

Comment on: Polarized absorption spectroscopy of lambda-doublet molecules: Transition moment vs electron density distribution

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Citation: *The Journal of Chemical Physics* **89**, 5965 (1988); doi: 10.1063/1.455524

View online: <http://dx.doi.org/10.1063/1.455524>

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Reply to the Comment on: "Analytic solution of relaxation in a system with exponential transition probabilities"

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(Received 18 March 1988; accepted 12 April 1988)

I believe Lim's conclusion¹ that linear decay is the consequence of constant $\langle \Delta E \rangle \equiv \langle \langle \Delta E \rangle \rangle$ is entirely correct. In fact, his argument can be taken one step further to show that the restriction to delta function initial distribution is unnecessary; it is sufficient that the initial energy have a definable average.

Suppose that at $t = 0$ the average initial energy in the bulk system is $\langle \langle E_0 \rangle \rangle$, and suppose that Eq. (5) of Ref. 1 is satisfied, i.e., that the average energy transferred per collision in the bulk system is $|\langle \langle \Delta E \rangle \rangle| = c$, where c is a constant independent of the number of collisions. Assuming that $\langle \langle E_0 \rangle \rangle$ is high and therefore the system relaxes by losing energy (but the total number of particles is conserved), the bulk-average energy after the first collision will be $\langle \langle E_0 \rangle \rangle - c$, and after n collisions will be

$$\langle \langle E_n \rangle \rangle = \langle \langle E_0 \rangle \rangle - nc. \quad (1)$$

For obvious physical reasons, Eq. (1) makes sense only for $nc < \langle \langle E_0 \rangle \rangle$. Since collisions are random, to convert from n dependence to time dependence $\langle \langle E_n \rangle \rangle$ must be averaged over the Poisson distribution

$$P(n) = (\omega t)^n e^{-\omega t} / n!, \quad (2)$$

where ω is the collision frequency. In the case of Eq. (1) this averaging is trivial leading directly to $\langle \langle E_t \rangle \rangle = \omega t c$, where $\langle \langle E_t \rangle \rangle$ is the average energy in the bulk system at time t after the initial excitation.

The same sort of argument can be used to deduce the decay of $\langle \langle E_n \rangle \rangle$ or $\langle \langle E_t \rangle \rangle$ in any system where, in addition to $\langle \langle E_0 \rangle \rangle$, the n dependence of $\langle \langle \Delta E_n \rangle \rangle$, the average energy transferred in the n th collision in the bulk system, is known. For example, if $\langle \langle \Delta E_n \rangle \rangle$ is a linear function of the average

energy in the bulk system after the preceding collision, i.e., if

$$\langle \langle \Delta E_n \rangle \rangle = a(\langle \langle E_{n-1} \rangle \rangle - b), \quad (3)$$

where a and b are constants, then the decay of average energy in the bulk system will be exponential in time. To show this (assuming again the system relaxes by losing energy), let $\Delta = (\langle \langle E_0 \rangle \rangle - b)$; thus the average energy in the bulk system after the first collision is $\langle \langle E_1 \rangle \rangle = \langle \langle E_0 \rangle \rangle - \Delta$; after the second collision it is $\langle \langle E_2 \rangle \rangle = \langle \langle E_1 \rangle \rangle - a(\langle \langle E_1 \rangle \rangle - b) = \langle \langle E_0 \rangle \rangle - 2a\Delta - a^2\Delta$, and so on. After some manipulation,

$$\langle \langle E_n \rangle \rangle - b = \Delta(1 - a)^n. \quad (4)$$

Averaging Eq. (4) over the distribution (2) yields the exponential decay

$$\langle \langle E_n \rangle \rangle - b = \Delta e^{-a\omega t}. \quad (5)$$

Note that it is the difference $\langle \langle E_n \rangle \rangle - b$ that decays exponentially and not $\langle \langle E_n \rangle \rangle$ alone. As $t \rightarrow \infty$, the system must reach equilibrium; thus $b = \langle \langle E \rangle \rangle_{\text{eq}}$, which is the average energy in the bulk system at equilibrium. Therefore, Eqs. (4) and (5), unlike Eq. (1), make physical sense for all n and t , respectively. It can be shown² that $a = 1/\omega\tau$ where $\omega\tau$ is the dimensionless relaxation time, and so Eq. (5) represents the familiar Bethe-Teller law, which is usually³ demonstrated as the consequence of the microscopic "linear sum rule," i.e., the linear dependence of $\langle \Delta E \rangle$ on energy.

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Comment on: Polarized absorption spectroscopy of lambda-doublet molecules: Transition moment vs electron density distribution

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Bigio and Grant (BG)¹ have reported laser analyses of NO. There they discussed our²⁻⁴ (AR) theoretical analysis of polarization data for OH (other portions of Refs. 2-4 are not at issue) from the photolysis of H₂O. They say: "Most seriously, the formalism established by (AR) fails to dis-

criminate between *isolated* main and satellite branches and *mixed* branches: Conclusions expressed there, relating degree of alignment to observed polarization ratio (R) as a function of J would be qualitatively correct only insofar as the mixed Q branches are concerned" and that "missing in

the treatment of (AR) is the fact that transitions of both $\Delta J = 0$ and $\Delta J = \pm 1$ exist for each lambda doublet. These yield opposite transition moment directionalities."

Such use of "fails" and "missing" to describe our *theoretical* treatment may lead a reader to the false inference that our *data* consist of mixed branches and that in our analysis we failed to include missing steps. With only two exceptions, our laser bandwidth was adequate to measure isolated branches. In fact we did observe that the main and satellite bands had opposite transition moment directionalities.

We reported^{2,3} LIF measurements with Q_1 - or Q_2 -branch excitation using the notation of Dieke and Crosswhite,⁵ where the Q refer to ΔN , because they yielded a maximum polarization effect. For Q_1 the neighboring satellite is Q_{21} . [In the notation of BG, these branches are Q_{11} and P_{21} , respectively, where Q and P refer to ΔJ .] Our laser bandwidth was $\approx 0.25 \text{ cm}^{-1}$. According to Table 14 of Ref. 5, which we used in carrying out our experiments, the Q_1 and Q_{21} were separated by 0.3, 0.58, 0.83, 1.01, 1.37, 1.50, 1.33, 1.91, and 2.23 cm^{-1} for N from 1–9, respectively. Clearly resolved peaks were obtained from $N = 3$ –9. A similar situation applies to Q_2 , except that $N = 2$ and 3 overlap. We explicitly recognized the effect of some main-satellite line overlap in Fig. 13 of Ref. 3 for $N = 1$ and 2.

The ability to separate main and satellite transitions, which is available for OH but not for NO, makes the former better suited for detailed polarization studies.

There is another point. Bigio and Grant correctly summarize our previous position that "for a given alignment, different ^2H molecules with different λ will show different polarization ratios $R (\equiv I_{\parallel}/I_{\perp})$, where the I_i are transition intensities) even for a given isolated branch." This was based upon increasing electron alignment with larger J as the molecule moves toward Hund's case (b) from case (a). In contrast, for Q excitation, they derive I_i that lead to Eq. (1), in which⁶ R is independent of λ for an isolated branch, i.e.,

$$R_{\text{theor}} = 4 \left\{ \frac{\sum_{M=-J}^{M=J} WM^2}{\sum_{M=-J}^{M=J} W} \frac{(J+M+1)(J-M)}{(J-M+1)(J+M)} \right\}, \quad (1)$$

where W is the M state distribution. This result is interesting, and is still surprising to us, because it means that although the alignment of the electrons and the I_i depend upon λ , their ratio R does not.

We agree that a BG-type of treatment should replace Eqs. (22) and (23) of Ref. 3 and the "polarization effects" section of Ref. 4 for the OH analysis. We say BG-type because (a) LIF was used in Refs. 2 and 3 which adds a small source of anisotropy and (b) because BG did not include dealigning effects of electron and nuclear spins. The latter occur because, e.g., the photodissociation is likely to be independent of nuclear spin,^{7,8} but it is the total angular momentum which is aligned in space. These effects are appreciable at low J for OH. We have not checked their effect upon NO.

In order to compare Eq. (1) with our data, we make an approximate correction for the fluorescence anisotropy, $R_{\text{exp}} = 1 + [6(R_{\text{LIF}} - 1)/7]$, where R_{LIF} are data from Fig. 13 of Ref. 3. We expect a $\cos^2 \theta$ distribution from our

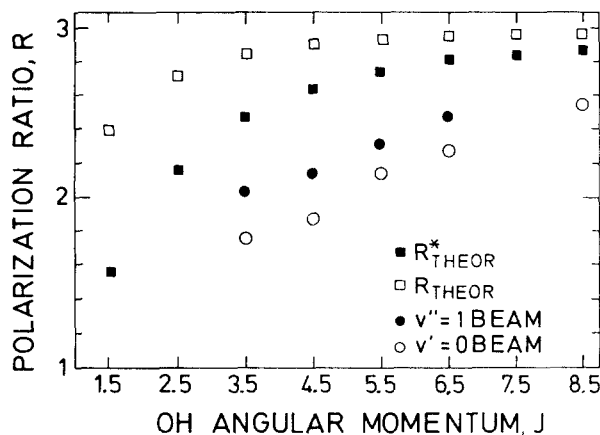


FIG. 1. Comparison of isolated Q_1 -branch polarization data of OH, R_{exp} , with the prediction of Bigio and Grant, R_{theor} , and with that modified for the effects of nuclear and electron spin, R^*_{theor} .

water photolysis, which implies that $W = M^2/[J(J+1)]$. Figure 1 contains R_{theor} and R_{exp} as a function of J . (Our data for $J = 1.5$ and 2.5 are omitted because these are not cleanly isolated branches.) Both R_{theor} and R_{exp} increase with J , but otherwise the agreement is unimpressive. At low J the agreement is improved when dealignment caused by precessions, arising from nuclear and electron spin, are considered.⁷ We estimate these here. For our assumed $\cos^2 \theta$ distribution of OH, the initial Green-Zare⁸ alignment parameter A_0 is $[4J(J+1) - 3]/5J(J+1)$. This A_0 is then reduced by the factors $1 - [6/(2J+1)^2]$ and $1 - [3/\{4J(J+1)\}]$ for nuclear⁸ and electron spin,⁹ respectively. The electron spin factor assumes Hund's case (b) coupling which is an approximation here. We converted these reduced alignments to $W(J, M)$, entered them in Eq. (1) and obtained an R^*_{theor} that is shown in Fig. 1.

Our main points are that (a) except for $J = 1.5$ and 2.5 , our data do not suffer from the main-satellite branch overlap problem described by BG and that their J dependence remains a good test for theory, (b) the BG approach is sounder than was ours, and (c) for low values of J the dealignments caused by nuclear and electron spins should be considered. As discussed in Ref. 4, a correct interpretation of such data is important for several applications.

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⁶This is the ratio of Eqs. 8(a) and 8(b) of Ref. 1. [Eq. 8(b) has two misprints: The $(2J+1)$ terms should be replaced by $(2J+1)^2$. L. Bigio and E. R. Grant, J. Chem. Phys. **89**, 5968 (1988)]. The λ dependent coefficients a_j and b_j vanish after the ratio is taken.

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