Reply to Comment by E. Pollak on "Photoisomerization of *trans*-Stilbene in Moderately Compressed Gases: Pressure-Dependent Effective Barriers" (*J. Phys. Chem. A* 1999, *103*, 10528−10529)

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Investigations of the photoisomerization of trans-stilbene in isolated molecules have led to specific rate constants $k(E)$ of the unimolecular reaction that can satisfactorily be reproduced by optimized RRKM modeling.[1] The quality of this modeling is such that thermal averaging should lead to a reliable limiting high-pressure rate constant k_∞ of the unimolecular isomerization in the excited electronic state. Surprisingly, the result is about a factor of 20 smaller than measurements in low-viscosity liquid solvents.[2] This is in striking contrast to the related photoisomerization of diphenylbutadiene where modeled k_∞ and measurements in low-viscosity solvents agree.[3,4] A convincing explanation of the stilbene "anomaly", and of the discrepancy between the stilbene and the diphenylbutadiene system, is still lacking.

Gershinsky and Pollak[5,6] attribute the factor of 20 increase in stilbene to Franck−Condon cooling upon excitation, which is not compensated by collisional heating in isolated molecules, in contrast to the liquid phase where collisional thermalization is supposed to precede isomerization. The discrepancy between the stilbene and diphenylbutadiene systems is not addressed in this work. It is also not realized that extensive Franck−Condon cooling or heating effects in photoexcitation experiments have not been demonstrated before in other molecular systems. On the contrary, other photochemical activation systems could be interpreted satisfactorily under the assumption that the thermal energy of the ground state in absorption together with the photon energy was carried up more or less undistorted into the excited electronic state. Examples of such systems are alkyl-substituted cycloheptatrienes[7] and benzenes,[8] 1,1′-(benzocyclobutylidene),[9] and also NO_2.[10] Why should *trans*-stilbene photoisomerization be governed by Franck−Condon cooling while all of these other systems do not show evidence for such effects?

We have recently done extensive new measurements of *trans*-stilbene photoisomerization in moderately compressed bath gases at pressures where the reaction is in the falloff range of a photochemically induced thermal unimolecular reaction approaching the high-pressure limit.[11,12] The differences between the various bath gases (from He to C_3H_8) are by far more pronounced than has been observed before in any other thermal unimolecular reaction in the falloff range.[13] Although we have not reached the maxima of the pressure dependent rate constants $k(P)$ before a transport-controlled decrease sets in, we can say that the observed $k(P)$ cannot be attributed to the usual falloff curve of a thermal unimolecular reaction. Our interpretation instead suggests a pressure dependence of the effective barrier height $E_0(P)$ and hence a pressure dependence of the effective specific rate constants $k(E,P)$ and the corresponding high-pressure "limiting" rate constant $k_\infty(P)$. The lowering of the effective barrier $E_0(P)$ with increasing pressure then leads to the factor of 20 anomaly of k_∞. In the preceding comment,[14] Pollak questions this conclusion and defends the Franck−Condon cooling hypothesis. However, apart from the more general considerations given above, our measurements from[12] in many aspects are also in conflict with a Franck−Condon cooling mechanism such as explained in the following.

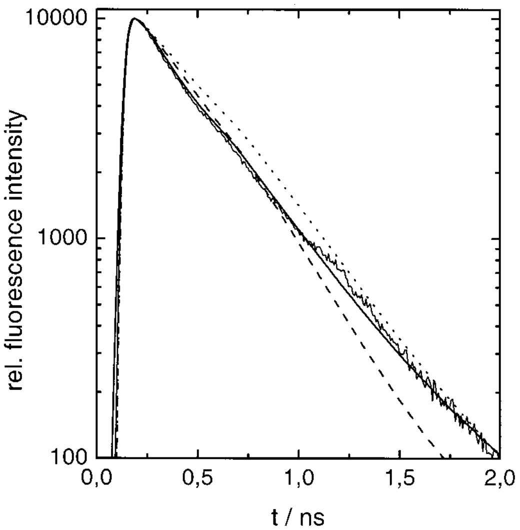

Figure 1. Measured fluorescence decay of *trans*-stilbene in 2 bar of N_2 at 323 K, following excitation at 310.4 nm (noisy line). Comparison with master equation simulations convoluted with instrument response function: (full line) without Franck−Condon cooling, (dashed line) with Franck−Condon cooling to 208 K and average energy transferred per deactivating collision of 100 cm^{-1}, (dotted line) 86 cm^{-1}. For details, see Figure 17 of 12.

Figure 1 (corresponding to Figure 17 from ref 12) illustrates the issue. The measured time dependence of the fluorescence decay is compared with three numerical modeling curves obtained by detailed master equation simulation. The dashed and dotted curves correspond to time dependences obtained assuming Franck-Condon cooling from an initial temperature of 208 K of the excited molecules (optimized fit), using $k(E)$ of isolated stilbene, and employing a collisional energy transfer model with average energies transferred per deactivating collision of 100 and 86 cm^{-1}, respectively. The results clearly differ from the experimental trace. Instead a modeling without Franck−Condon cooling with a pressure dependent $k(E,P)$ agrees with the experiment (full curve in Figure 1): in the first stage, the excited molecules react with a thermal equilibrium population carried up from the ground state and, in the final stage, the depletion of excited states, such as typical in the falloff range of unimolecular reactions, develops and leads to a slower rate. The initial decay within this analysis is determined by the high-pressure rate constant $k_\infty(P)$ convoluted with apparatus response, whereas the latter stage corresponds to the rate constant $k(P)$ of the falloff range.

Measurements of the temperature dependence of the derived $k_\infty(P)$ and of the corresponding barrier heights $E_0(P)$ are consistent with our interpretation. Figures 2 and 3 show Arrhenius plots of $k_\infty(P)$ and the corresponding barrier heights $E_0(P)$ for a series of densities of the bath gas N_2. The results of

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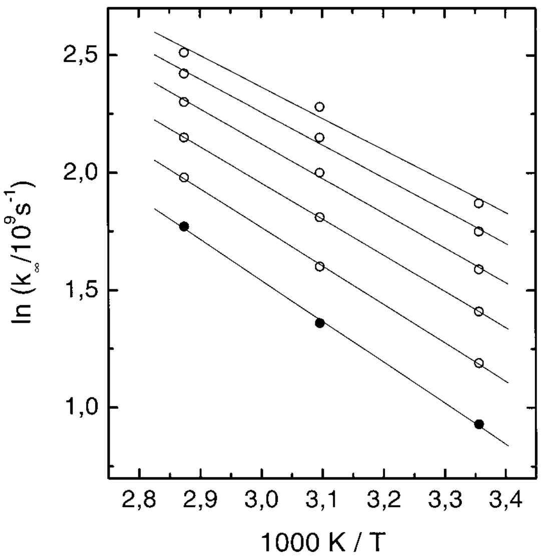

Figure 2. Temperature dependence of high-pressure "limiting" rate constants $k_\infty(P)$ of *trans*-stilbene in N_2 at different bath gas concentrations: (○) from 5×10^{-5} mol cm^{-3} to 2.5×10^{-4} mol cm^{-3} in increments of 5×10^{-5} mol cm^{-3} from bottom to top; (●) values from extrapolation to $k_\infty(P \rightarrow 0)$.

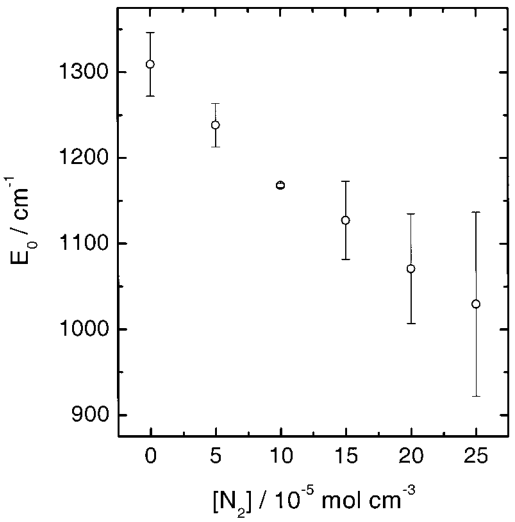

Figure 3. Dependence of effective barrier heights $E_0(P)$ on the bath gas concentration (obtained by simulations of traces such as Figure 1). $E_0(P)$ is not identical with the Arrhenius activation energies of Figure 2.

Figures 2 and 3 have not been published before. One clearly notices a decrease of $E_0(P)$ with increasing bath gas density.

Although we have no explanation why the stilbene system is characterized by such a "labile" reaction barrier, which already at low pressures shows a marked "solvent shift", at least we have an internally consistent interpretation of the available experimental observations. We emphasize that our interpretation of experiments in the fall off range is independent of the extent of reaching the plateau of $k_\infty(P)$ or $k(P)$, although more experiments at pressures above 20 bar would clearly be desirable. Some discrepancies between various earlier experimental studies were due to experimental difficulties such as incomplete analysis of the complete time dependence of the fluorescence decay and other problems. Nevertheless, the general agreement between our data and the earlier measurements from Fleming's[15] and from Hochstrasser's[16] laboratories is satisfactory, such as demonstrated in Figure 6 from ref 12. Because of some experimental inconsistencies, it appears not acceptable to compare arbitrarily chosen single values of $k(P)$, such as done in ref 14.

We conclude by emphasizing that the *trans*-stilbene photoisomerization in moderately compressed bath gases shows unusual pressure and bath gas dependences; see Figures 12 and 14 of 12. These can neither be rationalized by collisional energy transfer properties, such as typically encountered in falloff ranges of thermal unimolecular reactions, nor by collisional energy transfer properties such as observed in unimolecular reactions with chemical or photochemical activation.[13] The Franck–Condon cooling mechanism, which would correspond to a photochemically activated unimolecular reaction, therefore, first can be ruled out on the basis of the observed bath gas dependences of the experimental isomerization rates. Second, we have shown that a detailed master equation simulation of the time dependence of the fluorescence decay is in contrast to the Franck–Condon cooling mechanism while a modeling with pressure dependent effective specific rate constants $k(E,P)$ under all conditions reproduces the experimental results; see Figure 1. Finally, our detailed experimental results for the temperature dependence of the rate constants in the bath gas N_2, such as illustrated in Figures 2 and 3, clearly demonstrate the decrease of the apparent threshold energies $E_0(P)$ with increasing density. This confirms the internal consistency of our interpretation. Temperature dependences of the rate constant in the transport-controlled range in high-pressure liquids should not be compared with the present low-viscosity results, because new effects such as the multidimensionality of the barrier crossing may become relevant.[4] Since Franck-Condon cooling apparently has also not played a role in the series of other photoexcitation systems cited at the beginning of this Comment, we find no argument for its singular presence in the stilbene system. We close by adding that, at this stage, we cannot comment on the recent work from ref 17 alluded to in ref 14, because the data and their analysis have not yet been presented in a sufficiently detailed way.

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