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Quantum Interference Scattering of Aligned Molecules: Bonding in O_4 and Role of Spin Coupling

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Molecular beam experiments on collisions between oxygen molecules were performed at low energy and high angular resolution to permit observation of the "glory" interference effect. A novel technique for aligning the rotational angular momentum of the colliding molecules is exploited. Analysis of total scattering cross section data yields for the O_2-O_2 bond an energy of 1.65 ± 0.08 kJ $\cdot$ mol^{-1} for the most stable configuration (parallel molecules) at a distance of 0.356 ± 0.007 nm. These results indicate that most of the bonding in the dimer comes from electrostatic (van der Waals) forces but chemical (spin-spin) contributions are not negligible. [S0031-9007(98)08079-X]

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The interactions of molecular oxygen are of vital importance in a number of fields such as combustion and, particularly, atmospheric physics and chemistry. Despite continuing efforts, some of the processes linked to the release and recombination of oxygen in its various forms are still far from being properly understood. Among these, those involving the oxygen dimer $(O_2)_2$ are particularly interesting both for the peculiar nature of the bond [1,2] and for their relation to the atmospheric ozone and atomic oxygen balance, through the highly endothermic reaction $2O_2 \rightarrow O_3 + O$, or its inverse [3]. Comparison between observations [4] and predictions of reactive dynamical calculations [4–6] points out the need for a characterization of the O_4 potential energy surfaces [7] more accurate than those presently available. Interaction in the dimer strongly influences also gaseous transport properties [8], heterogeneous matrix spectroscopy [9], and magnetic couplings and dynamics in solid O_2 [10]. For the latter, three different phases, two of which are paramagnetic, are known but their modeling is not fully understood. Finally, spectra of the dimers show several weak absorption bands [11]. They are observed in the atmosphere and in oxygen under pressure or as a liquid and their assignment is far from complete. Some occur in the same wavelength range as the Chappuis bands of ozone, hence affecting measurements of stratospheric ozone [11]. The intermolecular potential in the oxygen dimer continues to pose a challenge to the theory of weak chemical bonds, beyond van der Waals forces. Indeed, because of the open shell nature of the oxygen molecules in their $^3\Sigma_g^-$ ground electronic state, the interaction in the dimer depends not only on the intermolecular distance and on the relative orientation between two molecules, but also on the coupling of their spins [12]. This originates a singlet ground potential energy surface and two excited ones, of triplet and quintet character.

Ewing *et al.* [13] were the first to reveal clearly the presence of $(O_2)_2$ dimers in the gas phase, by spectroscopic studies at low temperature in the IR and visible range. From the analysis of the collision induced absorption spectrum they concluded that the dimer, a floppy molecule, is stabilized both in the ground and the excited electronic state [dissociating to O_2 $(^1\Delta)$ + O_2 $(^1\Delta)$] by a weak bond of van der Waals nature with well depths of 1.0 and 0.6 kJ $\cdot$ mol^{-1}, respectively. They also give an equilibrium distance of ~0.35 nm tentatively associated with a parallel (H-like) geometry but provide no information on spin coupling and on the dependence of the interaction on the mutual orientation of the molecules.

As for the magnetic properties of oxygen dimers in the gas phase an early study [14] of Stern-Gerlach deflection spectra found O_4 molecules, formed in a supersonic molecular beam, to be paramagnetic. More recently [15], similar deflection spectra have lead to the conclusion that the ground state is a singlet and there is no net population in the beam of the paramagnetic triplet state.

Among the large number of theoretical calculations for the dimer potential energy surfaces, we mention recent use of *ab initio* [12], semi-*ab initio* [16], and semiempirical [6] methods. For the singlet ground state, values for the well depth in the D_{2h} configuration ranging from 0.29 [17] to 2.36 kJ $\cdot$ mol^{-1} [18] are reported.

This report presents the first detailed experimental characterization of the interactions in the gas phase O_2-O_2 dimer, including an assessment of the spin-spin coupling, from molecular beam scattering studies. In these experiments total cross section data, as a function of the collision velocity v, are obtained by measuring the attenuation of a velocity selected O_2 molecular beam when it crosses a scattering chamber filled with the O_2 target gas.

The total scattering cross section is a quantum-mechanical observable which finds its optical analog as the "shadow" which the target molecules cast on the detector when struck by the wave of the projectile molecules. Superimposed to its monotonic decrease as a function of v one may see an oscillatory behavior, the "glory," which arises because of interference effects due to different pathways in the forward direction. The high angular resolution of these experiments ($\simeq 5 \times 10^{-4}$ rad), where the lowest detectable deflection angle is much smaller than a critical angle arising because of the uncertainty principle, is crucial to measure the true quantum cross section. Furthermore, the collision energy is so low that attractive interactions prevail. These interactions vary with intermolecular distance R, as R^{-6}, and this leads to an average dependence of the cross section on relative velocity as $v^{-2/5}$. The glory pattern, observable when the de Broglie wavelength is of the same magnitude as the range of the potential, provides unique information on the features of the well.

Following the guidelines of our previous determination of potential energy surfaces interaction of O_2 with rare gases [19], we have measured total integral cross sections in the thermal energy range using beams of oxygen molecules in different internal states, as produced under both effusive and supersonic conditions. Hot effusive beams contain fast rotating and randomly oriented molecules, while the "seeding" phenomenon associated with the supersonic expansion naturally leads to a rotational cooling and to a strong alignment of the rotational angular momentum. This phenomenon can be exploited to produce beams of projectile molecules slowly rotating with a controlled alignment degree [20]. Collisional experiments with "hot" effusive beams mainly probe the isotropic component of the interaction potential while those performed with aligned oxygen molecules uniquely probe the anisotropy of the surfaces [19].

An early attempt [21], made with no alignment control, leads to an estimate of the interaction averaged over all mutual molecular orientations (the suggested well depth, 1.10 kJ $\cdot$ mol^{-1}, at a distance of 0.394 nm, has to be compared with the spin averaged V^{000} in Table I).

Total cross sections $Q(v)$ from an effusive beam of O_2 are plotted in the upper panel of Fig. 1 as a function of collision velocity. The high rotational temperature of oxygen projectiles ($\sim 10^3$ K, several rotational states result populated, with $K = 9-13$ as most probable) and the low translational temperature of the target O_2 molecules (frozen at 90 K) allow the resolution of three glory extrema (two minima and one maximum).

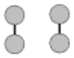
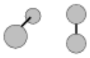
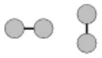
Total cross sections from supersonic seeded beams of O_2 (essentially in the ground rotational state, $K = 1$ [20,22]) have been measured at various alignment degrees of the O_2 projectile molecule, given by the ratio W_0/W_1 of the weights for the two possible K projections (0 or 1). The alignment degree, obtained by paramagnetism measurements [20] and confirmed by molecular scattering experiments [19], can be varied in a controlled way [19]. The two extreme cases are reported in the lower panel of Fig. 1 where each point is the average of several measurements. The dependence on velocity is obtained from 20 different mixtures of 2.5% O_2 in carrier gases such as H_2, He, and Ne in varying compositions [19].

The figure clearly shows that, to an increase of W_0/W_1—in comparison with the rotationally hot beam case—there correspond both an increase in the average absolute value of the cross sections and a shift of the glory extrema towards higher velocities. Both these effects are a manifestation of the anisotropy of the interaction.

In the analysis of the present experiments we provide a representation of the surfaces as a harmonic expansion whose moments depend on intermolecular distance, while the dependence on the three angles describing mutual orientations is given by spherical harmonics. A minimum of four moments, to be determined by fitting experimental data, are needed to characterize the four basic configuration of the dimer (to be referred to in Table I). The first term of the expansion, $V^{000}(R)$, represents the isotropic component of the interaction (the average on the relative molecular orientations), while the other three $[V^{202}(R), V^{220}(R), V^{222}(R)]$, describe the overall anisotropy. The spin-spin interaction is included in all terms although its main contribution is expected in V^{000}.

Data from rotationally hot effusive beam scattering give the input for the initial estimate of V^{000}, to be further refined by trial and error. The oxygen molecules in the scattering chamber have a sufficiently high rotational temperature ($\sim$90 K) to be considered as fast rotating and to behave effectively as a spherical target for the projectiles. Under these conditions (fast rotating molecules) the orientation anisotropy is expected to average out (as in the similar case of the N_2-N_2 system [23]) while the

TABLE I. Equilibrium distances R_m and binding energies E for singlet, triplet, quintet, and for spin-averaged potentials in selected geometries for the oxygen dimer system as obtained in present work. Corresponding results for the N_2-N_2 interaction (reported in parentheses) are shown for comparison.

Configuration	Singlet		Triplet		Quintet		Spin averaged	
	E^b	R_m^c	E^b	R_m^c	E^b	R_m^c	E^b	R_m^c
	1.65	0.356	1.54	0.360	1.37	0.368	1.45	0.364
							(1.06	0.368)^a
	1.49	0.363	1.50	0.362	1.53	0.361	1.52	0.362
							(1.11	0.367)^a
	1.55	0.374	1.43	0.379	1.25	0.388	1.33	0.384
							(1.16	0.410)^a
	0.87	0.427	0.82	0.431	0.74	0.438	0.78	0.435
							(0.33	0.481)^a
V^{000}	1.28	0.381	1.20	0.386	1.07	0.394	1.13	0.390
							(0.92	0.410)^a

[a] These numerical values correspond to data shown graphically in Fig. 12 of Ref. [23].

[b] kJ mol^{-1}.

[c] nm .

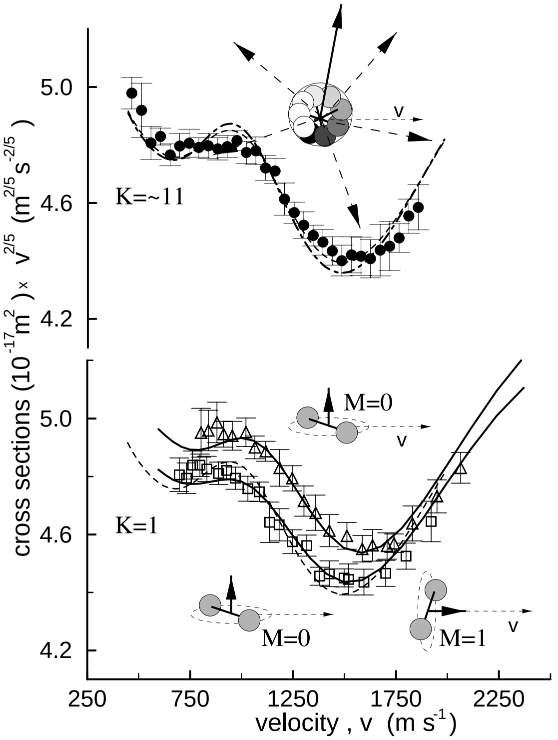


FIG. 1. Cross sections $Q(v)$ for the O_2-O_2 system (multiplied by $v^{2/5}$ to emphasize the glory structure; see text) as a function of the beam velocity v. Upper panel: Scattering of a rotationally "hot" effusive beam of O_2 with a rotational distribution peaked around $K \simeq 11$. In this case, anisotropy effects due to the relative mutual orientations can be neglected: dot-dashed curve is calculated excluding spin-spin interactions, dashed curve is obtained considering the scattering on the three potential energy curves of singlet, triplet, and quintet character. Lower panel: Typical data for scattering of rotationally "cold" supersonic seeded beams of molecular oxygen at alignment ratios $W_0/W_1 = 1/2$ (squares) and 4 (triangles). Continuous curves are quantum mechanical close coupling calculations (see text). Dashed curve is as above and is repeated for comparison.

spin-spin interaction removes the degeneracy of the three spin surfaces and manifests itself in a quenching of the glory amplitude. The minor but not negligible quenching effect of the glory undulations (see the upper panel of the figure and compare also with Fig. 2 of [23]) is direct evidence of the relatively small but measurable role of the spin-spin interaction with respect to electrostatic (van der Waals) forces. These data allow us to give a quantitative estimate of such a role.

The supersonic beams contain aligned oxygen molecules which are in their ground rotational state and therefore experience a much longer rotational period with respect to the molecules in the scattering chamber. The cross sections measured under these conditions are a source of information for the term V^{202} of the orientational anisotropy (which represents the effective anisotropy for a "diatomic-pseudoatom" interaction [23]). Such a term provides the main contribution to the interaction anisotropy, particularly for the approach of the molecules at long range and at distances relevant for the bonding in the dimer.

The final analysis includes simultaneously scattering data and second virial coefficients [24,25], allowing the determination of the two remaining (smaller but not negligible) contributions to the interaction anisotropy [26]. Curves in the lower panel of the figure are the results of quantum mechanical close coupling scattering calculations on our best-fit potential energy surfaces using as before [19] the MOLSCAT [27] package. The second virial coefficients are reproduced within experimental errors over the entire temperature range. Functional forms for the moments which allow the representation of the three surfaces are given in full form in Ref. [26] and are available for distribution on request.

Table I reports two main features (equilibrium distances R_m and binding energies E) for singlet, triplet, and quintet potential energy surfaces for the four basic geometries. Absolute uncertainties are estimated as ± 0.1 kJ/mole for E and ± 0.01 nm for R_m. Relative values are accurate to the digits given. Data for the average over spin states, which represent the pure van der Waals interaction, are also shown. The corresponding data for the N_2-N_2 system as determined very recently in our laboratory [23] are given for comparison. The planar rectangular H geometry is seen to be the most favorable for the ground singlet state of the dimer (this is in agreement with a recent theoretical result [16]) while a geometry quite close to the T shape is the most stable for $(N_2)_2$. This can be attributed to the non-negligible role of quadrupole-quadrupole interaction for the nitrogen case [23].

Indeed, the nature of these interactions can be shown to be mainly due to pure van der Waals forces [28], the spin-spin interaction being only of the order of ~15%—perhaps less than would have been anticipated by Pauling [2], but larger than maintained by others [12].

Our estimate of the spin-spin coupling term in the distance range corresponding to that for the equilibrium of the dimer can be an ingredient for modeling magnetic properties in solid O_2. The characterization of the three surfaces will contribute to assign features of absorption spectra, and of spectral line broadening due to dimer formation. Moreover, since the bond length and thus the polarizability of O_2 molecules, do not appreciably change for excitation to the metastable electronic excited states $^1\Delta$ and $^1\Sigma$ (see also [16]), the corresponding excited surfaces of the dimer, for which the spin-spin coupling is absent, are expected to behave similarly to the van der Waals component of the ground state.

All these surfaces are relevant for the elementary processes of atmospheric science and in general are expected to be of use for calculations of transport properties and for modeling the gas dynamics of systems involving oxygen molecules, oxygen atoms, and ozone.

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[1] The existence of a weak chemical bond between two oxygen molecules was first postulated in 1924 by G. N. Lewis [J. Am. Chem. Soc. **46**, 2031 (1924)] who, from the magnetic susceptibility of liquid oxygen, concluded that oxygen is a mixture of O_2 and O_4 species, the paramagnetic character being given by O_2, and that O_4 *"is chemically saturated and also magnetically saturated in the sense that it is not paramagnetic."* He gave a value of $0.54\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$ for the heat of dissociation of O_4 in two O_2 molecules.

[2] L. Pauling, in *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1964), p. 5, pointing out the role of spin coupling, writes: *"In general we do not consider the weak van der Waals forces between molecules as leading to chemical-bond formation; but in exceptional cases, such as that of the* O_4 *molecule … it may happen that these forces are strong enough to make it convenient to describe the corresponding intermolecular interaction as bond formation."*

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