and J P. Toennies, Z.Physik **177** (1964), 84.
- BEN 65 H G Bennewitz and H.D. Dohmann, Vakuum Tech **14** (1965), 8
- BEN 69 H G Bennewitz, R Haerten and G Muller, Z.Physik **226** (1969), 139
- BFN 69a H G Bennewitz, R Gengenbach, R Haerten and G Muller, Z Physik **226** (1969), 279
- BEN 69b H G Bennewitz and R Haerten, Z.Physik **227** (1969), 399
- BtR 62 K Berkling, R. Helbing, K. Kramer, H. Pauly, Ch. Schlier and P. Toschek, Z Physik **166** (1962), 406
- BtR 63 R B Bernstein, A Dalgarno, S W Massey, F.R S. and I.C. Percival, Proc.Roy. Soc.A **274** (1963), 427.
- BER 63a R B. Bernstein and K H. Kramer, J.Chem Phys. **38** (1963), 2507.
- BER 63b R.B. Bernstein, J Chem Phys **38** (1963), 2599.
- BER 66 R.B. Bernstein, Advances in Chemical Physics, Vol **10** (1966), 75, Interscience Publishers, New York
- BRI 62 D M Brink and G.R. Satchler, 'Angular momentum', Oxford University Press, Oxford (1962).
- BRI 66 N.J Bridge and A D Buckingham, Proc.Roy.Soc.A **295** (1966), 334.
- BUC 67 A D Buckingham, Advan.Chem Phys. **12** (1967), 107
- BUC 71 U Buck, K.A Kohler and H. Pauly, Z Physik **244** (1971), 180.
- BUC 71a U Buck, M. Kick and H. Pauly, International Report **121**, (to be published in J Chem Phys.), Max Planck Institut für Strömungs Forschung, Göttingen, Germany (1971)
- BUS 66 F von Busch, Z Physik **193** (1966), 412
- BUS 67 F. von Busch, H J Strunck and Ch. Schlier, Z.Physik **199** (1967), 518.
- BUT 71 H P Butz, R. Feltgen, H Pauly and H. Vehmeyer, Z Physik **247** (1971), 70.
- CRO 66 R J Cross and R G Gordon, J Chem Phys. **45** (1966), 3571.
- CRO 66a R J. Cross Jr., E.A. Gislason and D R Herschbach, J Chem.Phys **45** (1966), 3582.
- DAV 64 W D Davison, Proc.Roy.Soc.A **280** (1964), 227.
- DAV 70 R. David, W Spoden and J P Toennies, Internal Report **112** Max Planck

Institut für Stromungs Forschung, Göttingen Germany (1970)

- DUR 68 R Duren G P Raabe and Ch Schlier Z Physik 241 (1968), 410
- FDM 60 A R Edmonds 'Angular momentum in Quantum Mechanics', Princetown University Press Princetown, New Jersey (1960)
- FEL 70 R Feltgen, Thesis, Institut für Angewandte Physik, Bonn (1970)
- FRE 70 H Fremery, Internal Report 117, Max Planck Institut für Stromungs Forschung Göttingen Germany (1970)
- FRI 55 G Fricke Z Physik 114 (1955), 166
- GIS 67 F A Gislason and G H Kwei, J Chem Phys 46 (1967), 2838
- GOR 69 R G Gordon, J Chem Phys 51 (1969), 14
- GRO 61 W Grobner and N Hofreiter, Integral Tafel Vol 2 Springer Verlag, Wien, Austria (1961)
- GRO 67 F Grosser, Rev Sci Instr 38 (1967), 257
- HAW 68 R Hawley, Vacuum 18 (1968), 383
- HFL 64 R K Helbing and H Pauly, Z Physik 179 (1964) 16
- HFL 68 R K Helbing and F W Rothe J Chem Phys 48 (1968), 3945
- HFS 65 M M Hessel and P Kusch, J Chem Phys 43 (1965), 305
- HIR 65 J O Hirschfelder C I Curtiss and R B Bird, 'Molecular theory of Gases and Liquids', Wiley, New York (1965)
- JOH 66 B R Johnson and D Secrest J Math Phys 7 (1966), 2187
- KRA 65 K H Kramer and R B Bernstein, J Chem Phys 42 (1965), 767
- KUIJ 69 J W Kuipers, Quarterly Report no 25 p 32, Atomic and Molecular Research Group Katholieke Universiteit, Nijmegen The Netherlands (1969)
- LAN 51 Landolt Bornstein, Zahlenwerten und Functionen, Band II, Part 8, Springer Verlag Berlin (1951)
- LAN 59 L D Landau and E M Lifshitz, 'Quantum Mechanics', Pergamon Press, London (1959)
- LAW 67 K P Lawley, Mol Phys 13 (1967), 131
- LES 67 W A Lester and R B Bernstein, Chem Phys Letters 1 (1967), 207, 347
- MAR 69 H Margenau and N Kestner, 'Theory of intermolecular Forces', Pergamon, Oxford (1969)
- MAS 64 F A Mason, J T Vanderslice and J G Raw J Chem Phys 40 (1964), 2153
- MCD 70 E W McDaniel, V Cermak A Dalgarno, F F Ferguson and L Friedman, 'Ion molecule reactions', Wiley, New York (1970), 212
- MFE 70 W L Meerts, Quarterly Report no 26 p 9, Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1970)
- MEF 72 W L Meerts and A Dymanus (to be published), Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1972)
- MFS 64 A Messiah, 'Quantum Mechanics', North Holland Pub Company, Amsterdam (1964)
- MEU 71 J J ter Meulen, Quarterly Report no 28 p 72, Atomic and Molecular

- Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1971)
- MIL 69 W H Miller J Chem Phys **50** (1969), 3410
- MOE 70 H Moerkerken, M Prior and J Reuss, Physica **50** (1970) 499
- MOE 71 H Moerkerken and J Reuss, Electronic and Atomic Collisions, VII ICPEAC p 663, North-Holland Pub Company, Amsterdam (1971)
- MUL 71 G Muller Private Communication, Physikalisches Institut der Universität Bonn (1971)
- NFU 70 R M Neumann, The Astrophysical Journal **161** (1970), 779
- OLS 68 R F Olson and R B Bernstein, J Chem Phys **49** (1968), 163
- OLS 69 R E Olson and R B Bernstein, J Chem Phys **50** (1969), 246
- PAU 65 H Pauly and J P Toennies, Adv in Atomic and Molecular Physics **1** Academic Press, New York (1965), 201
- PIE 49 J R Pierce, 'Theory and design of electron beams', p 168, D van Nostrand Comp Inc, New York (1949)
- RAB 71 H A Rabitz, J Chem Phys **55** (1971), 407
- RAG 72 J A A Ragas, Internal Report (in preparation), Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1972)
- REE 62 R I Reed, 'Ion production by electron impact', Academic Press, New York (1962)
- REE 71 J van de Ree and J G R Okel, J Chem Phys **54** (1971), 589
- RFU 64 J Reuss, Physica **30** (1964), 1465
- RFU 65 J Reuss, Physica **31** (1965), 597
- REU 69 J Reuss and S Stolte, Physica **42** (1969), 111
- RIC 70 E Richmann and L Wharton, J Chem Phys **53** (1970), 945
- ROB 63 C S Roberts, Phys Rev **131** (1963), 203
- SAM 69 W N Sams and D J Kouri, J Chem Phys **51** (1969), 4809
- SCH 70 G Schonk, Internal Report, Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1970)
- SCH 71 W Schrader, Private Communication (1971), Physikalisches Institut der Universität Bonn, Germany
- STO 66 D E Stogryn and A P Stogryn, Mol Phys **2** (1966), 371
- STO 67 S Stolte, Monograph no 4, Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1967)
- STO 67a S Stolte and H Moerkerken, Quarterly Report no 16, Atomic and Molecular Research Group, Katholieke Universiteit, Nijmegen, The Netherlands (1967)
- STO 68 S Stolte, *ibid* no 20 (1968)
- STO 70 S Stolte, *ibid* no 26 (1970)
- STO 70a S Stolte, *ibid* no 27 (1970)
- STO 71 S Stolte, J Reuss and H L Schwartz, 'Electronic and Atomic Collisions', VII ICPEAC, p 658, North-Holland Pub Comp, Amsterdam (1971)
- STO 72 S Stolte, J Reuss and H L Schwartz, Physica **57** (1972), 254

STW 68 W C Stwalley and K L Kramer, J Chem Phys **48** (1968), 5555
TOE 66 J P Toennies, Z Physik **193** (1966), 76
VIC 70 G A Victor and A Dalgarno, J Chem Phys **53** (1970), 1316
ZUG 66 P Zugenmaier, Z Ang Physik **20** (1966), 184

STELLINGEN

1

De sterkte van de hoekafhankelijkheid der intermoleculaire potentiaal bij circa $10 \text{ \AA}$ wordt niet beschreven door de tot nu toe algemeen aanvaarde waarde van $\frac{\Delta\alpha}{3\alpha}$.

Dit proefschrift.

2

De anisotropie van de intermoleculaire potentiaal ter plaatse van het potentiaalminimum kan bepaald worden met behulp van de glorie-undulaties, waargenomen in de anisotropie van de totale botsingsdoorsnede.

Dit proefschrift.

3

De argumenten welke Kittel gebruikt voor de afleiding van de entropie in diverse modellen zijn hetzij onvolledig hetzij onjuist.

Ch. Kittel, 'Thermal Physics', Wiley, New York (1969),
Eq. (3.1) p.167 en Eq. (4.4) p.91.

4

Voor de hoekverdeling van een secundaire molecuulbundel die uit een lange buis stroomt, kan de gecompliceerde uitdrukking van Zugenmaier in goede benadering vervangen worden door een verdeling, die onafhankelijk is van de moleculaire vrije weglengte, buislengte en straal, zolang maar de lengte en de vrije weglengte tenminste 3 maal groter zijn dan de buisdiameter.

P. Zugenmaier, Z.Ang.Physik 20 (1966), 184.

5

De uitdrukking (Eq. 7.20), die Alonso en Finn berekenen voor de totale botsingsdoorsnede voor verstrooiing met lage energie ($E \rightarrow 0$) aan een recht-hoekige potentiaalput dient vervangen te worden door: $\sigma = 4\pi a^2 \cdot \left(1 - \frac{\tan Ka}{Ka}\right)^2$ met $K = \sqrt{\frac{2m}{\hbar^2} (E + E_0)}$.

M. Alonso en E.J. Finn, 'Quantum and statistical Physics', Addison-Wesley, Reading (Massachusetts), p.306 (1966).

V L Tal'Rose, A.F Dodonov, I O Leipunskii en I I. Morozov dienen in hun beschouwingen over moleculaire focusatie ook de mogelijkheid van dubbel-focusatie op te nemen

V L Tal'Rose, A F Dodonov, I O Leipunskii en I I Morozov, Int J Mass Spectrom Ion Phys , 7 (1971), 363

Informatie over de intermoleculaire potentiaal kan verkregen worden door moleculaire bundelspectroscopie

Het verdient aanbeveling om de sportbeoefening van studenten en personeel aan deze universiteit niet te scheiden