COMMENTS

Comment on "Rotational Alignment in Supersonic Seeded Beams of Molecular Oxygen" (*J. Phys. Chem.* 1995, *99,* 13620)

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Expanding O_2 in a light carrier gas, Aquilanti, Ascenzi, Cappelletti, and Pirani (referred to hereafter as AACP) found a non-zero, speed-dependent quadrupolar alignment, $A_0^{(2)}$, of the molecular angular momentum with respect to the beam axis.[1] However, the detailed results are in serious disagreement with those of Harich and Wodtke for alignment of CO in a supersonic beam.[2] Harich and Wodtke find that the fastest CO molecules are aligned with $\mathbf{J} \parallel \mathbf{v}$, while AACP find that the fastest O_2 molecules are aligned with $\mathbf{J} \perp \mathbf{v}$. These have been considered to be the only reliable, direct measurements of velocity-dependent alignment of molecules in beams. The discrepancy between the two results is disturbing, since one might expect O_2 and CO to behave similarly in a seeded supersonic expansion.

As one of the referees has pointed out, there are three possibilities to explain the observed differences: (1) the alignment determined by Harich and Wodtke is incorrect, (2) the alignment determined by AACP is incorrect, or (3) both trends are correct, but there is some subtle difference between the two experiments which gives rise to the differing results. It is important to understand which of these possibilities is the case.

We have found an error in the analysis of AACP, correction of which must significantly reduce the magnitude of the alignment they measured. Thus, the differences between the two experiments may not be as large as previously thought. However, from our analysis alone, it is impossible to determine whether AACP's results are not qualitatively correct or to eliminate the third possibility. Rather, more work is clearly called for on velocity-dependent alignment in seeded beams.

AACP measure O_2 ($^3\Sigma_g^-$) ground state transmission through a magnetic analyzer as a function of field strength. The populations of spin-rotation states that have the same transmission curves are adjusted to give the best fits to the measurements. Nuclear spin symmetry restricts $^{16}O_2$ to rotational states with odd rotational angular momentum, **K**. For Hund's case (b) coupling, both K and the spin angular momentum, **S**, are good quantum numbers, as is the total angular momentum, $\mathbf{J} = \mathbf{K} + \mathbf{S}$. AACP state that strong cooling in the expansion limits K to 1, and since $S = 1$, only $J = 0$, 1, and 2 states will be observed. We will show below that the highest alignment polarizations reported by AACP are physically impossible and the cases with lower alignment polarizations give improbable $|J, M_J\rangle$ population distributions. This problem occurs because AACP have not used the full experimental symmetry to constrain their fitting procedure.

In the experiments of AACP, both the molecular beam axis and the perpendicular analyzer magnetic field direction are quantization axes. Below, large M refers to angular momentum magnetic quantum numbers measured with respect to the beam axis (**v**) and small m refers to those measured with respect to the analyzer axis (**B**).[3] After determining the alignment of **J** or **K** along **B**, the alignment along **v** may be inferred. The experiment cannot differentiate between $|J, +m_J\rangle$ and $|J, -m_J\rangle$ states, or between the states ($|J = 2, \pm1\rangle$ and $|J = 1, 1\rangle$) or between ($|J = 0, 0\rangle$ and $|J = 2, 0\rangle$). Symmetry about **v** guarantees that pairs of states, ($+M$, $-M$) and ($+m$, m), must have equal populations. AACP[4] go from the fitted populations $w(J,m_J)$ to populations in the uncoupled representation $w(K{=}l,m_K)$ using Clebsch−Gordan coupling coefficients $\langle...|...\rangle$,

$$w(K = 1,m_K) = \sum_{Jm_J} \langle K{=}\ 1,\ m_K,\ S = 1,\ m_S|J,\ m_J\rangle^2 w(J,m_J) \quad (1)$$

thus determining the populations of the three $|K = 1, m_K\rangle$ states in the **B**-frame. These can be related to populations of the $|K = 1, M_K\rangle$ states in the **v**-frame, via the operator, $\mathbf{R}_Y(\pi/2)$, which rotates the quantization axis 90° from the **v**- to the **B**-frame,[5]

$$\mathbf{R_Y}(\pi/2)|j,\ M\rangle_\mathbf{v} = \sum_{m=-j}^{j} d^j_{mM}(\pi/2)|j,\ m\rangle_\mathbf{B} \quad (2)$$

For small j, the d^j_{mM} are tabulated in the literature.[6]

Using the cylindrical symmetry along **v**, eq 2 can be recast to give the fitted **B**-frame populations, $w(K = 1, m_K)$, in terms of the **v**-frame populations $W(K = 1, M_K)$

$$w(K{=}1,m_K) = \sum_M [d^{K=1}_{mM}(\pi/2)]^2\ W(K{=}1,\ M_K) \quad (3)$$

This set of equations can be inverted to give the $W(K{=}1,M_K)$ in terms of the $w(K{=}1,m_K)$. Once the $W(K{=}1,M_K)$ are known, it is trivial to calculate the alignment polarization, $P_{K=1}$,[1c] or the quadrupolar alignment, $A_0^{(2)}$, of **K** along **v**.

AACP used the method outlined to obtain, $P_{K=1}$ as a function of velocity and backing pressure. The fastest groups of molecules had values of $P_{K=1}$ ranging between +0.6 and +0.8. The very large polarizations of **K** with respect to **v** reported by AACP are surprising, since **K** should be naturally depolarized as it precesses about **J**, when the *incoherently* excited molecules travel down the beam to the detector. The largest polarizations reported by AACP are, in fact, larger than is physically possible. This can be shown by calculating the alignment polarization of **K** along **v** that results for various quadrupolar alignments of **J** along **v**. The results of this calculation are shown in Figure 1. In all cases, $P_{K=1} \leq +0.6$, for both $J = 1$ and 2. In fact, the maximum value, $P_{K=1} = +0.6$, would occur only in the unlikely case where multiple, random collisions produce a beam of pure $|J = 2, 0\rangle_\mathbf{v}$.

The reason that AACP could obtain alignment polarizations larger than physically possible is that they have not completely taken into account all of the constraints placed upon their fits

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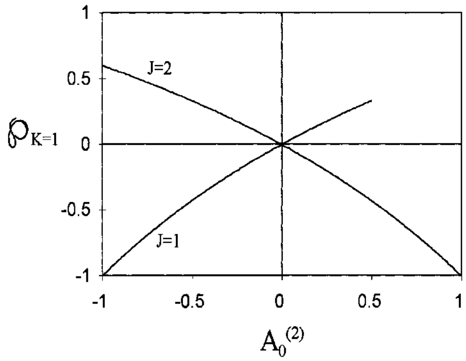

Figure 1. Calculated alignment polarization of K, $P_{K=1}$, shown as a function of the quadrupolar alignment of J, $A_0^{(2)}$, for $J = 1$ and $J = 2$. Both alignments are with respect to the beam axis.

by the cylindrical symmetry of the experiment. This may be seen most clearly if the fitted $w(J,m_J)$ in the **B**-frame are first rotated to obtain the $W(J,M_J)$ population distribution in the **v**-frame, followed by uncoupling of angular momenta in the **v**-frame. To do this, one must separately rotate the states that have different total angular momentum quantum numbers $J =$ 0, 1, and 2, using rotation matrix elements similar to those in eq 3. This yields a set of six linear equations for the $W(J,M_J)$, in terms of the fitted $w(J,m_J)$:

$$W(J{=}2,0) = w(J{=}2,\pm2) - w(J{=}2,\pm1) + w(J{=}2,0) \quad (4a)$$

$$W(J{=}2,\pm1) = {}^2/_3 w(J{=}2,\pm2) + {}^4/_3 w(J{=}2,\pm1) - 2w(J{=}2,0) \quad (4b)$$

$$W(J{=}2,\pm2) = -{}^2/_3 w(J{=}2,\pm2) + {}^2/_3 w(J{=}2,\pm1) + 2w(J{=}2,0) \quad (4c)$$

$$W(J{=}1,0) = w(J{=}1,\pm1) - w(J{=}1,0) \quad (4d)$$

$$W(J{=}1,\pm1) = 2w(J{=}1,0) \quad (4e)$$

$$W(J{=}0,0) = w(J{=}0,0) \quad (4f)$$

Following AACP, $W(J,\pm M_J) = W(J,+M_J) + W(J,-M_J)$ and $w(J,\pm m_J) = w(J,+m_J) + w(J,-m_J)$.

These six equations constrain the population distributions that can be measured in the **B**-frame, limiting the relative size of several $w(J,m_J)$ elements. For example, from eq 4d, $w(J{=}1,\pm1) \geq w(J{=}1,0)$, else $W(J{=}1,0)$ would be negative. Similarly, $w(J{=}2,\pm2)$, $w(J{=}2,\pm1)$, and $w(J{=}2,0)$ are limited. By first uncoupling in the **B**-frame and then rotating to the **v**-frame, AACP arrive at constraining equations for the $w(K{=}1,m_K)$ that are formally identical to eqs 4d and 4e, with J replaced by K. However, by first uncoupling, AACP have effectively disregarded the additional constraints on the populations $w(J,m_J)$, which allows them to fit their data with physically impossible population distributions.

The original fits to $w(J,m_J)$ from ref 1c are reproduced in Table 1. At a backing pressure (P_0) of 800 Torr and a velocity (v) of 1.73 km/s, the populations in the first column include $w(J{=}1,0) = 0.25 > 0.10 = [w(J{=}2,\pm1) + w(J{=}1,\pm1)]$, which implies that $W(J{=}1,0) < 0$. The same conclusion can be drawn by inspection for fits when P_0 is 300 and 100 Torr at $v = 1.73$ km/s. Table 2 shows calculated[7] $W(J,M_J)$, $P_{K=1}$, and $A_0^{(2)}$ for the two other data sets in Table 1. The alignment polarization, $P_{K=1}$, is close to that of AACP, as it should be since both our analysis and the analysis of AACP are mathematically correct. However, the $W(J,M_J)$ populations they provide are unreasonable. Some states have essentially no population and others have

TABLE 1: Population Data for O_2 (2.5%) Seeded in He

	$P_0 = 800^a$			$P_0 = 300^a$	$P_0 = 100^a$
$w(J,m_J)$	$v = 1.73^b$	$v = 1.60^b$	$v = 1.35^b$	$v = 1.73^b$	$v = 1.73^b$
$w(J{=}2,\pm2)$	0.50	0.17	0.05	0.42	0.25
$w(J{=}2,\pm1) + w(J{=}1,\pm1)$	0.10	0.38	0.40	0.16	0.30
$w(J{=}2,0) + w(J{=}0,0)$	0.15	0.19	0.35	0.10	0.07
$w(J{=}1,0)$	0.25	0.26	0.20	0.32	0.38

[a] Backing pressure (Torr). [b] Beam velocity (km/s).

TABLE 2: Average Populations $W(J,M_J)$, Alignment Polarization, and Quadrupolar Alignment of K in the Molecular Beam-Backing Pressure 800 Torr, O_2 (2.5%) Seeded in He

	$v = 1.60$ km/s	$v = 1.35$ km/s
$W(J{=}2,\pm2)$	0.08	0.16
$W(J{=}2,\pm1)$	0.08	0.03
$W(J{=}2,0)$	0.16	0.02
$W(J{=}1,\pm1)$	0.52	0.40
$W(J{=}1,0)$	0.04	0.10
$W(J{=}0,0)$	0.12	0.28
$P_{K=1}$	$+0.24 \pm 0.04^a$	-0.03 ± 0.06^a
$P_{K=1}$	$+0.40 \pm 0.10^b$	0.00 ± 0.05^b
$A_0^{(2)}$	-0.17 ± 0.03^a	$+0.02 \pm 0.02^a$

[a] The standard deviation over all populations subject to the constraints. [b] Reference 1c.

populations approaching 50%. The difference between the calculated $|J = 2, \pm1\rangle$ and $|J = 1, \pm1\rangle$ populations is particularly odd since these states have almost identical uncoupled representations. We conclude that AACP's least-squares fits of the experimental beam transmission curves to population distributions are not reliable, as demonstrated by their finding values of $P_{K=1}$, which are larger ($>+0.6$) than possible for any J of O_2 ($K = 1$, $S = 1$), and their finding unreasonable population distributions in the **v**-frame for other cases. The source of these nonphysical fits was a failure to use all constraints on the populations implied by the cylindrical experimental symmetry.

We cannot say what the actual alignment of O_2 in a supersonic seeded expansion is. We can say only that the analysis of AACP is flawed. The sign of the actual alignment of O_2 might be opposite from that found for CO by Harich and Wodtke, but the actual alignment is certainly different (quantitatively and perhaps qualitatively) from that reported by AACP. The analysis of magnetic transmission experiments is clearly quite complex. In light of this, a more direct determination of the alignment of O_2 in seeded beams is clearly desirable.

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References and Notes

(1) (a) Aquilanti, V.; Ascenzi, D.; Cappelletti, D.; Pirani, F. *Nature* **1994,** *371,* 399. (b) Aquilanti, V.; Ascenzi, D.; Cappelletti, D.; Franceschini, S.; Pirani, F. *Phys. Rev. Lett.* **1995,** *74,* 2929. (c) Aquilanti, V.; Ascenzi, D.; Cappelletti, D.; Pirani, F. *J. Phys. Chem.* **1995,** *99,* 13620.

(2) Harich, S.; Wodtke, A. *J. Chem. Phys.* **1997,** *107,* 5983.

(3) Note that the present notation differs from that of AACP and has been adopted for clarity.

(4) Equations 1 and 3 appearing here are identical to eq 3.2 and 3.3 of ref 1, with small changes to conform with our notation.

(5) Zare, R. N. *Angular Momentum;* John Wiley & Sons: New York, 1988; Chapter 3.

(6) Zare, R. N. *Angular Momentum*; John Wiley & Sons: New York, 1988; p 89.

(7) Using the constraints described above, calculations of all possible distributions in the beam were carried out for the data with $P_0 = 800$ Torr and $v = 1.60$ and 1.35 km/s. This was done by allowing $w(J{=}1,\pm1)$ and $w(J{=}0,0)$ to vary over their respective ranges in step sizes of 1%. If any of the populations $W(J,M_J)$ in the beam were less than 0%, the configuration was not counted as possible. The uncertainties on the average quadrupolar alignment and alignment polarization were calculated from the standard deviations of values from all possible configurations.