Reply to the Comment on "Rotational Alignment in Supersonic Seeded Beams of Molecular Oxygen" (by Charles D. Pibel, Joshua B. Halpern)

Vincenzo Aquilanti,* Daniela Ascenzi, David Cappelletti,† and Fernando Pirani

Dipartimento di Chimica dell'Università, I-06123 Perugia, Italy

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In 1994 we documented for the first time a strong dependence on the final velocity for the rotational alignment of molecules emerging from supersonic expansions.[1,2] The experiments involved the measurement of the variation of paramagnetism of O_2 in continuous seeded beams of molecular oxygen (O_2 has an open shell: the electronic spin **S** and the nuclear rotation angular momentum **K** are coupled to give the total angular momentum **J**).

Further evidence of a marked dependence of the alignment on the speed of the oxygen molecules, within the same supersonic velocity distribution, came from measurements of collision cross sections for the O_2-Xe system,[3] where the observed anisotropy effects were larger for faster molecules.

After our initial reports on this subject, some related works using laser probing appeared (for N_2^+ drifted in He[4] and for CO in a He-seeded pulsed beam[5]), accumulating further evidence of the dramatic correlation between molecular alignment and the final velocity.

All these experiments provide alternative views toward an understanding of the phenomenon of collisional alignment. Specifically in our work[1,2] it was shown that O_2 molecules in their rotational ground state $K = 1$ were not significantly aligned at low velocities v, while the population of those flying edge-on (*i.e.*, with $\mathbf{K} \perp \mathbf{v}$) was found to increase, over those flying broadside ($\mathbf{K} \parallel \mathbf{v}$), with the molecular speed.

This was initially contrasted by C. D. Pibel and J. B. Halpern[6] (PH in the following) with the findings that CO molecules (as reported in ref 5 for $J = 4$ and 6) with $\mathbf{J} \perp \mathbf{v}$ are dominant at the lower velocities while those with $\mathbf{J} \parallel \mathbf{v}$ prevail at intermediate velocities (for this spinless molecule J is also the rotational quantum number). However, we note that the maximum alignment was found to be about the same in both experiments,[1,2,5] even if the velocity integrated alignment is lower for the CO case.

PH claimed that such differences could not be real and focused their attention on a possible reanalysis of our paramagnetism data to obtain new values for the populations $w(J,m_J)$ (m_J is the **J** component along the analyzing magnetic field). These data provide information on rotational alignment, the analysis involving[1,2,6] a $\pi/2$ rotation from the magnetic field axis to the beam velocity direction **v**. The latter is the relevant quantization axis for the collisional alignment phenomenon, and the interesting quantities that are obtained are the populations $W(K,M)$ (M defines the projection of **K** along **v** and the notation here is the same as in our previous papers[1,2] PH suggest one use exactly the same mathematical formulas employed in our previous analysis[1,2] and make the additional observation that further constraints arise when the beam velocity direction **v** is considered as a good quantization axis for **J**.

The application of these further constraints to the analysis of our data, measured under moderate velocity and source pressure conditions, allows the determination of population weights in substantial agreement with our previous analysis,[7] but with smaller uncertainties. However, these constraints appear to be too severe to account for the paramagnetism data measured under the extreme velocity and pressure conditions of our experiments. Even with the PH constraints, the analysis indicates that our conclusions on the general trend of the velocity dependence of the alignment (*i.e.*, molecules in the edge-on configuration prevailing at higher velocities) are qualitatively unaffected, but the maximum alignment values are smaller than in our original analysis. A further test comes from the scattering studies on O_2-Xe and O_2-Kr systems[8] for which we measured, under extreme pressure and velocity conditions, an increase of ~2.5% in the total cross section and a shift of ~8% in the "glory" location (with respect to the case of an unaligned beam). The PH constraints would account for these effects only up to 1.5% and 4%, respectively.

The focus on **v** as the appropriate quantization axis to describe the alignment arises from the physics of the phenomenon under study—alignment by collision—and from its suitability for perspective applications to scattering experiments with aligned molecules. For collisions of molecular oxygen, the **v** direction is the proper quantization axis for the rotational angular momentum **K**, its projection M correlating asymptotically with a collision helicity quantum number. Indeed, **K**, and the electronic spin angular momentum **S** are decoupled by the inhomogeneous electric field due to the forces that are operative during a collision. In a supersonic expansion, because of the high number of collisions experienced by each molecule with the faster carrier atoms, these electrostatic forces are those that are mainly responsible for the rotational alignment. Alignment can occur through elastic scattering, bending of the rotational plane and inelastic rotational cooling.[1] However, no guarantee can be given for **v** being a good quantization axis either for **S** decoupled from **K** and for **J**, especially for collisions involving low helicities. A natural quantization direction for the spin, which couples only through a magnetic interaction, may rather be the direction of the orbital angular momentum of the colliding system, orthogonal with respect to the rotational plane of the van der Waals complex and therefore orthogonal to **v**. This interaction, which depends on the anisotropy of the charge distribution in the collisional complex, on the impact parameter, and on the orbital velocity, is expected to be slowly varying with the intermolecular distance.[9] A similar sequence of angular momentum coupling schemes is reminiscent of the Hund's (b) and (e) cases, describing rotational levels of diatomic molecules.

From this point of view a breaking of the PH constraints[6] is evidence of the failure for the direction of **v** to be a good quantization axis for **J**. Therefore our attention is attracted to the spin decoupling and to its possible polarization during the process of collisional alignment.[10]

Further scattering experiments, performed by using supersonic seeded beams of nitrogen and exploiting anisotropy effects in the measured cross sections, yielded information on the rotational alignment along **v** for the case of N_2 and, therefore,

† Istituto perle Tecnologie Chimiche, Universitá di Perugia, I-06125 Perugia, Italy.

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in absence of electronic spin.[11] Comparison of the anisotropy effects measured in the scattering experiments of O_2 and N_2, carried out under similar supersonic seeded expansion conditions, provides further support for the $W(K,M)$ populations obtained from the paramagnetism measurements, especially those under the extreme velocity and pressure conditions of our experiments.

The PH comment also stimulates some remarks on the differences in the findings of the various cited experiments. Such differences have to be interpreted by taking into explicit account that each experiment probes a different piece of a complicated mosaic—that of collisional alignment—which is expected to depend on the nature of the investigated system, on the intermolecular potentials, and on the number and nature of the collisions that occur during the expansion. The understanding of the phenomenon will require us to account, in addition to the change of the alignment with the molecular velocity, for other experimental evidences, such as the observed dependence of alignment on the tested rotational level at various source conditions and expansion geometries.[12−16] and also on the sampling angle along the beam profile.[16,17]

Collisional alignment is the result of hundreds of collisions. The final outcome depends on propensities of the single collision whose properties are thus fundamental for mechanistic interpretations. A key role is played by the impact parameter, which manifests in the angular dependence of the outcome of collisions.

As already authoritatively pointed out,[4,18] close attention must be paid to the quantum differential state-to-state cross sections,[19] which, according to the experiment under consideration, have to be partially or fully integrated, on the angle and on the velocity distribution. For the atom−molecule collisions of interest here, state-to-state differential cross sections can be classified as *elastic* (when the rotational quantum number K and helicity are both conserved or when K is conserved but the helicity varies) and *inelastic* (when K varies and helicity is conserved or when both K and helicity vary). Exact quantum mechanical studies of these phenomena are now feasible. Using an accurate interaction potential for O_2−He,[20] we performed extensive close-coupling scattering calculations[21] of state-to-state differential cross sections at various collision energies in the range pertinent to the alignment experiments.

Some results for O_2 in the rotational state $K = 5$[22] and for a center-of-mass collision energy of 6.8 meV (corresponding to a relative velocity of about 600 m/s) are anticipated here and reported in the figure. It is important to note how for high center-of-mass scattering angles and for particular molecular orientations, the helicity changing and the rotational inelastic cross sections may be comparable to, or even larger than, the pure elastic ones. Further calculations are providing information on dependences on both the collision energies and the involved rotational levels.

In our experimental configuration, the beam is analyzed well downstream (about 1 m after the expansion and with a final defining slit of 0.7 mm). The cone of acceptance is therefore $\leq 10^{-6}$ steradians. This unusually high angular resolution allows the sampling of the molecules that have suffered the largest number of those elastic and inelastic collisions, leading to a final transversal velocity close to zero.

Small and intermediate angular momentum scattering events enter the laboratory forward component of the differential cross sections (backward in the center-of-mass; see Figure 1). Relevant here are the *inelastic* events, which account for the nearly complete relaxation even from highest populated levels down

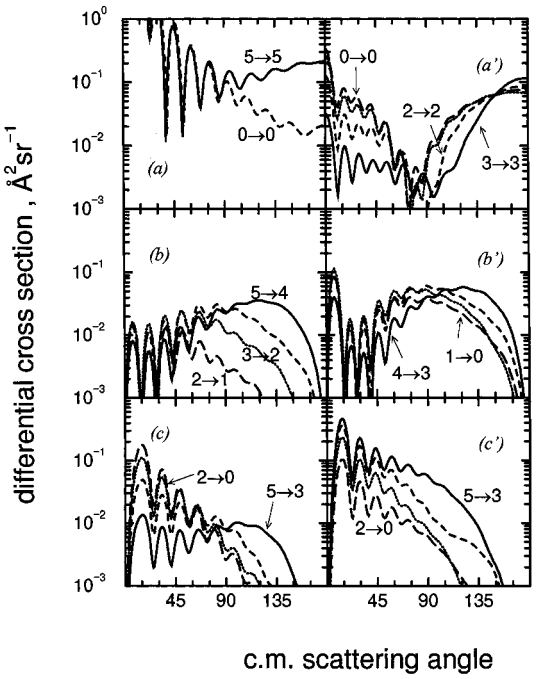

Figure 1. Quantum mechanical state-to-state differential cross sections for the O_2−He system for a center-of-mass collision energy of 6.8 meV and O_2 in the initial rotational level $K = 5$. Numbers indicate initial and final helicities M. Panels a, b, c: elastic processes (final rotational state, $K = 5$). Panels a′, b′, c′: inelastic processes (final rotational state, $K = 3$). Among the results not reported, those for leading to an increase of helicities are similar to those reported for elastic events but much smaller for inelastic events. Also negligible are events involving rotational and/or helicity jumps larger than ±2.

to $K = 1$[23] (the ground rotational state, which is the one being analyzed). Therefore, these calculations support the cartoon previously presented,[1] *i.e.*, that inelasticities involving small and intermediate impact parameters are most effective for molecules flying edge-on, rather then for those flying broadside. The latter must bend (see b and c in the figure) before relaxing or relax but bend at the same time (see b′ and c′). The figure shows that these processes occur sideways in the center-of-mass and therefore at large impact parameters. For the edge-on flying molecules in high rotational levels, the propensity to relax to the ground state, by collisions at small and intermediate impact parameters and involving a few helicity changes, is enhanced by the occurrence of a large sequence of inelastic collisions. This route, which involves large momentum transfer, leads to the observation of high speed $\mathbf{K} \perp \mathbf{v}$ molecules, in the beam. See also a relevant discussion based on a classical trajectory analysis.[18]

In the experiments, which probe not fully relaxed rotational states and which are carried out by analyzing a much wider molecular beam profile,[5,16] a crucial role is played by the elastic contributions to the differential cross section, to be integrated on the proper range of scattering angles. Indeed, for these levels, the selectivity and role of inelastic collisions are expected to decrease. Molecules, as for the example of $K = 5$, when flying broadside, may dominate at high final speeds, being accelerated by elastic events in the forward direction for the laboratory frame, or backward in the center-of-mass (see the case $5 \rightarrow 5$ in a panel a of the figure). We can argue that to this class belong also the molecules that in a drift tube offer the highest resistance to the flow.[4]

In conclusion, in agreement with point (3) in ref 6, we believe that progress has been made and will be made by explicitly taking into proper account the different experimental observa-

tional conditions as a basic requirement to approach a very complex and stimulating problem from complementary viewpoints.

References and Notes

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(7) Note that values of the degree of alignment reported in Table 2 of ref 2 must be considered as the average of several measurements performed under slightly different experimental conditions, while the weights $W(J,m_J)$ reported in Table 1 of the same paper refer to one sample set of data and are not sufficient to fully reconstruct results in Table 2.

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(9) An example of the important role of this coupling is given in: Happer, W.; Miron, E.; Schaefer, S.; Schreiber, D.; van Wijngaarden, W. A.; Zeng, X. *Phys. Rev. A* **1984**, *29*, 3092.

(10) The recoupling of polarized **K** with **S** to give **J**, which occurs also between successive collisions in the expansion, would lead to a natural depolarization effect in the case of unpolarized spin (see: Altkorn, R.; Zare, R. N.; Greene, C. H. *Mol. Phys.* **1985**, *55*, 1). In such conditions the maximum alignment observable for $K = 1$ should be even lower with respect to that obtained according to PH.

(11) Aquilanti, V.; Ascenzi, D.; Cappelletti, D.; Fedeli, R.; Pirani, F. *J. Phys. Chem. A* **1997**, *101*, 7648. In this paper anisotropy effects for the N_2-Xe system on the value of the cross section and on the position of "glory" extrema have been measured. The observed effects are of the same magnitude as in a pioneering work on the scattering of NO, state selected by a hexapolar field and oriented by means of a magnetic field (see: Thuis, H. H. W.; Stolte, S.; Reuss, J. *Chem. Phys.* **1979**, *43*, 351. Thuis, H. H. W.; Stolte, S.; Reuss, J.; van den Biesen, J. J. H.; van den Meijdenberg, C. J. N. *Ibid.* **1980**, *52*, 211.

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(19) Simple models based on classical mechanics cannot be exhaustive in the comprehensive of a phenomenon where the rotational relaxation plays such a dominant role.

(20) Beneventi, L.; Casavecchia, P.; Volpi, G. G. *J. Chem. Phys.* **1986**, *85*, 7011.

(21) In ref 8 close-coupling quantum-mechanical calculations have been reported supporting the experimentally observed effects for O_2-Kr and O_2-Xe systems. The same code is used here for the O_2-He system. See: Aquilanti, V.; Ascenzi, D.; de Castro Vítores, M.; Pirani, F.; Cappelletti, D. *J. Chem. Phys.*, in press.

(22) The O_2 molecules in the beam source exhibit a broad distribution of rotational levels (significantly populated up to $K = 21$). The level $K = 5$ is among the most populated ones.

(23) See for instance: Kuebler, N. A.; Robin, M. B.; Yang, J. J.; Gedanken, A.; Herrick, D. R. *Phys. Rev. A* **1988**, *38*, 737. Matsumoto, T.; Kuwata, K. *Chem. Phys. Lett.* **1990**, *171*, 314.