Scattering of Rotationally Aligned Oxygen Molecules and the Measurement of Anisotropies of van der Waals Forces

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Measurements are reported for the scattering of molecular oxygen with both a hot rotational energy distribution and cooled at its ground rotational state with a controlled alignment of the rotational angular momentum. The cooling and control of the alignment are achieved using supersonic expansion in beams of molecular oxygen seeded in various mixtures of Ne, He, and H_2 and monitored by a Stern-Gerlach magnetic deflection technique. It is shown by the example of integral scattering cross section with Xe in the glory energy range that information can be obtained on the isotropic and anisotropic components of intermolecular van der Waals interactions.

This Letter reports the first application to molecular scattering of a natural and facile technique for alignment of molecular rotations by *seeded* supersonic expansions of gaseous mixtures [1,2]. The seeding phenomenon provides a general way not only to molecular acceleration and cooling of the heavier components of the mixtures but also to polarization of their rotational angular momentum [1]. This alignment has been found [2] to be drastically dependent on final speed: In the prototypical case of oxygen molecules diluted in mixtures with lighter gases such as H_2, He, and Ne, cooling occurs down to the rotational ground state $K = 1$ and strongly nonstatistical distribution is observed for the rotational angular momentum projections along the propagation direction (helicities) $M = 0$ and 1 (either +1 or −1).

We denote the relative number of molecules with $M = 0$ as w_0: For them the rotational angular momentum is perpendicular to the propagation direction. The relative number of molecules pertaining to the other possibility, i.e., corresponding to helicity $M = 1$, will be denoted as w_1—this number is the same in both the +1 and −1 cases, which only differ by the sense of rotation, irrelevant under the axial symmetry of the molecular beam expansion. Alignment is conveniently measured by the ratio w_0/w_1, which is 1 in the statistical case (no alignment). It had been found [2] that, within a seeded supersonic expansion, fast molecules are much more highly aligned than slower ones and, specifically, states of zero helicity are strongly favored for those molecules that travel faster ($w_0/w_1 > 1$): Thus by changing the gas mixture and its composition we can prepare molecules with well-defined velocities and alignment ratios. Pictorially, zero helicity molecules can be considered as traveling edge-on and those with helicity $M = 1$ as traveling broadside towards a scatterer, and therefore an alignment control opens up the possibility of carrying out experiments with the aim of assessing the role of spatial aspects in the dynamics of atomic and molecular collisions.

A demonstration of the potentiality of this novel technique is presented here for the case of experimental measurements for O_2-Xe scattering with a controlled alignment ratio w_0/w_1; an outline is also given of the theoretical analysis for the extraction of information on the interaction from data on integral cross sections and their energy dependence in the "glory" range [3]. To exhibit the effect of cooling and alignment and to facilitate the final analysis, measurements have also been taken with the same apparatus and are reported here for scattering by a rotationally hot beam of oxygen molecules.

The experimental apparatus (see Fig. 1) is the same as used [2] for the characterization of the rotational alignment—a set of several differentially pumped vacuum chambers where, after the supersonic expansion, the seeded beam is mechanically velocity selected by rotating
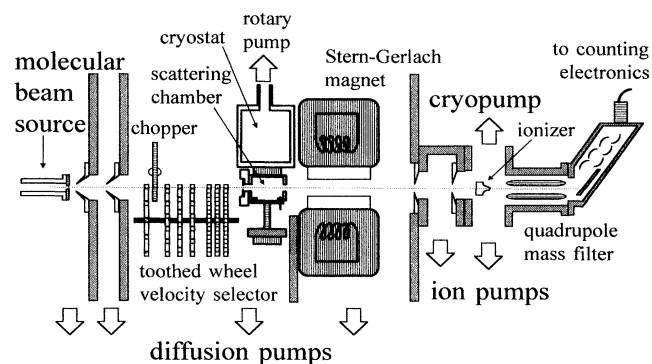

FIG. 1. The experimental apparatus. The seeded beam is formed by expansion of mixtures at typical stagnation pressures of 1 atm out of a nozzle of ~0.1 mm diam in a region of two differentially pumped vacuum chambers. The beam is velocity selected to within ~ ±20 m s⁻¹ and detected by quadrupole mass spectrometry as in Ref. [2], where the Stern-Gerlach magnet is exploited to analyze the molecular alignment of oxygen molecules. In the scattering chamber (~7 cm long) the target gas is kept at a pressure $10^{-2}-10^{-3}$ torr and can be cooled by a cryostat to solid air temperature.

slotted disks and detected by electron bombardment ionization and quadrupole mass filtering. The alignment of oxygen molecules could be monitored exploiting their paramagnetism by a Stern-Gerlach type magnet, which serves only to establish the connection between measured velocity and alignment for different mixture compositions of the seeding gases and is not used in the cross section measurements. In the present configuration a small scattering chamber is placed immediately after the velocity selector and before the magnetic analyzer (see Fig. 1). For details on aspects related to integral cross section measurements (procedure, calibration of target pressure, geometrical features, angular resolution, etc.) see, e.g., Ref. [4].

Sample results are shown in Fig. 2, which illustrates how information on the cross section dependence on both velocity and alignment has been obtained. About 20 different seed gas compositions have been used to accelerate oxygen molecules to different narrow velocity ranges, and for each composition cross section measurements were taken at four alignment ratios. These data, and about twice as many not shown, allow us to plot the velocity dependence of the cross sections as a function of velocity for specific alignment ratios. The two extreme cases are reported in Fig. 3, which also shows, in the upper panel, another set of results pertaining to scattering of beams of rotationally hot oxygen molecules produced by microwave discharge heating of a pure O_2 effusive beam (thermal distribution of rotational levels peaked at $K = 13$)—the dis-

FIG. 3. Selected scattering data for the O_2-Xe system. The product $Q(v)v^{2/5}$, where $Q(v)$ are the integral cross sections and v the oxygen beam velocity, is reported as a function of v to emphasize the glory interference pattern. The upper part of the figure refers to the case of a rotationally hot effusive beam (Boltzmann distributions of K levels peaked at $K = 13$), and the continuous curve is the result of a calculation assuming that the O_2-Xe interaction is represented by a single potential function corresponding to an essentially isotropic interaction, V_0 in Fig. 4. In the lower part, two sets of data are shown for scattering of rotationally cooled oxygen molecules with $K = 1$, corresponding to the two extreme cases (alignment ratios $w_0/w_1 = 1$ and 8) extracted from data such as those shown in Fig. 2. The continuous curve is the same as before, while the dashed curves are calculated as indicated in the text and illustrated in Fig. 4.
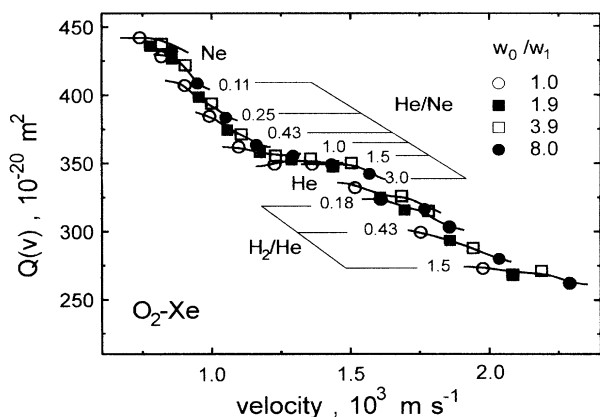

FIG. 2. Cross section data for scattering of oxygen molecules by Xe. Lines through data connect measurements taken with a supersonic beam of oxygen molecules seeded in various gaseous mixtures at near atmospheric pressure, the relative partial pressure for O_2 being in all cases 2.5%. Seed gases employed are Ne, He, and H_2—either pure or in mixtures whose compositions are varied as indicated to cover an ample velocity range. As shown for each mixture composition, four different measurements where taken at different velocities corresponding to different alignment ratios. About twice as many points corresponding to different mixture compositions had been taken (not shown for clarity).
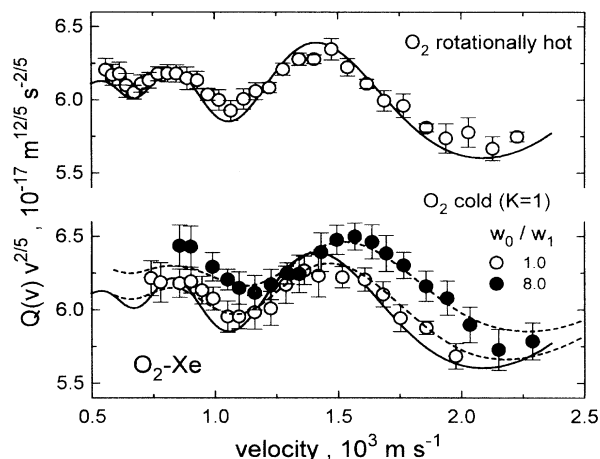
cussion of these results will appear to be relevant for a comparative analysis of the observed effects.

A simplifying assumption of the following analysis (to be relaxed in subsequent work) is that the interaction is represented by an angular independent potential curve, $V_0(R)$—the isotropic component—and that the anisotropy is restricted to only the second order Legendre moment $V_2(R)$, where R is the distance between the Xe atom and the center of mass of the oxygen molecule. The relation between these interaction functions and those corresponding to the two limiting geometrical configurations $V_\parallel(R)$ and $V_\perp(R)$ (see Fig. 4) is simple; $V_0 = (V_\parallel + 2V_\perp)/3$ and $V_2 = 2(V_\parallel - V_\perp)/3$. The analysis follows closely previous work from this laboratory [5] and main features can be discussed by reference to Fig. 4.

Data for the scattering of rotationally hot molecules (Fig. 3) exhibit a well-developed glory pattern, three minima and two maxima being clearly displayed. A natural starting point for the analysis is to attempt their fit with a single potential curve, to be interpreted as the effective spherical potential which exerts the interaction between the partners when the molecule is rotating fast enough to average its anisotropy. That this is indeed the case is shown by the full curve in Fig. 3, which appears as a reasonable fit to
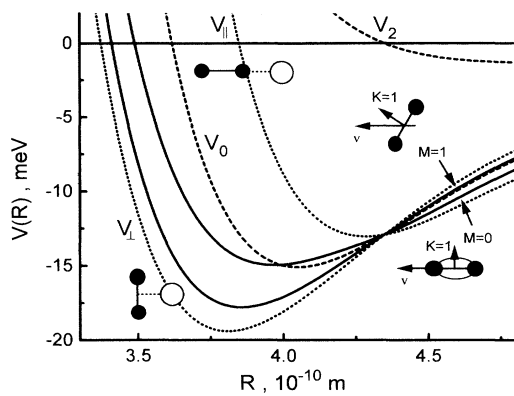
FIG. 4. The interaction between xenon atoms and oxygen molecules for the two limiting configurations—collinear and perpendicular—are depicted as dotted lines and labeled as $V_\parallel$ and $V_\perp$. The corresponding interactions isotropic V_0 and anisotropic V_2 are shown as dashed curves. V_0 governs the rotationally hot case of Fig. 3. Solid lines represent effective potentials as obtained by introducing molecular rotations, and correspond to the two different helicity cases $M = 0$ and 1 (M is the projection of the rotational angular momentum K along the propagation direction v). In the experiments with the rotationally cold oxygen molecules ($K = 1$), a variation in the alignment ratio varies the entrance helicity: Absolute values of integral cross section are sensitive to long range helicity splitting, while glory patterns are sensitive to wells and therefore to helicity mixing induced by Coriolis coupling at the crossing at $R \sim 4.35 \times 10^{-10}$ m. Such a coupling has been taken into account in the calculations of Fig. 3, together with radial coupling to the $K = 3$ state (see Ref. [5]).

the data and corresponds to a flexible Morse spline van der Waals [4] potential model with a well depth ϵ, a distance of the minimum R_m, and an effective C_6 constant listed in Table I. It can be shown that these values are fully consistent with that expected for the isotropic component $V_0(R)$ [6], and as such this potential is plotted in Fig. 4. Therefore a comparison between the rotationally cold scattering results with controlled alignment and the full curve in Fig. 3 provides a dramatic view of the sensitivity of these measurements to the interaction anisotropy.

In fact, for the case of greater alignment, both a sizable increase in the absolute cross section values and a variation in the amplitudes and locations of the glory extrema appear as salient features in Fig. 3: They have to be attributed to molecular anisotropy effects and therefore

TABLE I. Parameters of the potential energy surface for the O_2-Xe interaction.

	$V_0(R)$	$V_\parallel$	$V_\perp$
ϵ (meV)	15.1	13.0	19.4
R_m (m)	4.05×10^{-10}	4.28×10^{-10}	3.81×10^{-10}
C_6 (MeV m^6)	1.02×10^{-55}	1.28×10^{-55}	0.89×10^{-55}

the analysis will provide detailed information on $V_2(R)$ and possibly on higher order terms. Dashed curves have been obtained using an analysis carried out along the lines developed in Ref. [5] and appear to satisfactorily account for observed trends. As is well known [3–5], average values of cross section are sensitive to the effective long range $C_6 R^{-6}$ behavior, so that their increase for the edge-on traveling molecules ("pinwheel" configuration [7]) allows us to estimate for the C_6 in the collinear and perpendicular limiting configurations $V_\parallel$ and $V_\perp$ values given in Table I. As for the glory pattern, which is sensitive to the interaction region around the minima, the picture which emerges is that of an essentially adiabatic evolution along potential curves corresponding to well-defined helicity states (the solid curves of Fig. 4 labeled by either $M = 0$ or $M = 1$), but nonadiabatic transitions are important between the $K = 1$ and $K = 3$ rotational states, and Coriolis coupling induces helicity mixing [8]. Collinear and perpendicular values for well depths ϵ and minimum locations R_m are reported in Table I. It is interesting to note that these parameters have been taken so as to agree with expectations [6] from the known polarizability anisotropy of the oxygen molecules: A full close-coupling calculation for the dynamics, which is in progress, is expected to provide a more accurate and detailed description of the interaction.

Essentially similar results have been obtained also for Kr as the scattering partner of O_2, the choice having been so far restricted to the heavier rare gases, in view of their less stringent kinematic requirements for the energy resolution in the measurements of the true quantum integral scattering cross section, but other partners can obviously be studied.

Finally these experiments also show that scattering in the glory region can be an effective probe of alignment for diatomic molecules (such as, for example, N_2) for which we may suspect a velocity dependence of the alignment in gaseous expansions similar to that demonstrated for oxygen molecules, but for which a direct measurement by the present technique is difficult for lack of magnetic moment.

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[5] V. Aquilanti, L. Beneventi, G. Grossi, and F. Vecchiocat-tivi, J. Chem. Phys. **89**, 751 (1988). The procedure of this reference is extended here to the case of a manifold of odd K states, as appropriate for O_2.

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[7] As opposed to "airplane" states, see V. Aquilanti, S. Cavalli, G. Grossi, and R. W. Anderson, J. Phys. Chem. **95**, 8184 (1991).

[8] It is worth while to mention that nonadiabatic transitions between $K = 1$ and $K = 3$ states lead to rotationally inelastic collisions, while helicity mixing induced by Coriolis coupling is the probable bottleneck to collisional alignment (see Ref. [2]): the insight provided by such an analysis will be detailed elsewhere.