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Cite as: J. Chem. Phys. **147**, 013918 (2017); <https://doi.org/10.1063/1.4981023>

Submitted: 27 February 2017 . Accepted: 04 April 2017 . Published Online: 24 April 2017

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The Journal of Chemical Physics **147**, 013906 (2017); <https://doi.org/10.1063/1.4973677>

Imaging diffraction oscillations for inelastic collisions of NO radicals with He and D₂

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(Received 27 February 2017; accepted 4 April 2017; published online 24 April 2017)

We present state-to-state differential cross sections for collisions of NO molecules ($X^2\Pi_{1/2}$, $j = 1/2$, f) with He atoms and *ortho*-D₂ ($j = 0$) molecules as a function of collision energy. A high angular resolution obtained using the combination of Stark deceleration and velocity map imaging allows for the observation of diffraction oscillations in the angular scattering distributions. Differences in the differential cross sections and, in particular, differences in the angular spacing between individual diffraction peaks are observed. Since the masses of D₂ and He are almost equal and since D₂ ($j = 0$) may be considered as a pseudo-atom, these differences directly reflect the larger size of D₂ as compared to He. The observations are in excellent agreement with the cross sections obtained from quantum close-coupling scattering calculations based on accurate *ab initio* NO–He and NO–D₂ potential energy surfaces. For the latter, we calculated a new NO–D₂ potential energy surface. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4981023>]

I. INTRODUCTION

Crossed molecular beam scattering provides one of the most accurate and widely used approaches to probe the interactions between gas-phase particles.¹ In this type of experiment, the angular distribution of the scattering products, i.e., the differential cross section (DCS), can be measured under well-defined conditions in order to characterize the collisional dynamics and the underlying interactions between the collision partners. These interactions are captured theoretically by the potential energy surface (PES) of the collision complex, which can be determined via *ab initio* quantum mechanical calculations. Since the deflection of the scattering products depends on the paths, the molecules take over the PES, precise measurements of DCSs probe the quality of theoretically determined PESs.

For rotationally inelastic collisions, systems that involve the NO radical are among the most intensely studied subjects.² This popularity has both experimental and theoretical reasons. Due to its open-shell nature, the NO radical's interactions with its scattering partners are governed by two Born-Oppenheimer PESs that are non-adiabatically coupled, giving rise to collision dynamics beyond the Born-Oppenheimer approximation. Experimentally, beams of NO with high density and low rotational temperature are readily produced, and the radical can be detected state-selectively with sensitive and easy to implement spectroscopic methods.

Over the last decades, a wealth of experimental data has become available for scattering of NO with rare gas (Rg) atoms or molecules. For NO–Rg collisions, near-exact quantum scattering calculations are possible nowadays that predict scattering cross sections that are in excellent agreement with experimentally determined cross sections. The bimolecular scattering of NO with other molecules, however, is significantly less well understood. The added complexity introduced by the molecular collision partner makes a theoretical description of the collision much more challenging.

To elucidate inherent differences between NO–Rg and NO-molecule interactions, collisions of NO with He and D₂ molecules appear particularly interesting. Both collision partners have the same mass, which yields identical kinematic conditions at identical collision energies. In addition, when D₂ is prepared in its $j = 0$ rotational quantum level (*ortho*-D₂), the effect of the orientation of D₂ on the NO–D₂ interaction potential is practically eliminated and D₂ ($j = 0$) may be considered as a pseudo-atom. Therefore, He and D₂ ($j = 0$) are rather similar scattering partners for the NO radical and, at first sight, one may expect similar collision cross sections. The subtle differences in cross sections that are actually found for these systems, thus reflect directly the effect of the different size and polarizability of the molecular and the He collision partners.

Several experiments have been performed in which the comparison was made between DCSs for NO–He and NO–D₂ collisions. Using velocity map imaging (VMI) detection in a crossed-beam collision experiment, Westley *et al.* studied the inelastic scattering of these systems for multiple rotational excitation channels of ground state NO molecules, for both spin-orbit conserving and spin-orbit changing

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collisions.³ Rotational rainbows were observed in the DCSs for both complexes and it was found that, although the DCSs were very similar, the corresponding rainbow angles were consistently smaller for the NO–D₂ collisions, i.e., more forward scattering was observed. This is an indication for a stronger anisotropy in the NO–D₂ interaction, in comparison with NO–He. In a different study, hexapole state selection of the NO radicals was applied to investigate the parity dependence of these rainbows.⁴ Recently, the DCSs, as well as the rotational polarization moments, have been measured for electronically excited NO(*A*²Σ⁺) colliding with He and D₂.⁵

The NO–He system has been the subject of several high-level *ab initio* studies and its PES is well-known.^{6–8} The scattering cross sections computed with these PESs are generally in very good agreement with experimentally determined cross sections. To the best of our knowledge, the PES governing the collisions between NO and H₂, the simplest molecular scattering partner, has been the subject of only one published *ab initio* theoretical study.⁹ Another, yet unpublished NO–H₂ PES was recently computed by Klos and made available to us.¹⁰ The work described in the present paper involves the *ab initio* calculation of a new NO–H₂ PES and the application of this potential in scattering calculations, but we also computed the scattering cross sections with the NO–H₂ PES of Klos for comparison.

Here, we present high-resolution measurements of DCSs for the scattering of NO radicals with He atoms and *ortho*-D₂ molecules, for collision energies between 54 and 267 cm^{−1}. We use the combination of Stark deceleration and VMI in a crossed beam experiment to record the state-to-state DCSs with sufficient angular resolution to resolve diffraction oscillations.^{11–14} These diffraction oscillations are the finest structures occurring in a DCS, and they are one of the most sensitive gauges for the PES.^{15,16} We developed a new *ab initio* PES for NO–D₂ that predicts state-to-state scattering cross sections in excellent agreement with the experimental observations.

II. METHODS

A. Experiment

The experiments were performed in crossed molecular beam apparatus that is shown in Fig. 1 and that has been described in detail previously;^{17,18} we here only describe the

most important features. A mixture of 5% NO seeded in krypton, with a typical backing pressure of 1 bar, was expanded through a Nijmegen Pulsed Valve.¹⁹ The beam was passed through a skimmer before entering a 2.6 m long Stark decelerator, operated at a guiding phase angle in *s* = 3 mode.²⁰ The manipulation process inside the decelerator resulted in a state-selected and well-defined packet of NO radicals residing in the *X*²Π_{1/2}, *v* = 0, *j* = 1/2, *f* state, referred to hereafter as (1/2, *f*), with a mean velocity of 390 m/s and a velocity spread of 4.8 m/s (FWHM). The velocity of the NO molecules is kept constant for all experiments reported here. At a distance of 69 mm from the exit of the decelerator, the radical beam intersected with a neat beam of He atoms or D₂ molecules at a 45° angle of incidence.

The He and D₂ beams were created with a commercially available Even-Lavie (EL) valve.²¹ The valve was cooled to temperatures between 50 K and 240 K in order to alter the velocity of the He atoms or D₂ molecules, and thereby the collision energy in the experiment. For the He beam, the backing pressure was altered depending on the valve temperature, with pressures ranging from 3 bars at low temperatures to 10 bars at high temperatures. To avoid condensation, a backing pressure of 3 bars was used for the D₂ molecules at all temperatures. The velocity spread of the part of the He and D₂ beams contributing to the collision signal was estimated to be 2.5% of the mean beam velocity.

Before expanding the D₂ molecules, the D₂ gas is cryogenically cooled in a *para-ortho* converter containing a magnetic catalyst that effectively reduces the population in any of the *para*-D₂ levels with odd values of the quantum number *j*. During the supersonic expansion, the majority of the D₂ molecules cooled to the lowest rotational energy level. The rotational state distribution in the beam was probed spectroscopically using a 2 + 1 resonance-enhanced multi-photon (REMPI) scheme.²² From this we estimated that the population in the *j* = 1 level of *para*-D₂ is below 22% under all experimental conditions.

The scattered NO radicals were detected via a (1 + 1') REMPI scheme, using two Nd:YAG pumped pulsed dye laser systems. The resulting NO ions were extracted by VMI optics following the design of Suits and co-workers,²³ using a voltage on the repeller plate of 3000 V and a grounded time-of-flight tube of approximately 1 m length. The accelerated ions impinged on a microchannel plate (MCP) detector that was coupled to a phosphor screen. Mass-gating of the detector

FIG. 1. Schematic view of the experimental setup.

ensured suppression of the signal from other ionized particles. The resulting phosphor screen ion signal was recorded by a CCD camera.

For both the NO–He and NO–D₂ scattering systems, we studied the inelastic process that excites NO radicals from the initial $(1/2, f)$ state to the final $X^2\Pi_{1/2}, v = 0, j = 3/2, e$ state (hereafter referred to as $(3/2, e)$), as we found that diffraction oscillations are most pronounced for this transition. We recorded scattering images at collision energies of 54, 87, 133, 170, and 267 cm⁻¹ that were reached by tuning the temperature of the EL valve to produce beam velocities between 815 and 1590 m/s. The collision energy spread was estimated from simulations of the scattering process and beam distributions and ranged from ≈ 3.4 cm⁻¹ at the lowest collision energy to ≈ 16 cm⁻¹ at the highest collision energy.

Special care was taken to record these images at near-identical collision energies for both systems. It was found that at a given valve temperature, beams of He and D₂ are produced with slightly different velocities. Although He and D₂ have equal mass, the rotational degrees of freedom of the D₂ molecule result in different expansion dynamics and consequently different beam velocities. To obtain equal collision energies for both scattering systems, the temperature of the valve was adjusted to obtain equal beam velocities for He and D₂. Depending on the collision energy, the temperature used for He expansions was about 5–15 K lower than for D₂ expansions. For each collision energy, it was verified that both NO–He and NO–D₂ collisions were studied at the same collision energy by analyzing the radii of the resulting scattering images.

B. Data analysis

With the VMI detection method, the three-dimensional Newton sphere on which all the scattering products lie is projected on a two-dimensional detector, resulting in various blurring effects. This is illustrated in Fig. 2(a) that shows the experimental raw image for the NO $(1/2, f) + \text{He} \rightarrow \text{NO} (3/2, e) + \text{He}$ scattering process at a collision energy of 133 cm⁻¹. The structured angular scattering distribution

FIG. 2. Parts of the experimentally obtained ion images for NO–He scattering at a collision energy of 133 cm⁻¹ before (a) and after (b) applying the finite slice analysis image reconstruction method. The presented images are rotated such that the relative velocity vector points horizontally to the right.

featuring diffraction oscillations is clearly visible on the rim of the image, but there is also significant signal intensity in the inner part of the image. Image reconstruction methods are available to mitigate these effects, such that angular scattering distributions can be retrieved from the images with optimal angular resolutions. For instance, in collision experiments using a counter-propagating molecular beam geometry, the inverse Abel transformation can be applied to the images. However, these methods require full cylindrical symmetry of the recorded images and can therefore not be applied to the experiment presented here.¹²

An image reconstruction method that does not assume cylindrical symmetry was developed recently by Thompson *et al.*²⁴ This so-called finite slice analysis method assumes a symmetry axis running through the forward and backward directions of the scattering image. The two halves of the image divided by this symmetry axis are then analyzed separately without prior knowledge of the angular distribution. The program is developed in two forms: a polar treatment described in detail elsewhere in this issue²⁴ and a Cartesian form to be described in a future publication. The Cartesian form has been used here.

We used this reconstruction method to analyze all scattering images. As an example, Fig. 2(b) shows the reconstructed ion image corresponding to the raw experimental image of Fig. 2(a). Clearly, the signal intensity in the inner part of the image is much diminished, reducing the blurring effects caused by the projection of the three dimensional Newton sphere. The angular scattering distributions were extracted from the reconstructed ion images by examining the distribution of the ion signal within a thin annulus on the outer rim of each image, resulting in an intensity distribution that is a function of the scattering angle θ . The kinematics of the experiment, however, lead to additional effects that cause a bias in this distribution. To correct for these effects, ion images were simulated with the assumption of an isotropic DCS such that the influence of kinematic effects on the image intensity became apparent. These images were then analyzed with the same procedure used for the experimental ion images in order to obtain the detection probability as a function of the scattering angle, as described previously.¹³ Finally, the experimentally obtained intensity distribution was divided by this function to obtain the DCS of the scattering process.

C. Theory

1. Scattering calculations

We performed coupled-channels scattering calculations to obtain the DCSs for NO–D₂ and NO–He collisions. The basic theory of this approach is described for atom-molecule collisions in Ref. 25; we have extended it to molecule-molecule collisions. Here, we give only details pertaining to the NO–D₂ and NO–He systems and numerical aspects.

We used a primitive Hund's case (a) basis set to describe the NO molecule, and the *diabatic* electronic wavefunctions of the complex are given as products of rotated monomer wavefunctions.²⁶ Matrix elements of the potential energy surface in this diabatic electronic basis are given by the

expansion,²⁷

$$\begin{aligned} \langle \Lambda | \hat{V} | \Lambda' \rangle = & \sum_{L_{\text{NO}}, L_{\text{D}_2}, L} V_{L_{\text{NO}}, L_{\text{D}_2}, L}^{\Lambda, \Lambda'}(R) \\ & \times \sum_{M_{\text{NO}}, M_{\text{D}_2}, M} \langle L_{\text{NO}} M_{\text{NO}} L_{\text{D}_2} M_{\text{D}_2} | LM \rangle \langle LML - M | 00 \rangle \\ & \times D_{M_{\text{NO}}, \Lambda - \Lambda'}^{(L_{\text{NO}})*}(\hat{\mathbf{r}}_{\text{NO}}) C_{L_{\text{D}_2}, M_{\text{D}_2}}(\hat{\mathbf{r}}_{\text{D}_2}) C_{L, M}(\hat{\mathbf{R}}), \quad (1) \end{aligned}$$

where $D_{m,k}^{(j)}(\hat{\mathbf{r}})$ is a Wigner D-matrix element and $C_{j,m}(\hat{\mathbf{r}})$ are the Racah-normalized spherical harmonics. The directions of the NO, D₂, and intermolecular axes are denoted by $\hat{\mathbf{r}}_{\text{NO}}$, $\hat{\mathbf{r}}_{\text{D}_2}$, and $\hat{\mathbf{R}}$, respectively, and $\langle j_1 m_1 j_2 m_2 | jm \rangle$ is a Clebsch-Gordan coefficient. The index $\Lambda = \pm 1$ denotes the two orbital angular momentum components of the NO(²Π) ground state. For the *diagonal* ($\Lambda = \Lambda'$) diabatic potentials $K = \Lambda - \Lambda' = 0$ and the Wigner D-matrix elements are the Racah-normalized spherical harmonics. Wigner-D matrix elements with body-referred projection $K = \Lambda - \Lambda' = \pm 2$ were used for the *off-diagonal* elements which couple the asymptotically degenerate $\Lambda = \pm 1$ sub-states of the NO(²Π) state.²⁷ For NO–D₂ we used the diabatic potentials computed for NO–H₂, the calculation of these diabatic potential energy surfaces is discussed in Sec. II C 2. The diabatic potentials for NO–He were obtained from Ref. 7.

The channel basis in the scattering calculations consists of the same functions as used in the expansion of the potential in Eq. (1), but Clebsch-Gordan coupled to definite values of the conserved total angular momentum quantum number $\mathcal{J}$ and adapted to the overall parity. Due to identical particle symmetry, we can further limit the rotational states of D₂ to even or odd j_{D_2} , depending on whether they refer to *ortho* or *para* D₂. For NO–D₂ the basis sets were truncated at $j_{\text{NO}} = 13.5$ and $j_{\text{D}_2} = 3$, and calculations were performed for both parities and $\mathcal{J}$ up to 60.5. The maximum number of channel functions amounts to more than 2500. The radial propagation grid ranges from $R = 4.5$ to $40 a_0$ with a grid spacing of $0.1 a_0$. For NO–He we used even higher maximum j_{NO} and $\mathcal{J}$ values, although convergence was reached already at lower values, with a radial grid of $R = 2.5$ – $40 a_0$ and a grid spacing of $0.1 a_0$. Scattering calculations were performed at the experimental collision energies of 54, 87, 133, 170, and 267 cm^{-1} . In order to account for the spread in collision energy in the experiments, the cross sections were actually calculated for energies in a range from -10% to $+10\%$ of each collision energy, in steps from 0.25 cm^{-1} for the lowest to 5 cm^{-1} for the highest collision energy. The calculated DCSs are then input to simulations which account for the experimental conditions.

2. Diabatic potential energy surfaces for NO–H₂

At high-symmetry geometries with either all four atoms in the same σ_h -plane or with the H₂ molecule perpendicular to that plane, the NO–H₂ system possesses C_s symmetry. The two relevant adiabatic states, correlating to the two degenerate components of the ²Π ground state of the NO molecule, carry different irreducible representations which are designated by A' and A'' . This simplifies calculations on the NO–H₂ system in two ways. First, the A' and A'' adiabatic states and the

$\Lambda = \pm 1$ diabatic states are related by a fixed known transformation, such that one can transform to the diabatic representation analytically. Second, the relevant adiabatic states are the lowest states in their respective symmetries, such that one can apply accurate single-reference coupled-cluster theory for this open-shell system.

We first performed benchmark calculations to gauge the accuracy of different *ab initio* approaches at two high-symmetry geometries. These geometries are defined by the Jacobi coordinates $R = 6.25 a_0$, $\theta_{\text{NO}} = 90^\circ$, $\theta_{\text{H}_2} = 60^\circ$, $\phi = 180^\circ$, corresponding to the A' minimum, and $R = 6.5 a_0$, $\theta_{\text{NO}} = 60^\circ$, $\theta_{\text{H}_2} = 67.5^\circ$, $\phi = 180^\circ$, corresponding to the A'' minimum. For values of θ_{NO} smaller than 90° , the N atom is closer to the H₂ midpoint than the O atom. All calculations reported here were performed using the MOLPRO 2012 suite of programs,²⁸ and all energies were corrected for the basis set superposition error (BSSE) using the counter-poise procedure of Boys and Bernardi.²⁹ We performed partially spin-restricted coupled-cluster calculations with single and double excitations and perturbative triples [RCCSD(T)], where orbitals were obtained from Hartree-Fock calculations, all separately for both A' and A'' states. We performed calculations in aug-cc-pV ζ Z basis sets with $\zeta = T, Q, 5, 6$. Extrapolations to the complete basis set (CBS) limit were estimated, assuming a ζ^{-3} basis-set dependence of the correlation energy. We formed different estimates using all subsets of two or three basis sets with ζ increasing in unit steps. Additional CBS estimates are given by performing F12-RCCSD(T) calculations in $\zeta = T, Q$ basis sets. All of these CBS estimates lie scattered within 0.6 cm^{-1} of the simplest estimate based on the $\zeta = T, Q$ basis sets. This is an error smaller than 1% of the well depth, which is approximately 84 cm^{-1} for both A' and A'' states. Further corrections should be small but, for example, an approximate F12 correction for the triples energy, by scaling with the ratio of F12-MP2 and MP2 correlation energies, amounts to 1.5 cm^{-1} . This may give a more conservative indication of the uncertainty in the well depth. Based on these benchmark calculations, we have decided to compute global RCCSD(T) potentials extrapolated to the CBS limit using $\zeta = T, Q$ basis sets.

Next, we extended the *ab initio* approach outlined above to low-symmetry geometries, such that we could perform calculations for arbitrary orientations of the molecules and hence accurately sample the anisotropy of the potential. At these low-symmetry geometries, the two relevant adiabatic states no longer carry different irreducible representations and hence are not the lowest adiabatic states in their respective symmetries. Hence, one might conclude that one cannot apply the single-reference coupled-cluster method for low-symmetry geometries. Our modified approach is as follows: We obtained orbitals from state-averaged two-configuration self-consistent field (2C-SCF) calculations, which is a complete active space SCF calculation with one open-shell electron in two NO π^* orbitals. For this effective one-electron system, one can always describe both 2C-SCF states exactly as single determinants by using natural orbitals. We computed pseudo-canonical orbitals, in terms of which both states are generally still close to a single determinant form. These single determinants were subsequently used as reference states

in single-reference RCCSD(T) calculations. This approach relies on an accurate description of the mixing of the two states at the 2C-SCF level of theory and effectively neglects mixing at the post-SCF level by applying the single-reference RCCSD(T) method. The validity of this approach was monitored throughout by comparing the RCCSD(T) energy difference between the lowest two adiabatic states to what is obtained from multi-reference configuration interaction (MRCI) calculations. At $R = 6 a_0$, the RCCSD(T) and MRCI excitation energies differ by less than 3.7 cm^{-1} for all orientations included, which is to be compared to the mean excitation energy of 71 cm^{-1} .

For low-symmetry geometries, the calculations of diabatic potential energy surfaces are further complicated since the transformation between the diabatic representation and the adiabatic representation in which *ab initio* potential energies are computed is not known analytically. We determine this transformation numerically using the multiple-property-based diabaticization algorithm of Ref. 30. As properties we included all components of the electric quadrupole tensor and all components of orbital angular momentum. These properties are computed from MRCI wavefunctions using the same 2C-SCF reference states. At high-symmetry geometries, our diabaticization algorithm recovers exactly the symmetry-determined transformation between the diabatic and adiabatic representations. However, our approach also allowed us to diabaticize at low-symmetry geometries, i.e., to explore more orientations and to sample the anisotropy of the interaction more accurately.

The monomer bond lengths were kept fixed at the ground state vibrationally averaged values: $r_{\text{NO}} = 2.1803 a_0$ and $r_{\text{H}_2} = 1.448 a_0$. Although the vibrationally averaged bond length of D_2 is somewhat smaller than that of H_2 , we used the NO-H_2 potential also for NO-D_2 without modification. In the radial grid, we used the points $R = 4, 4.25, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 10, 12, 15, 18, 20 a_0$. The Jacobi angles θ_{NO} , θ_{H_2} , and ϕ were sampled using 10, 8, and 10-point grids of Gauss-Legendre and Gauss-Chebyshev quadrature points, respectively. The range of θ_{H_2} was limited to angles between 0° and 90° . This permitted evaluation of the expansion coefficients in Eq. (1) up to $L_{\text{NO}} = 9$ and $L_{\text{H}_2} = 6$ by numerical integration. The expansion, which was subsequently truncated to $L_{\text{NO}} \leq 8$ and $L_{\text{H}_2} \leq 4$, reproduces the *ab initio* points for $R = 7 a_0$, i.e., near the minimum of the isotropic potential with a depth of 44 cm^{-1} , to root-mean-square errors of 0.02 and 0.11 cm^{-1} for the diagonal and off-diagonal potentials, respectively. At $R = 6 a_0$, which is at shorter separation than the anisotropic minima with depths of approximately 84 cm^{-1} , these errors increase to 0.08 and 0.34 cm^{-1} . At $R = 4 a_0$, where the isotropic potential is repulsive by 7000 cm^{-1} , they are up to 16 and 40 cm^{-1} . That is, the angular expansion used here is more accurate than the uncertainty in the *ab initio* points, as indicated by the benchmark calculations discussed above.

To obtain a global representation of the diabatic potential energy surfaces, we fitted the R -dependence of the angular expansion coefficients. We determined first-order long-range interactions from multipole moments of rank $L \leq 3$, which were obtained from finite-field CCSD(T) calculations for the

monomers. Other long-range terms proportional to R^{-n} with $n \leq 7$ were fit in a R^n -weighted linear least squares fit to the *ab initio* points with $R \geq 12$. This long-range potential was then damped by multiplication with Tang-Toennies damping functions with $\beta = 2 a_0^{-1}$.³¹ The short-range potential, defined as the difference between the *ab initio* points and the damped long-range potential, was then interpolated using the reproducing kernel Hilbert space method,³² with the long-range extrapolation determined by the leading long-range term which is not included explicitly. SCILAB routines for evaluating the R -dependent expansion coefficients are made available in the [supplementary material](#).³³

Finally, we note that we made the following modifications to the procedure outlined above, in order to obtain smooth long-range interactions with the correct R^{-n} radial dependence for the off-diagonal potential. Before applying the counterpoise correction, the adiabatic monomer states were transformed to the same diabatic representation as the adiabatic states of the complex, with the same diabaticization procedure. Second, the off-diagonal potential was not extrapolated to the CBS limit, but given in the $\zeta = Q$ basis set. The diagonal potential was extrapolated as discussed.

III. RESULTS AND DISCUSSION

The inelastic scattering of NO with He and *ortho*- D_2 was probed for the $(1/2, f \rightarrow 3/2, e)$ channel for five different collision energies. The raw ion images are shown in Fig. 3, in which the upper and lower rows pertain to NO-He and NO- D_2 collisions, respectively. The collision energy is indicated above each set of images. All images are presented with the relative velocity vector of the scattering partners oriented horizontally, such that the forward scattering direction ($\theta \approx 0^\circ$) is found on the righthand side of the circular distribution. In each image, a small area around this forward scattering angle is affected by imperfect state selection of the NO molecules. This region is therefore cut from the experimental image.

For each collision energy, the diameters of the scattering images are seen to be equal for both collision systems, indicating that NO-He and NO- D_2 collisions are probed at near-identical collision energies. All images show a clear presence of diffraction oscillations, although they are more pronounced at lower collision energies. Due to the projection of three-dimensional Newton spheres onto a two-dimensional detector plane, the oscillatory diffraction patterns cause vertical stripes in the images. These stripes are clearly visible in the images as well, in particular for NO- D_2 at the lowest collision energies probed.

Each image was analyzed using the procedure described in Section II B, and a DCS was subsequently extracted from the reconstructed image. The resulting experimentally obtained DCSs are presented in Fig. 4 (solid lines), together with the DCSs that are predicted by theory (dashed lines). For the latter, we show effective DCSs obtained by averaging the DCSs from our scattering calculations over the collision energy distributions present in the experiment. Each panel corresponds to a specific collision energy and displays the results for both NO-He (blue curves) and NO- D_2 scattering (red curves). The

FIG. 3. Experimentally obtained velocity mapped ion images for the inelastic scattering of NO with He and *ortho*-D₂ ($j = 0$), in which the NO molecules are rotationally excited from the $(1/2, f)$ to the $(3/2, e)$ state at various collision energies. Colors indicate the signal intensity and the collision energy (E_{coll}) is given in cm^{-1} . For He (D₂) collisions, pixels with an intensity lower than 5% (1%) of the maximum value are omitted from the image in order to reduce the visibility of the background signal. Note that the color scale is defined relative to the maximum intensity of each individual image. Therefore, the difference in signal intensities between images does not reflect the difference in integral cross sections. The images are displayed such that the relative velocity vector of the scattering partners is oriented horizontally. A small area around the forward scattering direction is masked due to imperfect state selection of the initial NO packet.

traces corresponding to NO–D₂ collisions are given a vertical offset for clarity. The DCSs are normalized by the area under the curve, taking the angles of the extracted experimental DCS as the limits for the integration, i.e., omitting the part of the forward scattering region that is masked by the imperfect state selection of the parent NO beam.

In general, the cross sections observed for NO–He and NO–D₂ are quite similar, which is to be expected from the similarity of He and D₂ ($j = 0$) as collision partners. However, some subtle differences become apparent after closer inspection of the results. At a given collision energy, the DCSs for NO–He collisions have larger sideways and back-scattered components compared to NO–D₂ collisions. In addition, the individual diffraction peaks appear closer spaced for NO–He than for NO–D₂. For both collision partners, the experimentally determined cross sections show excellent agreement with the DCSs predicted by theory. Both the overall shapes of the DCSs and the positions of individual diffraction peaks are reproduced well by the calculations, providing a rigorous test for the new NO–D₂ PESs that were calculated for this work. We also computed the cross sections for NO–D₂ collisions with the NO–H₂ potentials of Klos;¹⁰ the results were very similar to those obtained with the NO–H₂ potentials described in Sec. II C 2.

The differences observed between the two scattering systems can be rationalized from the differences in interaction potentials. The D₂ molecule has a quadrupole moment, but the anisotropic contributions to the NO–D₂ PES that this quadrupole moment produces are averaged out in the $j = 0$ rotational state of D₂, and the energy spacing with the $j = 2$ rotational state is so large that the admixture of

this state during the collision with NO has hardly any effect. What remains, however, is that D₂ is larger than He, i.e., it repels NO at larger distances R , and it also has a larger polarizability, which results in stronger attractive dispersion interactions at long range. Consequently, for a given collision energy and inelastic transition, larger impact parameters can induce transitions for NO–D₂, while for NO–He more head-on collisions are required. This results for NO–D₂ in a more forward scattered angular distribution of the scattered products.

The larger size of D₂ also explains the slightly smaller angular spacing $\Delta\theta$ between the diffraction peaks, which is observed for NO–D₂ in comparison to NO–He. In a semi-classical picture, diffraction oscillations can be understood to originate from matter waves that diffract from a target particle. In the limit of hard-sphere scattering, the spacing between the diffraction oscillations $\Delta\theta$ is given by¹¹

$$\Delta\theta = \frac{\pi}{kR_0}, \quad (2)$$

where $\Delta\theta$ is given in radians, k is the size of the wavevector of the impinging matter wave, and R_0 is the radius of the sphere. The wavevector is related to the collision energy as $k = \sqrt{2\mu E_{\text{coll}}}/\hbar$, with μ the reduced mass of the scattering partners. In this model, we may take for R_0 the effective shell radius of the interaction potential at the collision energy of the experiment. A larger size of a collision partner yields a larger value for R_0 , resulting in closer spaced diffraction peaks.

We can use the observed diffraction patterns to estimate the value of R_0 , i.e., the size of the collision complex at closest

FIG. 4. Extracted differential cross sections for the inelastic excitation of NO($1/2$, f) to the final state ($3/2$, e) through collisions with He (blue curves) and D₂ (red curves) at various collision energies. Solid lines show the experimentally obtained DCSs, whereas dotted lines represent the DCSs predicted by theory. The red curves are given vertical offsets for reasons of clarity. All DCSs are normalised according to the area under the experimentally obtained curve. Note the different scales on the horizontal axes.

approach. It should be noted, however, that this will merely give an indicative number, as the semiclassical model discussed above is rather crude. In addition, the DCSs do not feature a regular diffraction pattern that is characterized by a single value for $\Delta\theta$. Instead, the interference pattern originates from a combination of multiple Bessel functions, resulting in a spacing between adjacent diffraction peaks, which changes slightly over the full DCS.¹⁴ Nevertheless, it is insightful to quantify the values for $\Delta\theta$ from the measured diffraction patterns, and to compare these to theory. For this, we analyzed the spacing between the diffraction peaks in the angular region where the oscillatory pattern is most pronounced and regular. This region is found for scattering angles between 30° and 50° and about 170° . This window thus excludes forward scattered angles where irregular diffraction patterns are typically found, and backscattering angles where the amplitude of the diffraction peaks is typically low.

The results are presented in Fig. 5, together with the spacings predicted by the theoretically obtained DCSs. It is seen that good agreement between the experiment and theory is obtained for both collision partners, although the experiment seems to systematically overestimate the angular spacing, which we attribute to blurring effects in particularly the backward parts of the images. Fig. 5 further illustrates that the spacing between the diffraction oscillations is

consistently smaller for the NO–D₂ system, indicating that the size of the collision complex is larger for NO–D₂ than for NO–He, in accordance with the observations made above. The values for $\Delta\theta$ follow a $1/\sqrt{E_{\text{coll}}}$ dependence on

FIG. 5. Double logarithmic plot of the angular spacing of the diffraction oscillations as a function of the collision energy. Results for D₂ are shown in red, whereas the results for He are shown in blue. Circles show the theoretically predicted values, whereas the asterisks show the experimental results. Error bars indicate the 95% confidence interval for the experimental values. To guide the eye, logarithmic fits of the experimental data are shown by the solid lines.

collision energy, in accordance with Eq. (2). For each collision complex, a rough estimate for the effective radius of the sphere, R_0 , can be obtained from the logarithmic fits shown in Fig. 5 by evaluating Eq. (2). This leads to a value of $(6.2 \pm 0.2)a_0$ for the NO–He system and a value of $(6.7 \pm 0.1)a_0$ for the NO–D₂ system.

IV. CONCLUSION

We have presented high-resolution measurements of state-to-state differential scattering cross sections for collisions of state-selected NO radicals with He atoms and *ortho*-D₂ ($j = 0$) molecules. Cross sections for the $X^2\Pi_{1/2}, j = 1/2, f \rightarrow X, ^2\Pi_{1/2}, j = 3/2, e$ transition are probed as a function of collision energy between 54 cm⁻¹ and 267 cm⁻¹. Diffraction oscillations are fully resolved for both systems and at all collision energies. Subtle differences are found in the DCSs for the kinematically identical NO–He and NO–D₂ systems, particularly in the angular spacing between the diffraction peaks. The cross sections are in excellent agreement with the cross sections derived from quantum close-coupling scattering calculations that are based on recent NO–He PESs and newly developed NO–D₂ PESs. The differences in the diffraction structure found here between NO–He and NO–D₂ collisions reflect the larger size of D₂ in comparison to He as a collision partner.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for Scilab routines for evaluating the potential energy surfaces.

ACKNOWLEDGMENTS

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013/ERC Grant Agreement No. 335646 MOLBIL). This work is part of a research program of the Netherlands Organization for Scientific Research (NWO). A.G.S. acknowledges support from the National Science Foundation (Award No. CHE-1634760) and from the Radboud Excellence Initiative through a visiting professor award. The expert technical support of C. Berkhout and N. Janssen is gratefully acknowledged. The authors thank J. Klos for providing the PESs of NO–He and NO–H₂.

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