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COMMENTS

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

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In a recent article published in this Journal, Kühne and Vöhringer[1] reported transient anisotropy measurements on I_2^- after photodissociation of triiodide in ethanol solution. On the ultrashort time scale, a Gaussian decay of the initial nonequilibrium orientational distribution of the dissociation products was observed from changes in the anisotropy, indicating a significant inertial contribution to orientational relaxation. A Gaussian correlation time constant of 450 fs was attributed to this inertial decay. Since the free rotor orientational correlation time of I_2^- at room temperature is 950 fs, it was concluded that the photodissociation of I_3^- yields I_2^- with significant rotational excitation. The collinear dissociation of a linear molecule is not expected to yield products with excess rotational energy, so it also was proposed that I_3^- is bent in solution.

The experimental results of Kühne and Vöhringer are very similar to previous results on the photodissociation of HgI_2 in ethanol, where a 500 fs Gaussian component in the anisotropy decay of the HgI photoproduct was reported,[2] which incidentally has a moment of inertia very similar to I_2^-. However, good agreement between the time dependence of the HgI anisotropy decay and MD simulations of the HgI rotational correlation function at 300 K was observed, indicating that the photodissociation of HgI_2 does *not* yield HgI with significant rotational energy[2] probably because of the linear geometry of the parent molecule. Furthermore, MD simulations showed that the rotational energy relaxation time of HgI in ethanol is 160 fs.[2]

Thus, the results of Kühne and Vöhringer[1] seem to imply that rotational energy relaxation is significantly slower for I_2^- than for HgI. This result would be of great interest in the context of a detailed understanding of solute−solvent interactions. However, the conclusion that I_2^- is created rotationally hot rests on the discrepancy between the room-temperature free rotor correlation time constant of 950 fs and the value of 450 fs for the Gaussian correlation time constant found by fitting the experimental data to the *sum* of a Gaussian and two exponentials. A thorough analysis shows that this fitting function is nonphysical and does not reproduce the correct correlation time constant of the initial inertial component.

If the rotational behavior is that of an impulsively created ensemble of free rotors, the initial time dependence of the anisotropy decay is Gaussian with a time constant τ_c, calculable from the moment of inertia and the temperature. This Gaussian signal will constitute *100% of the initial anisotropy*; i.e., all molecules will contribute to the initial coherent rotational response. Collisions with solvent molecules cause the functional form of the anisotropy decay at larger delay times to evolve into one or more exponentials describing rotational diffusion. In contrast, Kühne and Vöhringer[1] assume the anisotropy should fit to a function that is the *sum* of a Gaussian and (slower) exponentials at all delay times. The Gaussian component represents only 10−20% of the initial anisotropy (with the exact result depending on the probe wavelength). It is straightforward to show that this Gaussian contribution necessarily has a significantly shorter time constant than the free rotor decay constant correctly reproducing the initial behavior.

TABLE 1: Time Constants Obtained by Fitting the Data of Ref 1 to Eq 2

λ_{probe}/nm	Γ_1/ps	Γ_2/ps	τ_c/ps	τ_t/ps
800	10.5	1.12	1.01	0.28
730	10.0	1.38	0.86	0.35
700	9.8	1.46	0.85	0.41
680	8.5	1.64	0.89	0.44
650	10.3	1.61	1.18	0.60
630	11.5	1.27	0.92	0.45
610	11.3	1.45	1.21	0.68
530	15.6	0.61	0.85	0.34

Analytic forms for the time-dependent rotational diffusion coefficient were deduced,[3] and an empirical function describing the evolution of the anisotropy $r(t)$ of an ensemble of rotors from Gaussian to exponential diffusional behavior was introduced in earlier studies of inertial motion:[4]

$$r(t) = F(t)\exp[-t/\tau_t] + (1/\tau_t)\int_0^t \mathrm{d}T\,\exp[-(t-T)/\Gamma] \times F(T)\exp[-T/\tau_t] \quad (1)$$

Here, $F(t)$ corresponds to the pure free rotor decay, which can be approximated by a Gaussian with correlation time constant τ_c, $F(t) = r_0\exp[-(t/\tau_c)^2]$, τ_t describes the (exponential) transition from free rotor to diffusional behavior, and Γ is the rotational diffusion time constant. If the transition from free rotor to diffusional behavior is faster than the anisotropy decay, eq 1 can be approximated by

$$r(t) = r_0\exp[-(t/\tau_c)^2]\exp[-t/\tau_t] + r_0(A_1\exp[-t/\Gamma_1] + A_2\exp[-t/\Gamma_2])(1-\exp[-t/\tau_t]) \quad (2)$$

(here, eq 1 was adapted to allow for *bi*exponential diffusional behavior with time constants Γ_1 and Γ_2 and relative amplitudes A_1 and A_2, i.e., $A_1 + A_2 = 1$). Unlike the sum of Gaussian and exponential(s), this function yields the correct behavior also at early times and therefore should be used to extract the free rotor correlation time associated with the early part of an experimental anisotropy decay.

We reanalyzed the results of Kühne and Vöhringer on the anisotropy decay of I_2^- to investigate how the use of this physically more relevant fit function will affect the resulting free rotor time constants. For this purpose, we simulated the experimental data with the help of eq 3 and Table 1 of ref 1 and performed a nonlinear least-squares fit of these simulated data to eq 2, using a Levenberg−Marquardt routine. The results

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are summarized in Table 1.[5] The values for the rotational diffusion time constant Γ_1 are in good overall agreement with Kühne and Vöhringer's results, whereas the values for Γ_2 are somewhat smaller. Most prominently, the free rotor correlation time constant, τ_c, adopts values around 1 ps, which is in good agreement with the free rotor orientational correlation time constant of I_2^- *at room temperature*. Thus, I_2^- does not seem to be produced with significant rotational energy. Alternatively, it may undergo fast rotational cooling, in analogy to the fast rotational cooling of HgI, which was shown by MD simulations to occur with a time constant of 160 fs.[2] Our fits also show that the transition from free rotor to rotational diffusion behavior, as described by the time constant τ_t, occurs on the time scale of a few 100 fs. The apparent wavelength dependence of this value may be of particular interest in the context of a detailed understanding of solute−solvent interaction. Our preliminary results suggest that in molecules with higher vibrational excitation, which are predominantly detected at the shorter wavelengths,[6] this transition is slower.[7]

In summary, if anisotropy data show the transition from inertial to diffusive rotational behavior, the free rotor correlation time constant cannot be determined by fitting the data to the *sum* of a Gaussian and exponential(s). The fitting function must show the *evolution* from one type of behavior to another. Our preliminary analysis shows that the results of Kühne and Vöhringer[1] on the anisotropy decay of I_2^- do not require the invocation of rotationally hot molecules. Thus, no conclusions on slow rotational energy relaxation can be drawn. Furthermore, the results are consistent with I_3^- being approximately linear in ethanol solution.

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References and Notes

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(3) Steele, W. A. *Adv. Chem. Phys.* **1976**, *34*, 1.
(4) Myers, A. B.; Pereira, M. A.; Holt, P. L.; Hochstrasser, R. M. *J. Chem. Phys.* **1987**, *86*, 5146.
(5) For these fits, the time constants Γ_1, Γ_2, τ_c, and τ_t and the amplitudes r_0, A_1, and A_2 were set as free fit parameters (under the constraint $A_1 + A_2 = 1$). For all wavelengths, good fits were obtained. Small discrepancies between simulated data and fit results (not significantly larger than the experimental accuracy) were observed for delay times within the temporal overlap of pump and probe laser pulses. These discrepancies may be due to the fact that the proper convolution of the signals with the finite instrument response was neglected in the original data analysis (see ref 1). It was not possible to obtain good fits with τ_c fixed to a value of 500 fs.
(6) Kühne, T.; Vöhringer, P. *J. Chem. Phys.* **1996**, *105*, 10788.
(7) The fit results for the data at 530 nm seem to be in contradiction to this suggestion. However, at this wavelength, I_3^- is expected to contribute significantly to the signals (ref 6), thus distorting the anisotropy data.