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COMMENTS

Comment on "Photoisomerization of *trans*-Stilbene in Moderately Compressed Gases: Pressure Dependent Effective Barriers" (*J. Phys. Chem. A* 1999, *103,* 10528−10539)

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Some years ago, Gershinsky and Pollak[1] provided a new interpretation for the factor of 20 difference between the fluorescence decay rate of pure stilbene vapor and stilbene in liquid ethane. We showed, that upon excitation, the lowering of vibrational frequencies in the excited state causes a lowering of the effective vibrational temperature of the nascent vibrational distribution. This cooling leads to a decay that is much slower than the decay that would be measured without cooling. In the liquid, the bath rapidly heats the cold molecule and the rate is increased by over an order of magnitude. In the presence of a bath gas, increasing the pressure will lead to an increase of the rate, due to the partial reheating of the cold nascent stilbene.

In a recent paper, Meyer et al.[2] reported a systematic experimental study of the bath gas and pressure dependence of the photoisomerization dynamics of *trans*-stilbene when excited at the 0−0 excitation frequency. They found that (a) at high pressure (7−20 bar), the decay rate depends on the identity of the bath gas and (b) at low pressure, the long time decay component of the fluorescence decay is pressure dependent. To explain both of these observations, the authors postulated that increasing the pressure of a bath gas causes a substantial lowering of the barrier height to isomerization, which depends on the identity of the bath gas. The cooling hypothesis, they argued, does not account for the observed bath gas dependence of the high pressure rate constant. They also presented in their Figure 17, the fluorescence decay in N_2 at $P = 2$ bar and claimed that their experimental decay curve is incompatible with a decay curve calculated on the basis of the cooling hypothesis. They also claimed that the reason we had to postulate a cooling hypothesis is because our RRKM computations imply a barrier height of 930 cm^{-1}, which is much lower than the experimentally measured barrier of $\sim$1250 cm^{-1}. They then concluded that vibrational cooling upon optical excitation of *trans*-stilbene is "definitely" not consistent with the experimental results.

In this Comment we would like to point out that, in fact, their experimental observations seem to support the cooling hypothesis.

(a) The supposed high-pressure rate constants presented in their Figure 14 are not really the high-pressure rate constants for all bath gases. Fleming et al.[3] found that the rate for methane at 296 K increases up to a value of $(30 \pm 10) \times 10^9\ \mathrm{s}^{-1}$ at a pressure of 100 bar. This is *larger* than the value of $17 \times 10^9\ \mathrm{s}^{-1}$ measured by Meyer et al. at a pressure of 20 bar and a (higher) temperature of 323 K. If methane has not reached the high-pressure limit, then He, Ne, and Ar, which are poorer colliders, have also not reached the true high-pressure limit.

(b) Meyer et al. do not present error bars on the data presented in Figure 14, but in a previous report[4] they find somewhat different results. For example, for propane and ethane they report rates of 20×10^9 and 18×10^9 in ref 4 as compared to 26 and 21 in ref 2. On the basis of these error bars, one would conclude that the "high-pressure rates" measured for CO_2, ethane, Xe, and propane are actually the same.

(c) In ref 4 a linear dependence of the rate on the pressure for N_2 up to a pressure of 10 bar is reported. There is no evidence for a plateau at this pressure. These data are not presented in Figure 14 of Ref 2.

(d) Schroeder et al.[5] measured the temperature dependence of the isomerization rate in liquid ethane and propane. At low liquid densities, they find that the rates at $T = 298$ K are 3.1×10^{10} and $2.5 \times 10^{10}\ \mathrm{s}^{-1}$, respectively. Assuming an activation energy of 1250 cm^{-1}, this would imply that at $T = 323$ K the rates in liquid ethane and propane would be 5.0×10^{10} and $4.0 \times 10^{10}\ \mathrm{s}^{-1}$, respectively. Both of these rates are substantially higher than the "high pressure" rates reported in ref 2 (2.1 and 2.6 respectively) at $T = 323$ K. This is another indication that Meyer et al. did not reach the true high-pressure limit.

(e) The Arrhenius activation energy obtained from the temperature-dependent rates in low-density liquids, reported in ref 6 is at least 1250 cm^{-1}. Nevertheless, Meyer et al., claim that the barrier in the presence of 10 bar of ethane is 900 cm^{-1}.

(f) The experimental results of ref 5 show that increasing the pressure on liquid ethane leads to a larger activation energy (see Figure 8 of ref 5). This experimental observation was corroborated by our molecular dynamics simulations.[1,7] This contradicts the hypothesis of Meyer et al., that increasing pressure causes a lowering of the barrier. The least that Meyer et al. should do to prove the barrier lowering hypothesis, is to present temperature-dependent rates for the different gases in the 10−20 bar range.

Some further observations are in order. Figure 17 of ref 2, which supposedly disproves the cooling hypothesis is misleading. As can be seen from Figures 4 and 5 of ref 2, the accuracy of the experimental curve is questionable for relative intensities lower than 10^{-2}. For the first two decades, the fit based on the cooling hypothesis is already quite good even though they did not attempt to fine-tune the parameters for the fit. Moreover, the noise in the reported fluorescence decay plot for N_2 at $P = 2$ bar is not negligible (Figure 5 of ref 4). The dashed line presented in Figure 17 does not reflect this noise, so that the comparison presented in Figure 17 is not meaningful. It also does not reflect the system response. Meyer et al. did not convolute an optimized cooling hypothesis theory with the system response and then compare with the measured signal. Neither do they present anywhere, deconvoluted decay curves. Not less disturbing is their attaching a very strong physical meaning to the two-exponential fit for the various decay curves. The only meaningful theoretical exponents are the eigenvalues of the master equation. But Meyer et al. do not report eigenvalues, rather they extract slopes from the simulated curves. We note that in all our computations, we used a barrier height of 3.5 kcal/mol. Our theoretical $k(E)$ is significantly lower (60%) than the experimental one[1] only for energies for which the

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measured lifetime $1/k(E) \geq 700$ ps, this would have very little impact on the high-pressure rate constants.

Finally, Meyer et al. should relate to our recent report on the pressure and wavelength dependence of the isomerization lifetime,[8] in which we show that the wavelength dependence in the presence of 1 bar of Ar is much smaller than for the isolated molecule, in agreement with expectations based on the cooling hypothesis.

In summary, Meyer et al. did not reach the true high-pressure limit. They ignore molecular dynamics simulations and experimental results in high-pressure liquids, which show that increasing pressure increases the barrier height instead of lowering it. Their theoretical analysis attempting to disprove the cooling hypothesis is incomplete and therefore not conclusive. The cooling hypothesis has not been disproved by the experiments of Meyer et al.

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