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The Ne–O₂ potential energy surface from high-resolution diffraction and glory scattering experiments and from the Zeeman spectrum

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The full anisotropic potential energy surface for the Ne–O₂ van der Waals molecule has been obtained from the simultaneous analysis of total differential cross section data with well resolved diffraction oscillations and of absolute total integral cross section data with glory structure measured in Perugia, of the Zeeman spectrum measured in Nijmegen, and of transport coefficients taken from literature. The anisotropy of the interaction is obtained from the Zeeman spectrum using both numerical and analytical approaches for the energy levels, and from the quenching of the diffraction oscillations in the total differential cross section within the infinite-order-sudden approximation. The latter approximation is practically exact under the experimental conditions, as previously shown for the similar Ne–N₂ system by comparison with exact close-coupling scattering calculations. The derived potential energy surface represents a dramatic improvement with respect to a previous approximate estimate.

I. INTRODUCTION

In recent years, much work has been devoted to the determination of potential energy surfaces (PES) for simple atom–molecule van der Waals systems. Unfortunately, quantum chemistry, even at the level of the most sophisticated \textit{ab initio} calculations, has thus far been of limited value in generating a reliable quantitative description of anisotropic van der Waals interactions in the attractive well, with the exception of a few light systems. Theory so far provides useful information on the long-range attraction and on the short-range repulsion. Generalization to atom–molecule interactions of atom–atom interaction modeling procedures has recently been applied beyond the H₂–rare gas systems with various degree of success.\textsuperscript{2–4} Our most detailed knowledge of anisotropic interaction comes from the experiment. The scattering method has proven to be a general and powerful tool for providing detailed information on both the attractive and repulsive parts of the interaction potential.\textsuperscript{5}

When the molecular species possesses a permanent dipole or quadrupole moment, spectroscopic techniques can successfully be applied for obtaining detailed information on the intermolecular potential near the equilibrium configuration of dimers and recently also far from equilibrium.\textsuperscript{6–8} In these cases, information away from the minimum and on the repulsive part of the interaction still relies on scattering experiments, which, in general, are complementary to spectroscopic studies. For van der Waals systems in which the molecular partner is a homonuclear diatomic, such as N₂ and O₂, interacting with a rare gas atom, scattering methods are practically the only source of detailed information on the intermolecular potentials, these systems still being out of reach of the state-of-the-art techniques of mid-infrared (IR)\textsuperscript{7} and far-infrared (IR) laser\textsuperscript{8} rovibrational spectroscopy. However, for the paramagnetic O₂–rare gas systems, Zeeman spectroscopy has recently become feasible.

Measurements of state-to-state rotationally inelastic differential cross sections (DCS) provide the most detailed information on the anisotropy of the interaction.\textsuperscript{1,5,9} When single rotational transitions cannot be experimentally resolved, differential energy loss spectra still provide a sensitive probe of the anisotropy, especially if rotational rainbows are observed.\textsuperscript{1} However, rotationally inelastic cross sections, as well as rotational rainbows, give information only on the relative anisotropy of a system, i.e., the difference between potential curves of different orientations.\textsuperscript{1} The determination of the absolute scale of the potential relies on additional information, as the precise measurement of diffraction oscillations in the total (elastic + inelastic) DCS. Total DCS data, measured under high-resolution conditions and presenting a well resolved diffraction structure, also provide indirectly quantitative reliable information on the anisotropy of the interaction.\textsuperscript{5,10–13} Measurements of the rainbow structure in the total DCS, and/or of the glory structure in the total integral cross section (ICS), or of the second virial coefficient down to low temperatures, allow the determination of the other relevant features of the attractive well of the full PES. The long-range part of the interaction can be obtained experimentally from the absolute value of the ICS measured as a function of collision velocity, if available, or from calculated \textit{ab initio} or semiempirical van der Waals coefficients. Transport data can then be used to check the validity of the potential so derived and, if available up to very high temperature, to extend its validity in the region of the repulsion.

The prescription outlined above has been followed in our laboratory for the determination of accurate intermolecular potentials for both atom–atom\textsuperscript{14} and atom–molecule systems.\textsuperscript{10,11,15} Advantage has been taken of the very detailed information content of precise diffraction scattering measurements, which coupled to all the other available ex-
perimental properties in a multiproperty analysis fashion, has led to the determinations of reliable PES for He–N₂, He–O₂, He–NO,¹⁰ He–CO,¹⁵ and Ne–N₂.¹¹ In all these cases, the scattering dynamics have been treated within the infinite-order-sudden (IOS) approximation.¹⁶ The accuracy of the IOS decoupling scheme for the analysis of total DCS data at relatively low collision energies is well established for He-containing systems.¹⁷ Recently, it was also checked for Ne-containing systems by performing exact close-coupling (CC) scattering calculations for Ne–N₂ at the energy of the experiment, and comparing the CC results with the IOS scattering results.¹¹

In the present study we have extended the same approach used for the He–molecule and Ne–N₂ systems to also Ne–O₂. In the Perugia laboratory, we have measured (a) the total DCS in a wide angular range at a collision energy of \( E = 74.9 \text{ meV} \) in high resolution conditions, which has permitted us to resolve clearly the closely spaced diffraction oscillations superimposed on the main rainbow oscillation, and (b) the absolute total ICS with a pronounced glory structure as a function of collision velocity using rotationally hot molecules. In the Nijmegen laboratory, the magnetic radio-frequency (r.f.) spectrum of Ne–O₂ has been measured by the molecular beam magnetic resonance technique.

The information content of these scattering and spectroscopic experiments has been coupled to that of transport (diffusion and viscosity) coefficients available from the literature to derive a reliable potential energy surface for the Ne–O₂ van der Waals molecule.

Prior to the scattering and spectroscopic studies reported here, the range of experimental data available for the Ne–O₂ system was somewhat limited. The interaction second virial coefficient was reported at only one temperature (90 K) by Knobler et al.¹⁸ in 1959. The viscosity and diffusion coefficients from 298 to 678 K were measured by Kestin et al.¹⁹ in 1977. The absolute total ICS as a function of velocity was measured by Luzzatti et al.²⁰ in 1977 and analyzed in terms of a spherical symmetric potential model. Pressure broadening cross sections were analyzed by Smith and Giraud²¹ in 1979 to generate a crude anisotropic interaction, which was later on modified in its anisotropy by Corey and McCourt²² to obtain improved agreement between their IOS calculations for the pressure broadening cross sections governing the magnetic dipole allowed transitions in Ne–O₂ and the experimental cross sections. A preliminary unpublished form of the present PES for Ne–O₂ was employed by Gianturco and co-workers to compute transport (diffusion and viscosity) coefficients within first-order kinetic theory in the 298–678 K temperature range²³ and the second virial coefficient at 90 K.²⁴

The paper is organized as follows: in Sec. II we briefly describe the apparatus and details of the experiments. In Sec. III we report the experimental results, illustrate the potential model used, present the data analysis which includes also transport coefficients, and discuss the results of the analysis. Conclusions follow in Sec. IV.

II. EXPERIMENTAL

The scattering measurements were carried out in Perugia by using two different molecular beam machines, while the Zeeman spectrum of the Ne–O₂ van der Waals molecule was measured in Nijmegen.

A. Total differential cross sections

The total DCS have been measured in a high-resolution crossed molecular beam apparatus which has been described in detail previously.¹⁰ Briefly, two well-collimated, differentially pumped, supersonic nozzle beams of Ne atoms and O₂ molecules are crossed at 90° in a large scattering chamber kept at about 3×10⁻⁷ torr in operating conditions, and the in-plane scattered Ne is detected by a rotating ultra-high-vacuum (UHV) quadrupole mass spectrometer detector kept in the 10⁻¹¹ torr range in the ionization region by extensive ion-, turbo-, and cryo-pumping.

The primary Ne beam was produced by expanding 18 Atm of pure Ne at room temperature through a 0.025 mm diam nozzle and defined to an angular divergence, \( \Delta \Theta \), of 0.4°. The expansion conditions of the secondary O₂ beam were 3 Atm with a nozzle diameter of 0.10 mm and at room temperature (\( \Delta \Theta = 1.8°\)). The velocity distribution of the Ne beam showed a peak velocity \( v \) of 797 m/s with a full-width-at-half-maximum (FWHM) \( \Delta v/v = 4.6\% \). The corresponding values for the O₂ beam were \( v = 735 \text{ m/s and } \Delta v/v = 10.9\% \). The beam pressures were chosen as to give the maximum signal intensity, while avoiding possible problems from condensation effects. Under our geometrical arrangement, which is the same used in previous experiments,¹⁰¹¹¹⁴¹⁵ the collision volume is always contained in the detector viewing angle, which, for a point collision zone, is 0.5°. Great care was devoted to the calibration of the velocity distributions of the two beams as well as of the angular positions, in order to obtain high accuracy in the determination of the absolute scale of the potential. The beam velocities were measured by the time-of-flight method to better than 0.6%, using a high-speed multichannel scaler and a CAMAC data acquisition system controlled by a microcomputer PDP-11/23. The location of the primary Ne beam was determined to better than 0.03°, as stressed in previous work,¹⁰¹¹¹⁴¹⁵ by carefully measuring the elastically scattered signals at known collision energies for the Ne–Ar and He–Ar systems for which the potentials are accurately known.

The translational temperature of the O₂ molecules in the beam has been estimated from the velocity distribution to be less than 10 K. Assuming equilibrium among the translational and rotational temperatures in the beam, all the O₂ molecules are expected to be in their lowest rotational levels (\( J = 1,3 \)). The laboratory total (elastic + inelastic) angular distribution \( J(\Theta) \), was obtained by taking at least four scans of 45–90° counts at each angle. The secondary beam was modulated at 160 Hz by a tuning fork chopper for background subtraction. The angular distributions were measured at both positive and negative angles with respect to the Ne primary beam, which turned out to be very useful for deriving an accurate absolute scale of the potential. In fact, the scattered Ne beam at negative laboratory angles has a lower velocity than the incoming beam before the collision: This "kinematic cooling" effect gives rise to a higher resolution.
which is manifested in an amplitude of the diffraction oscillations at negative angles slightly larger than at positive angles, and in a higher sensitivity to the absolute scale of the potential determined by the location of the diffraction structure.

B. Absolute total integral cross sections

The molecular beam apparatus employed for the measurement of the absolute total ICS is the same used in Perugia for a number of years, and is described in detail elsewhere. Briefly, an effusive beam of oxygen molecules, produced at high rotational temperature from a source kept at about $10^4$ K, is velocity selected by a slotted disk selector with 5% resolution (FWHM), and after mechanical modulation, crosses a scattering chamber cooled to liquid air temperature, containing the target Ne gas. The beam is detected by a quadrupole mass spectrometer detector with an electron bombardment ionizer kept in UHV conditions. Integral cross sections are obtained from measurements of beam intensities with and without target gas in the scattering chamber. In order to minimize random errors due to fluctuations and/or drifting of experimental conditions, the target gas is admitted continuously in the scattering chamber under flow conditions calibrated to reach the proper target gas pressure ($10^{-2} \div 10^{-3}$ torr), and the chamber can be emptied to background pressure ($\sim 10^{-6}$ torr) in less than one second through an additional hole opened by a magnetically operated valve. In this way, using measurement cycles of about 20 sec with and without target gas, a statistical error of the order of 1% is obtained with counting times of about 200 sec per point. The velocity dependence of the cross section is obtained by taking at least five scans of 200 sec counts at each velocity. The angular resolution of the apparatus is $8 \times 10^{-4}$ rad, less than the limiting angle for the present system. Absolute values of the cross sections have been obtained following the usual procedure, whereby the relative pressure of the target gas has been measured by a flow method, and the Ne–Ar cross section at a relative velocity of 1.797 km/sec reported by Nenner et al. has been used for the calibration. For each cross section, the overall error is not more than $\pm 3\%$.

The present measurements, obtained under high rotational temperature conditions of the $O_2$ molecules ($\sim 10^3$ K), cover an extended velocity range and therefore supercede the previous measurements.

C. Zeeman spectrum

The magnetic beam resonance apparatus for the Zeeman spectrum measurements has been described in Ref. 27, where results on Ar–$O_2$ were reported. In the present measurements, a stagnation temperature $T_0 = 100$ K was chosen for a mixture of 1% $O_2$ in Ne. In this way, $(O_2)_n$ clustering was unimportant, even at the employed stagnation pressure $P_0 = 900$ mbar. The measurements were performed setting the mass spectrometer detector on the mass of $O_2$–Ne$^+$. Particle counting yielded 600 counts/s of full beam signal to be compared to 150 counts of background, for this mass setting. A maximum beam attenuation of typically 3% was achieved by driving the strongest r.f. transition into saturation.

III. RESULTS AND ANALYSIS

A. Scattering data

The total DCS data of Ne scattered off $O_2$ at $E = 74.9$ meV are presented on a semilog scale in Fig. 1. Data measured at both positive and negative angles, with respect to the Ne primary beam, are shown. The laboratory angular distributions $I(\Theta)$ are multiplied by $\Theta^2$ in order to remove the steep angular dependence at small angles. Typical error bars are shown representing $\pm 1$ standard deviation. At angles between $11^\circ$ and $-11^\circ$, the error bars become smaller than the solid circles. As can be seen, the diffraction oscillations superimposed on the falloff of the main rainbow oscillation are clearly resolved. The diffraction structure appears strongly quenched with respect to the corresponding spherical systems Ne–Ar measured under the same geometrical arrangement. This is a manifestation of the anisotropy of the interaction potential. The dashed line at positive angles in Fig. 1 represents a calculation assuming a spherical interaction for Ne–$O_2$ (see Sec. III D 1), and the comparison with the continuous curve, obtained from the best-fit anisotropic potential surface, shows the amount of quenching due to the effect of the anisotropy. It has been shown clearly by Pack that the quenching of the diffraction oscillations in the total DCS is directly related to the anisotropy.
of the potential minimum position $R_m$ and that of the rainbow oscillations to the well depth $e$ anisotropy. Since Ar and O$_2$ have very similar polarizabilities, the Ne–Ar potential is expected to be very similar to the spherical potential of Ne–O$_2$. Therefore, by taking as standard Ne–Ar for which an empirical potential$^{14}$ accurate to better than 1% in $R_m$ and 2% in $e$ reproduces very well both amplitude and angular positions of the diffraction oscillations, we were able to estimate quantitatively the amount of quenching due to anisotropy, in addition to that produced by the finite resolution of the experiment. We have recently shown$^{10,11}$ that an accurate evaluation of the quenching of the diffraction structure for the related He–O$_2$, He–N$_2$, and Ne–N$_2$ systems within the IOS approximation has given a repulsive wall anisotropy in agreement with more direct determinations obtained from rotationally inelastic differential cross sections (available only for He–O$_2$ and He–N$_2$). The reliability of the IOS approximation for treating the scattering dynamics in the present experiments is supported by our previous work on the strictly related Ne–N$_2$ system,$^{11}$ for which total DCS were measured under analogous experimental conditions at practically the same collision energy as for Ne–O$_2$. By performing exact close-coupling calculations, it was shown$^{11}$ that for a system as Ne–N$_2$, (under conditions as those of the experiments) the use of the IOS decoupling method to calculate total DCS and extract the anisotropy of the atom–diatom potential from the quenching of the diffraction oscillations is certainly reasonable. IOS fails only for those inelastic transitions that make a negligible contribution to the total DCS.

The absolute total integral cross sections, measured in the 0.5–1.9 km/s velocity range using rotationally hot O$_2$ molecules, are reported in Fig. 2. A clear glory maximum of order one is exhibited over an average $\sim v^{-2/5}$ dependence at around 1.2 km/s. Since rotationally hot O$_2$ molecules are used in these experiments, the data are mainly sensitive to the isotropic component, $V_0(R)$, of the potential surface. In fact, the glory oscillation is well reproduced in amplitude and position using a potential which depends only on $R$, the separation between the atom and the center of mass of the diatom. This has been shown for O$_2$–Kr$^{31}$ for which the integral cross section data measured with O$_2$ emerging from a source at $\sim 10^3$ K were found to be very close to the corresponding atom–atom data (Ar–Kr) results, while the O$_2$–Kr data measured with O$_2$ rotationally cold, as from a supersonic expansion, showed a shifting and quenching of the glory structure with respect to Ar–Kr. This behavior has recently been rationalized also theoretically by Aquilanti et al.$^{32}$ who have explained the experimentally observed dependence of glory scattering in atom–diatom collisions from the rotational temperature of the diatom within an adiabatic representation in the coupled states framework.

The absolute value of the smooth component of the integral cross section is a probe of the long-range part of the $V_0$ potential. This is always true, even in the presence of anisotropy effects since anisotropy quenches the glory amplitude,$^{31,32}$ but does not affect the average value of the cross

![FIG. 2. Absolute integral cross sections for Ne–O$_2$ as a function of velocity obtained using rotationally hot O$_2$. The continuous curve is the best-fit calculation with the spherical average potential, $V_0(R)$, obtained from the full potential of Table III using Eq. (2).](image)

![FIG. 3. The measured Zeeman transitions, for $B = 2.60$ Gauss. Below 900 kHz, multiphoton transitions occur (see Ref. 33), prohibiting further analysis. The experimental uncertainty above 900 kHz is $\pm 25$ kHz, except for the doublets at 2794 kHz ($\pm 50$ kHz) and at 1048 kHz ($\pm 40$ kHz). Vertical lines indicate the position of the Zeeman transitions calculated from the best-fit anisotropic potential of Table III.](image)
TABLE I. The experimental results, for \( B = 2.60 \) Gauss, together with their assignment, are compared with calculations. For frequencies below 900 kHz the assignments become dubious since we enter the region of Zeeman multiphoton transitions (see Ref. 33); therefore, no real confrontation with calculations has been attempted. For the last two columns we have used a somewhat out-dated potential. The purpose of this calculation was to convince ourselves that our analytical calculation is sufficiently near to the results of the numerical approach to warrant a meaningful comparison (Ref. 27). The two parameters on top of the middle columns stand for the values of \( B_2/A_1 \) of the potential of Eq. (1). The recommended values are those in the first column. The ladder-2 results are most meaningful in this comparison with calculated values, though (in contrast to Ref. 27) there is no strict selection rule limiting Zeeman transitions to ladder-2 levels.

<table>
<thead>
<tr>
<th>Ladder</th>
<th>( F )</th>
<th>Parity</th>
<th>Experiment</th>
<th>Analytical</th>
<th>Numerical</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>+</td>
<td>413</td>
<td>0.125/ - 0.425</td>
<td>484/ 417</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>-</td>
<td>462</td>
<td>0.135/ - 0.472</td>
<td>505/ 447</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>+</td>
<td>462</td>
<td>0.115/ - 0.325</td>
<td>532/ 490</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>-</td>
<td>529</td>
<td>0.125/ - 0.425</td>
<td>560/ 539</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>+</td>
<td>594</td>
<td>0.115/ - 0.325</td>
<td>583/ 586</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>+</td>
<td>900</td>
<td>0.125/ - 0.425</td>
<td>2737/ 2728</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>-</td>
<td>1045</td>
<td>0.135/ - 0.472</td>
<td>2747/ 2740</td>
</tr>
<tr>
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<td>+</td>
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<td>0.115/ - 0.325</td>
<td>2752/ 2746</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>-</td>
<td>1304</td>
<td>0.125/ - 0.425</td>
<td>2758/ 2748</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>+</td>
<td>1596</td>
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<td>2798/ 2790</td>
</tr>
<tr>
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<td>11</td>
<td>-</td>
<td>1752</td>
<td>0.125/ - 0.425</td>
<td>2798/ 2790</td>
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<tr>
<td>2</td>
<td>12</td>
<td>+</td>
<td>2798</td>
<td>0.115/ - 0.325</td>
<td>2798/ 2790</td>
</tr>
</tbody>
</table>

**C. The potential energy surface**

The interaction between a Ne \( (^1S_0) \) atom and an \( \text{O}_2 \) \( (^3\Sigma_u^+) \) molecule is described by single potential energy surface \( V(R, \gamma) \), which is a function of \( R \), the distance between the center of mass of the molecule, and the atomic partner, and \( \gamma \), the angle between \( R \) and the internuclear molecular axis. A potential model in which the angle dependence is obtained by making the size parameters, \( e \) and \( R_m \), angle dependent is conveniently used, while the reduced form is taken to be the same for all orientations, as stressed in previous work.\(^{10,11,15}\) The following analytical potential form has been used,

\[
V(R, \gamma) = \frac{e}{R} (x), \quad x = \frac{R}{R_m}(\gamma),
\]

where the parameters \( e(\gamma) \) and \( R_m(\gamma) \) are given by

\[
e(\gamma) = \bar{e}[1 + A_1 P_2(\cos \gamma)]
\]

\[
R_m(\gamma) = \bar{R}_m[1 + B_2 P_2(\cos \gamma)].
\]

The reduced curve \( f(x) \) is chosen to be the piecewise analytic Morse–Morse-spline-van der Waals (MMSV) form, given by,

\[
f(x) = \left\{ \begin{array}{ll}
\exp[-2 \beta'(R/R_m - 1)] & -2 \exp[- \beta'(R/R_m - 1)] \cdot \frac{e'}{e(\gamma)}, \quad 0 < x < \sigma/R_m(\gamma) \\
\exp[-2 \beta(x - 1)] - 2 \exp[- \beta(x - 1)], \quad \sigma/R_m(\gamma) < x < x_1 \\
b_1 + (x - x_1)b_2 + (x - x_1)(b_3 + (x - x_1)b_4), \quad x_1 < x < x_2 \\
-c_6x^{-6} - c_8x^{-8} - c_{10}x^{-10}, \quad x_2 < x < \infty
\end{array} \right.
\]

with

\[c_6 = C_6/\bar{R}_m^6, \quad c_8 = C_8/\bar{R}_m^8, \quad c_{10} = C_{10}/\bar{R}_m^{10},\]

and

\[
R'_m = \beta'(\sigma)/(\beta' - \ln 2),
\]

\[
\sigma = R_m(\gamma)(1 - \ln 2/\beta),
\]

\[
e' = e(\gamma)(R_m/\bar{R}_m(\gamma)\beta').
\]
The well region is described by a Morse function joined smoothly at \( \sigma \) [the distance at which \( V(R) = 0 \)] with another Morse function describing the repulsion. The outer well is joined smoothly to the long range van der Waals expansion by a cubic spline, whose parameters are fixed by smoothness conditions at the joining points \( x_1 \) and \( x_2 \), whose values were chosen to reflect the validity of the various potential pieces; in particular, \( x_1 \) was taken very close to the Morse inflection point. The \( C_{6}, C_{8}, \) and \( C_{10} \) coefficients have been obtained from the corresponding spherically averaged values derived from the absolute value of the integral cross section using for the \( C_{8,0}/C_{6,0} \) and \( (C_{10,0} \times C_{6,0})/C_{8,0}^{2} \) ratios the values of 4.95 \( \AA^{2} \) and 1.27, respectively, which are the values for the corresponding isotropic Ne–Ar system.\(^{14}\) The parameters of the present MMSV potential form which were subjected to adjustment during the best-fit multiproperty analysis were therefore only \( \tilde{\epsilon}, \tilde{R}_m, \beta, \) and \( \beta' \). Only even terms appear in the expansion (1), \( \tilde{O}_2 \) being homonuclear, and, as also found in similar systems,\(^{10,11,15}\) a \( P_{2} \) term is sufficient to describe the anisotropy effects observed in the present experiments.

**D. Data analysis**

The procedure of analysis consists in determining the parameters \( \tilde{\epsilon}, \tilde{R}_m, \beta, \) and \( \beta' \), which describe the attractive and low repulsive part of the “spherical limit” potential \( V_s(R) \) (obtained from the full potential by setting the anisotropy parameters equal to zero) from the coarse best fit of the general behavior of the total DCS (which is sensitive to the \( \tilde{\epsilon} \) and \( \tilde{R}_m \) parameters and somewhat less to the slope of the repulsion). Then, \( A_2 \) and \( B_2 \) anisotropy parameters are introduced in Eq. (1) until the location and amplitude of the diffraction oscillations, which are sensitive to the anisotropy of the repulsive wall, i.e., of the \( \sigma \) (and then \( R_m \)) parameter, are reproduced. The potential parameters so derived are then slightly adjusted by imposing the constraint that the spherical average of the surface \( V_0(R) \) has to reproduce the absolute total integral cross section at high rotational temperature as a function of collision velocity. A fine tuning of the well depth and \( \beta \) Morse parameter is so obtained, the location of the glory structure being sensitive to the product \( \epsilon_0 R_m6 \) and its amplitude to the width of the spherically averaged well.\(^{34}\) The repulsion (i.e., \( \beta' \) parameter) is then fine tuned to reproduce the diffusion and viscosity coefficients. Finally, the surface so far obtained is used to calculate the Zeeman spectrum. From a comparison with the measured spectrum, a further check of the spherical component of the interaction and of its anisotropy around the minimum is obtained.

In practice, the whole procedure has been rather simple and rapid since, once the total DCS data, which carry the largest amount of information on the potential among the examined properties, were fitted, only a minor fine tuning of the \( \tilde{\epsilon}, \beta, \) and \( \beta' \) parameters was found necessary to also reproduce accurately the integral cross section and transport data. At this point, also the Zeeman spectrum turned out to be well predicted. Sensitivity calculations with slightly modified potential parameters showed that the Zeeman spectrum is affected by variations in both the \( V_0(R) \) term and the anisotropy. Therefore, the spectroscopic data are found to corroborate the scattering results.

The anisotropy parameter directly determined from the total DCS data is \( B_2 \), which is obtained from the quenching of the diffraction oscillations. Sensitivity to \( A_2 \), which reflects the anisotropy of the well depth, is much lower, also because the main rainbow structure is not fully observed at the collision energy of the experiment. However, since \( A_2 \) and \( B_2 \) are not independent, by imposing the constraints that the long-range anisotropy had to be consistent with the anisotropy of the diatom polarizability and that the most stable configuration occurs for the \( T \)-shaped \( \tilde{O}_2 \) complex, a reliable value for the \( A_2 \) parameter has also been obtained. These assumptions are supported by the fact that the partial quenching of the rainbow observed experimentally is well reproduced. The anisotropy of the \( \tilde{O}_2 \) polarizability, \( \Delta\alpha/\tilde{\alpha} \), where \( \Delta\alpha = \alpha_\parallel - \alpha_\perp \) and \( 3\tilde{\alpha} = \alpha_\parallel + 2\alpha_\perp \), is taken to be 0.229.\(^{35}\)

**1. Total differential cross sections**

The differential cross sections were calculated for each orientation angle \( \gamma \) by partial wave analysis with JWKB phase shifts.\(^{36}\) A 32-point Gauss–Legendre quadrature was used to average the c.m. cross sections \( \sigma(\theta,\gamma) \) over \( \cos \gamma \), according to the IOS formula

\[
\sigma(\theta) = 1/2 \int_{-1}^{+1} \sigma(\theta,\gamma) d(\cos \gamma).
\]

For comparison with the experimental \( I(\Theta) \), the c.m. cross section \( \sigma(\theta) \) was transformed into the laboratory frame by using the elastic Jacobian and then averaged over the velocity distributions of the two beams and over the beam/detector geometry. Minimization of a chi-squared \( (\chi^2) \) factor was adopted as goodness-of-fit criteria. The best-fit total \( I(\Theta) \) is shown as a solid line in Fig. 1 at both positive and negative angles. The dashed curve in the same figure (shown only at positive angles) represents the \( I(\Theta) \) calculated with the spherical limit potential \( V_s(R) \) obtained from the full potential by setting the anisotropy \( A_2 \) and \( B_2 \) parameters equal to zero.

**2. Absolute total integral cross sections**

The integral cross sections, calculated in the center-of-mass frame, using an efficient semiclassical procedure,\(^{34(a)}\) have been convoluted to the laboratory system by averaging over the thermal distribution of the target gas in the scattering chamber and taking into account the transmission function of the velocity selector.\(^{34(b)}\) The calculated integral cross sections are compared with the experiment in Fig. 2.

**3. Diffusion and viscosity coefficients**

As we have previously done for the Ne–N\(_2\) system, the collision integrals needed for the evaluation of diffusion and viscosity coefficients have been calculated by using the IOS approximation. This approximation is equivalent\(^{27}\) to the Mason and Monchick scheme.\(^{38}\) Collision integrals are calculated for each \( \gamma \) angle and then spherically averaged. The collision integrals for each \( \gamma \) value have been obtained by

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using standard computer codes$^{19}$ and for the angular averaging procedure a 16-point Gauss–Legendre quadrature was used. The diffusion $D_{12}$ and the interaction viscosity $\eta_{12}$ coefficients are obtained from the collision integrals, $\Omega_{11}$ and $\Omega_{22}$, by the first order Chapman–Enskog formulas,$^{35(b),37}$ then corrected for the higher order terms.$^{35(b),37}$ As we have already observed in the Ne–N$_2$ system,$^{11}$ this correction is very small and in the whole temperature range we have considered, is always smaller than 1%. The diffusion coefficients as a function of the temperature calculated with the present best fit potential are compared with the experimental results by Kestin et al.$^{19}$ in Fig. 4. The viscosity coefficients of Ne/O$_2$ mixtures calculated for three different concentrations are compared with the experimental results by Kestin et al.$^{19}$ in Table II.

As can be seen from Table II and Fig. 4, the calculated values are lower by 1%–2% than the experimental values for $\eta_{12}$ and even less for $D_{12}$. Recent classical trajectory calculations$^{40}$ of viscosity and diffusion coefficient for the similar Ne–N$_2$ system in the 200–900 K temperature range have shown that IOSA calculations underestimate these transport properties typically by about 1% in the temperature range of interest here for Ne–O$_2$. It is reasonable to expect that similar deviations also hold for Ne–O$_2$. Taking this into account, we note that the predicted values of $D_{12}$ and $\eta_{12}$ for Ne–O$_2$ are in good agreement, well within experimental error, with the experimental data.

### 4. The Zeeman spectrum

The Zeeman spectrum has been calculated using a numerical approach within the correct angular momentum coupling scheme for the bound states of the van der Waals molecule, and using also approximate analytical methods, as previously done for Ar–O$_2$.$^{27}$ Comparison with experiment is reported in Fig. 3 and Table I.

### E. Results and discussion

The best-fit potential parameters for Ne–O$_2$ obtained from the above multiproperty analysis are listed in Table III. Two cuts of the potential energy surface for the parallel ($\gamma = 0^\circ$) and perpendicular ($\gamma = 90^\circ$) geometries are depicted as solid lines in Fig. 5, where also the previous surface, hereby called SGMOD, of Corey and McCourt$^{22}$ is shown with dashed lines for comparison.

For a given anisotropy, the frequency of the diffraction oscillations of the total DCS determines the absolute position of the repulsive wall of the spherical potential independently of the potential model and also of the shape and depth of the well, while the position of the main rainbow oscillation is a direct probe of the strength (well depth) of the interaction. The quality of the data shown in Fig. 1 has allowed us to

![FIG. 4. Diffusion coefficients for Ne–O$_2$. Experimental data from Ref. 19 are compared with the prediction of the best-fit anisotropic potential of Table III.](image)

![FIG. 5. Best-fit Ne–O$_2$ anisotropic potential (continuous curve) for parallel ($V_P$) and perpendicular ($V_L$) configurations compared to the SGMOD potential of Corey and McCourt (Ref. 22).](image)
determine for the spherical potential the $\alpha_0$ parameter, and then $R_{m,0}$, with a precision of better than $\pm$ 1%, and the well depth $\epsilon_0$ to about $\pm$ 3%. These uncertainties are similar to those for $\bar{\epsilon}$ and $R_{m}$ parameters (see Table III). The precision on the well depth was lowered to $\pm$ 2% by also including in the analysis the absolute total integral cross section measured using rotationally hot $O_2$ molecules. This type of data is sensitive to the spherical component of the interaction, $V_{0}(R)$, i.e., the first term of the Legendre expansion of the potential. For each trial potential surface, the spherically averaged potential was obtained by a 16-point Gauss–Legendre quadrature from the full surface according to

$$V_0(R) = \frac{1}{2} \int_{-1}^{+1} V(R,\gamma) d(\cos \gamma).$$

(2)

Integral cross sections calculated with this potential were compared with the experimental data and the parameters of the full surface adjusted to derive a best-fit $V_0(R)$. Once the minimum position was fixed from the diffractions to $\pm$ 1%, the position of the glory maximum (see Fig. 2), which is directly sensitive to the product $\epsilon_0, R_{m,0}$, allowed us to fix also $\epsilon_0$, and then $\bar{\epsilon}$, to about $\pm$ 2%. Moreover, the amplitude of the glory oscillation, which is sensitive somewhat to the width of the potential well, permitted us to refine the $\beta$ parameter of the Morse function describing the well to $6.4 \pm 0.2$. It has to be noted that $V_0(R)$ and $V_0(R)$ have the same reduced form. The absolute value of the integral cross section is a direct measure of the potential in the probed distance range, which in the present case is about 4.7–5.6 Å.

The van der Waals coefficients used to describe the long-range attraction are consistent with the measured experimental value of the spherically averaged potential. We note that the $C_6$ value of 12 893 meV Å$^6$ (see Table III) corresponds to a $C_{6,0}$ value of 12 200 meV Å$^6$, which can be considered in good agreement with the recent theoretical value of 11 650 meV Å$^6$ calculated by Rijks et al.$^{41}$

The ratio of rainbow to wide angle scattering intensities in the total DCS is sensitive to the low repulsion up to about 25 meV. The inclusion in the analysis of diffusion and viscosity data, which within a reasonable range of the anisotropy are essentially sensitive to the location and slope of the repulsive wall of the spherical interaction, has permitted us to derive the slope of the repulsive wall up to about 60 meV. As expected, calculation of the transport data using the full PES were found to be unsensitive to details of the anisotropic component of the interaction. In order to achieve a good fit of the transport data, the repulsion from $V_0(R) = 0$ up needed to be described by a separate piece of Morse function: Diffusion and viscosity have refined the $\beta'$ parameter, while $\beta$ was already very well fixed by the scattering data.

The main effect of anisotropy on the experimental data shown in Fig. 1 is the quenching of the diffraction oscillations, as already pointed out. As clearly shown in the figure, the calculation with the full anisotropic potential reproduces very well the experimental amplitude and location of the diffraction oscillations, while the diffractions calculated with the spherical limit potential are much more pronounced, having amplitudes more similar to those measured for the isotropic Ne–Ar system [see Ref. 11 and 14(a)] and being strongly shifted towards small angles with respect to the experiment. Figure 1 clearly indicates that a best-fit of the locations of the diffraction oscillations with a spherical potential would require a minimum position shifted by a significant amount (several percent) towards smaller inter­nuclear separations with respect to the present spherical limit potential. Since the amplitude of the diffractions are negligibly affected by physically reasonable small shifts of the absolute scale, by simultaneously fitting the locations and the amplitudes of the diffraction oscillations in the total DCS, independent estimates of the anisotropy ($B_2$ parameter) and of the absolute scale ($R_{m,0}$ parameter) were derived. The $B_2$ parameter obtained for Ne–O$_2$ is identical, within the sensitivity of the present type of data, to that previously derived for He–O$_2$, He–N$_2$, and Ne–N$_2$. However, the accuracy of the determination for Ne–O$_2$ is slightly smaller than for He–O$_2$ ($\pm$ 15% vs $\pm$ 8%), since for this heavier system the diffraction oscillations are much more closely spaced and have a much lower amplitude, which limits the accuracy of the evaluation of the quenching due to anisotropy effects with respect to that due to experimental averaging. No uncertainty is reported for the $A_2$ parameter in Table III since it has been linked to $B_2$ as described in Sec. III D (see also Ref. 10).

The Zeeman spectrum has been compared with exact numerical and approximate analytical calculations.$^{27}$ The potential parameters were changed in such a way that

$$A_2 + 6B_2 + \left(\frac{12}{7}\right)A_2B_2 = (\alpha_\parallel - \alpha_\perp)/\bar{\alpha}$$

assumes the value 0.229. In Table I, three sets of values $B_2/A_2$ are indicated, together with the corresponding positions of the Zeeman transitions. It appears that for a constant value of $(\alpha_\parallel - \alpha_\perp)/\bar{\alpha}$, the Zeeman transitions shift only very slightly for different $A_2$ and $B_2$ parameters, especially if one compares with the remaining differences between the experimental and the theoretical results. On the other hand, the difference between analytical and numerical calculations, although within the experimental error, is such that finer fitting of $A_2$ and $B_2$ values to the Zeeman results seems rather pointless (see Table 1).

A comparison of the spherically averaged scale parameters, $\epsilon_0$ and $R_{m,0}$, with those of Ne–Ar, shows only small differences, as one would expect considering that O$_2$ and Ar have very similar polarizabilities.

| TABLE III. Potential parameters for Ne–O$_2$. |
|-------------------|-------------------|
| $\bar{\epsilon}$ (meV) | 5.94 ± 0.12 |
| $A_2$ | -0.425 |
| $R_{m,0}$ (Å) | 3.58 ± 0.03 |
| $B_2$ | 0.125 ± 0.020 |
| $\beta'$ | 5.9 |
| $\beta$ | 6.4 |
| $C_6$ (meV Å$^6$) | 12 893 |
| $C_6$ (meV Å$^6$) | 63 044 |
| $C_{10}$ (meV Å$^{10}$) | 400 782 |
| $x_1$ | 1.108 30 |
| $x_2$ | 1.46 |
Finally, a comparison of the presently derived potential energy surface for Ne–O₂ with the results of previous determinations is in order: The rather crude anisotropic surface of Smith and Giraud was later on modified by Corey and McCourt to get improved agreement between computed pressure-broadening cross sections for the magnetic dipole allowed transitions and experimental measurements. The SGMOD potential surface remains still rather unrealistic, as can be seen from Fig. 5 and Table IV, where its main potential characteristics are compared with those of the present determination. The well depth for the most stable Ne–O₂ configuration is by far too deep and too inwardly located, for instance. The well depth and minimum position anisotropies are too large. That is, both the isotropic and anisotropic components of the SGMOD surface are incorrect. However, this is not surprising, the SGMOD surface being based on a very limited set of data. Predictions based on this surface of the experimental scattering cross sections reported in this work are completely off and are not shown here. It has recently been reported that diffusion and viscosity coefficients calculated with the SGMOD surface are about a factor of two too large with respect to the experiment, as a consequence of the mainly too inwardly located well of the spherical component.

IV. CONCLUSION

In this work, we have reported the first accurate determination of the full potential energy surface for Ne–O₂, through the simultaneous analysis of high-resolution scattering data (total differential and integral cross sections), of spectroscopic properties (Zeeman spectrum), and macroscopic data of transport properties (diffusion and viscosity). These experimental data probe the intermolecular potential over a wide range of internuclear distances, from the long range up to the high repulsion (≈ 60 meV), both in the isotropic and anisotropic components. The spherical part of the potential [i.e., the \( V_0(R) \) term] has been determined with an accuracy comparable to that achieved for the isotropic rare gas–rare gas systems (≈ ± 1% on the minimum position and ≈ ± 2% on the well depth). The anisotropic part of the interaction should also be rather accurate, being corroborated from both the damping of the diffraction oscillations in the total differential cross section and the Zeeman spectrum.

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39 See Appendix of Ref. 37.