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Reply to the Comment on “Transient Anisotropy and Fragment Rotational Excitation in the Femtosecond Photodissociation of Triiodide in Solution”

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We previously published experimental results on the transient anisotropic response of diiodide ions following femtosecond photolysis of triiodide in ethanol solution.[1] In this paper, the experimental anisotropy, $r(t)$, as a function of photolysis probe delay t could be fitted phenomenologically by a sum of two exponentials and a Gaussian. From the decay of the Gaussian component, we tried to obtain information regarding the degree of rotational excitation of the diatomic product. We assumed that the correlation time, τ_3, of this Gaussian contribution can be connected to specific parameters of the rotational product distribution responsible for the expected inertial decay of the anisotropy. For example, if the process of bond breakage generates a rotational Boltzmann distribution of product diatoms at room temperature, a free rotor correlation time of 0.94 ps can be predicted for a thermalized ensemble of diiodide ions. Instead, we recovered rotational correlation times that were significantly smaller, implying a substantial amount of rotational excess energy of the diatomic fragment. In addition, a classical model for bond breakage of an instantaneously bent triatomic parent ion was invoked to further establish the source of product rotational excitation.

In his comment, Dr. Volk points out that the functional form that was used in ref 1 to simulate the experimental data is nonphysical and does not reproduce the “true“ rotational correlation time constant, τ_c. Furthermore, he concludes that our results are fully consistent with a room temperature ensemble of product diatoms and that diiodide ions are not formed rotationally excited. In response to these comments, we discuss a few issues that are related to these criticisms.

First, we did not assume a priori that the anisotropy should obey the functional form that was used for fitting in ref 1. As Figure 5 in ref 1 demonstrates, it is the decay of the experimental anisotropy itself that suggests a fitting by a sum of two exponentials and a Gaussian over several orders of magnitude. We have chosen this fitting function because it gave the only acceptable approximation to the global data from time zero to infinite delays. Besides this semantic issue, we agree that for a perfectly coherent ensemble at $t = 0$, the correct functional form for $r(t)$ should transfer an initial Gaussian decay (with a relative amplitude of 1) continuously into a purely diffusive exponential decay for infinite delays. We did try to fit the experimentally observed anisotropy to empirical functions that describe this gradual evolution from inertial to diffusive-type motions (e.g., eq 12 in ref 2). In addition, a Langevin-type approach was used that was previously employed by Baskin et al.[3] Nevertheless, these models were unable to reproduce the global experimental data.

Most importantly, however, our interpretation of rotationally excited fragments was inspired by further findings that were not specifically included in ref 1. (i) We performed experiments related to the solvent dependence of the rotational dynamics in this system, and (ii) we did apply the proper time series expansion directly to the data as will be shown below. *These additional pieces of information corroborate our interpretation that the diatomic fragment is born rotationally excited from the femtosecond photolysis of triiodide solutions in ethanol.*

Acetonitrile is known to have a rather small symmetry-breaking ability with respect to triiodide ions (see, for example, refs 4 and 5). According to resonance Raman experiments conducted by Myers and co-workers, I_3^- in acetonitrile solution can be considered as a nearly perfectly centrosymmetric ion (point group $D_{\infty h}$).[6] Such an assignment is based on the lack of Raman activity of the antisymmetric stretching vibration in this solvent. Assuming I_3^- in acetonitrile is indeed perfectly linear in both the ground and excited states, one would expect a rotational temperature T of the I_2^- product of 300 K and, hence, a rotational correlation time of 0.94 ps.

Figure 1a displays our experimentally determined decays of $r(t)$ for triiodide solutions in acetonitrile and in ethanol. Both data were taken back-to-back and were obtained with detection near the center of the I_3^- resonance ($\lambda = 800$ nm). Subsequent normalization of the data with respect to their maximum facilitates a direct comparison of the rotational dynamics in these two solvents. First, we note that diffusive reorientation on longer time scales leads to a considerably faster decay for acetonitrile because of its lower visocosity. However, on ultrashort time scales below 1 ps, the same data clearly decay much more slowly compared to ethanol. Our fitting function returns a Gaussian correlation time of 0.85 ps with a corresponding relative amplitude of 0.14 for this solvent.

In Figure 1b, both data sets are plotted as a function of the squared time delay as suggested by the free rotor expression for the initial behavior of the anisotropy. The slope of the anisotropy extrapolated to $(t - t_{\max})^2 \rightarrow 0$ should be proportional to the inverse of the squared free rotor correlation time. Here, $t_{\max}$ denotes the pump−probe time delay at which the anisotropy reaches the maximum. For acetonitrile solution we find a free rotor time constant of 1.0 ps consistent with a fully thermalized ensemble at 300 K. In contrast, the slope of the ethanol data around $(t - t_{\max})^2 = 0$ is much steeper. From its value of -3.3 ps^{-2}, one would extract a free rotor time constant of 0.55 ps which is about a factor of 2 smaller than in acetonitrile. As we concluded in ref 1, this finding is entirely consistent with a substantial degree of rotational excitation of the diatomic fragment in ethanol solution.

It should be strongly emphasized at this point that the anisotropy is only proportional to t^2 strictly in the limit $t^2 \rightarrow 0$. In liquid solution, however, deviations from a linear behavior exist already at early times, which originate from solvent-induced damping of rotational motion. A functional form that

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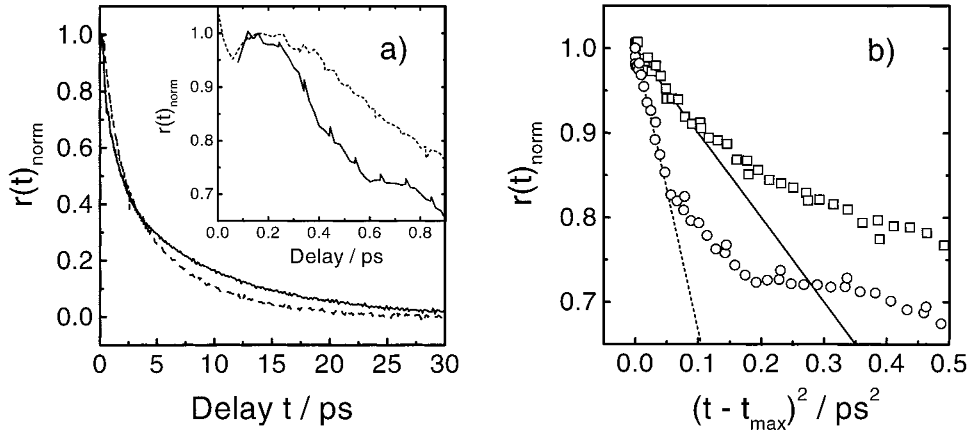

Figure 1. (a) Comparison of the anisotropy decay observed for acetonitrile (dashed) and ethanol (solid) solutions. Both data sets have been normalized with respect to their maximum. The inset emphasizes the ultrafast inertial contribution to $r(t)$ which decays considerably faster in ethanol solution. (b) Plot of $r(t)$ vs the squared time delay as suggested by the series expansion of the free rotor for ethanol (circles) and acetonitrile (squares). The solid and dashed lines indicate the slope of the anisotropy extrapolated to a squared time delay of zero. For ethanol, the slope is -3.3 ps^{-2}, suggesting a free rotor time constant of 550 fs. For acetonitrile, the slope is -1.0 ps^{-2}, implying that diiodide ions are formed rotationally cold in this solvent.

describes this early-time behavior exactly is the full time-series expansion as given by Gordon:[7]

$$r(t) = \frac{2}{5}\left\{1 - \left(\frac{3k_\mathrm{B}T}{I}\right)t^2 + \left[\left(\frac{2k_\mathrm{B}T}{I}\right)^2 + \left(\frac{\langle Q^2\rangle}{8I^2}\right)\right]t^4 \dots\right\} \quad (1)$$

Deviations from a linear behavior are clearly visible in Figure 1b and can be used to estimate mean squared torques, $\langle Q^2\rangle$, exerted by the solvent onto the rotor with moment of inertia I. Qualitatively, the influence of these torques is to decelerate the decay of $r(t)$ in the fourth power of t. The solid line in Figure 1b corresponds only to the free rotor part of eq 1 truncated after the quadratic term. Therefore, this line sets the fastest limit for the short-time decay of $r(t)$ if the fragments were born rotationally cold. Regardless of the correct functional form that should be used for fitting the global data, the anisotropy at early times cannot decay faster than this limit unless the diatomic fragments are born rotationally excited. Obviously, in ethanol solution, the early time anisotropy decays much faster than this limit indicating that, in fact, the fragments rotate faster than at room temperature.

To summarize, we feel that Dr. Volk's comments were very well made and we very much appreciate his response to our work. However, the full time series expansion for the early-time behavior of $r(t)$ and the solvent dependence of the anisotropy show indeed that *in ethanol solutions, diiodide ions are formed rotationally excited*. As we have already done in ref 1, we should mention again that triiodide is *not* necessarily bent in the electronic ground state. It is also possible that the ground state is linear while anisotropic gradients on the excited state lead to an evolution along the bending coordinate.

References and Notes

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