

Picosecond Kinetics of *trans-cis*-Photoisomerisations: From Jet-Cooled Molecules to Compressed Solutions

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The understanding of photoisomerisation reactions involving large amplitude motion is discussed with special emphasis on the merits of systematic studies over wide ranges of physical conditions. It appears that the friction β in such cases is proportional to macroscopic solvent viscosity η , and the original Kramers theory is sufficient to describe the effect of friction in the range from intermediate to strong damping, i.e. from low viscosity fluid to compressed high viscosity liquid solution. This one-dimensional model may be connected to multidimensional unimolecular rate theory to obtain a representation of the density dependence of the rate coefficient down to the thermal collisionless regime. The apparent failure of this approach in the case of *trans*-stilbene can be traced to modifications of the excited state PES by the solvent. This interpretation is consistent over the entire range of physical conditions studied, starting at the jet-cooled isolated molecule and solvent cluster and ending in compressed liquid solution at very high viscosities. It is shown that detailed information about the PES is urgently needed to provide safer ground for a profound understanding of the photoisomerisation dynamics.

1. Introduction

Photoisomerisation reactions in solution involving large amplitude motions often are controlled by a number of different superimposed physical processes whose individual significance may vary as the solvent environment changes. Therefore, a quantitative understanding of such reactions can only be reached, if one succeeds in disentangling them to characterise their specific effect on the photoisomerisation dynamics. A natural way of achieving this goal seems to be a systematic variation of the solvent environment, starting from isolated molecule conditions in a supersonic beam expansion or a collision-free thermal ensemble, and then gradually increasing the complexity of the environment towards common liquid solution conditions. In this manner, the reaction proceeds from a purely intramolecular process via the domain of single collision events or pair interactions in cooled 1:1-solute-solvent van der Waals complexes and the regime of larger clusters with multiple interactions in supercritical fluid solution towards the diffusive regime in liquid solvents. Accordingly, a separation of the individual contributions to the observed dynamics becomes increasingly difficult if not impossible, but as specific processes are expected to govern the reaction in the different regimes, they can be identified and characterised at least to a certain extent by considering the variation of the

photoisomerisation dynamics over the entire range of conditions.

Under collision-free conditions one expects that the photoisomerisation is governed by the intramolecular excited state potential energy surface (PES) and controlled by the excess internal energy above the lowest rovibrational level of the molecule which is determined by the initial optical excitation. If statistical redistribution of this energy over all vibrational modes of the molecule (IVR) after optical excitation is fast compared to photoisomerisation, statistical reaction rate theories may be applied to calculate microcanonical rate coefficients. As for large systems, however, the excited state PES in the reactant well and transition state regions in most cases is not known sufficiently well, one has to resort to fitting procedures to adjust statistical models.

In the low pressure gas phase binary collisions with solvent molecules lead to qualitative changes in the dynamics whose nature depends on the properties of the PES. If the reaction takes place on a PES with an adiabatic barrier, with increasing pressure the photoisomerisation will approach a thermal unimolecular reaction with rate coefficients showing fall-off behaviour as described, e.g., by the Lindemann model. If the PES for the reaction is diabatic with a barrier resulting from a crossing of different electronic states, collisions may influence the diabaticity factor leading to a more complicated overall pressure dependence of the reaction rate. If attractive solute-solvent interactions are sufficiently strong, with increasing pressure one has to consider cluster formation which can lead to significantly enhanced local solvent densities in the vicinity of the reactant. In such cases "static" solvent effects may change the PES of the isolated molecule, which, in principle, one can take into account by using the appropriate potential of mean force. The same interactions can also affect the photoisomerisation dynamics in jet-cooled reactant-solvent clusters. Here, in particular, the dependence on cluster size may contain valuable information concerning the effect that building up a solvation shell has on the reaction.

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Increasing the density further, one approaches the common liquid solution and additional "dynamic" solvent effects gradually gain control of the reaction, i.e. solvent friction starts to slow down the photoisomerisation. With knowledge of the isolated molecule PES and its modification by "static" solvent effects, one can analyse the density and solvent dependence of the friction on photoisomerisation rates and establish its relation to macroscopic solvent viscosity or other physical parameters describing the solvent response to the motion of the solute along the reaction path. If memory effects can be neglected and the Maxwell-Boltzmann distribution of velocities is maintained for the solvent molecules along the reaction path, the photoisomerisation is in the Smoluchowski limit and equivalent to diffusive motion on the potential surface of mean force. In this simplest case the rate coefficient is inversely proportional to the solvent viscosity η .

A reaction that has been widely studied and served as a model system to test a multitude of theoretical models in the different solvent density domains as outlined above is the *cis-trans*-photoisomerisation of diphenylpolyenes, in particular *trans*-stilbene. A number of excellent and comprehensive reviews on these reactions are available, covering the aspects of classical photochemistry [1–3] as well as picosecond dynamics and reaction kinetics [4–7]. The following will be no attempt at yet another one, but rather at an overall picture of our present understanding of the reaction in the different density regimes that, to a large extent, rests on results of high pressure experiments [8–14]. Starting from the photoisomerisation dynamics in the familiar liquid phase, questions arise that call for experiments at lower densities, bridging the gap to the isolated molecule at the other end of the scale.

2. Friction and Effective Photoisomerisation Barrier Height in Liquid Solution

In liquid solution, if the viscosity is sufficiently high for the reaction to be in the so-called high damping limit, the effect of friction on photoisomerisation taking place on an adiabatic S_1 -PES should lead to an expression of the type

$$k_{\text{iso}} \propto \frac{\omega_{\text{B}}}{\beta} \cdot \exp\left(-\frac{E_{0,\text{sol}}}{RT}\right) \quad (1)$$

for the reaction rate coefficient, where $E_{0,\text{sol}}$ is the photoisomerisation barrier height in solution, ω_{B} is the curvature of the parabolic barrier, and β is the friction coefficient divided by an effective reduced moment of inertia for motion along the reaction coordinate. Generally, it is assumed that $\beta \sim \eta$, so that k_{iso} should be inversely proportional to the viscosity of the solvent. Measurements of k_{iso} in the *n*-alkane solvent series for both *trans*-stilbene [15] and *E,E*-1,4-diphenyl-(1,3)-butadiene (DPB) [16] gave, however, a much weaker viscosity dependence $k_{\text{iso}} \propto \eta^{-\alpha}$ with $\alpha \approx \frac{1}{2}$. This observation prompted controversial interpretations, the most prominent of which are (i) the macroscopic

solvent viscosity is an inadequate measure for microscopic friction acting along the reaction path [17], (ii) it is the multidimensional character of the barrier-crossing process that causes the fractional power dependence [18], (iii) as the reaction is very fast, one has to take into account the finite response time of the solvent, i.e. the friction becomes frequency dependent [15, 16, 19], and (iv) the effective barrier height decreases with increasing electronic polarisability and polarity of the solvent [20]. To some extent one can test these hypotheses by studying molecular rotational relaxation and photoisomerisation independently in homologous solvent series [17], but corresponding measurements of the pressure dependence in single solvents give much better control over the physical parameters of the solvent environment. A few examples will serve here to illustrate the main conclusions that one can draw from such experiments.

Fig. 1 shows that the rotational relaxation time τ_{rot} of *trans*-stilbene in compressed liquid ethane and *n*-octane shows a perfectly linear viscosity dependence [21] with a slope that depends on the solvent. One may conclude that the macroscopic solvent viscosity η is proportional to the microscopic friction β_{rot} governing molecular rotational diffusion, while the solute-solvent coupling constant changes with solvent. Equivalent results were obtained for DPB and other compounds [21, 22]. One may, therefore, safely assume that the friction acting along the photoisomerisation reaction path in liquid solution is also proportional to η .

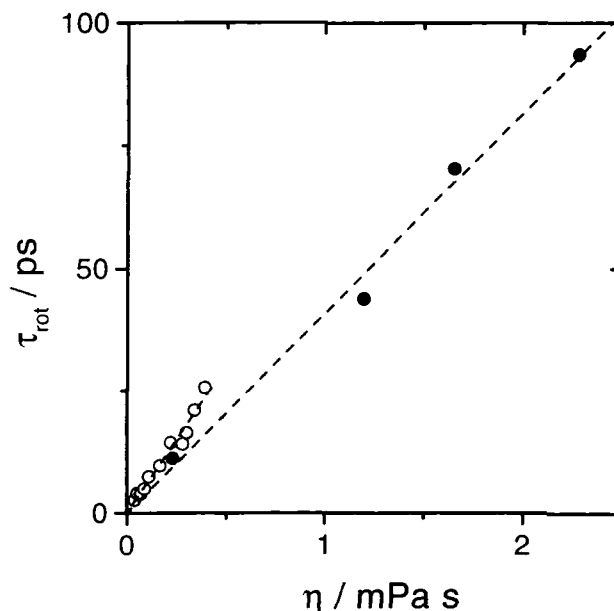


Fig. 1 Rotational relaxation times of *trans*-stilbene in the S_1 -state versus solvent viscosity in compressed liquid ethane (O) and *n*-octane (●) at 298 K

Illustrating results concerning reactive motion, Fig. 2 shows the measured viscosity dependence of rate coefficients for the reaction of DPB in compressed liquid *n*-hexane. Quite different from the results of the solvent series

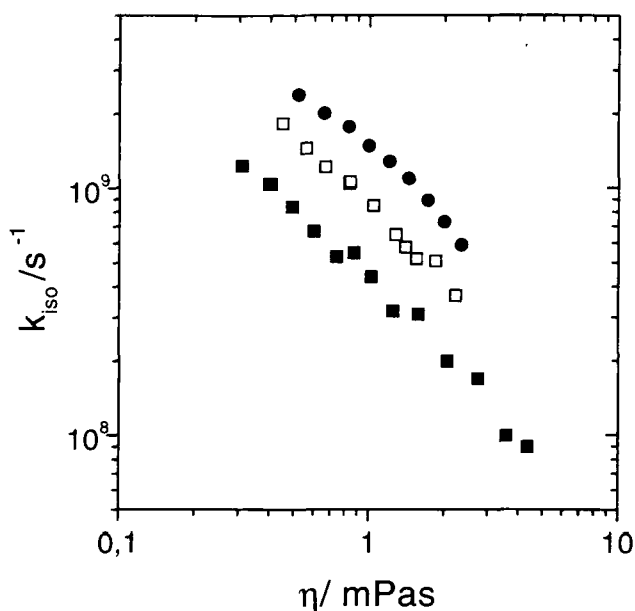


Fig. 2 Photoisomerisation rate coefficients of DPB in compressed liquid *n*-hexane versus solvent viscosity at 298 K (■), 320 K (□), and 340 K (●)

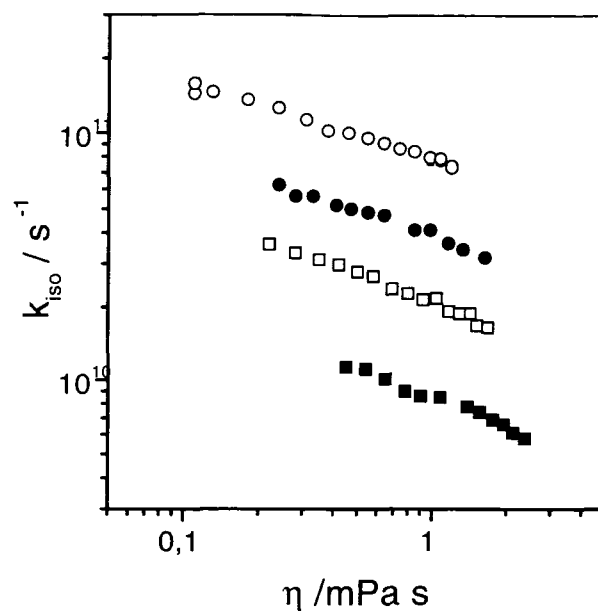


Fig. 3 Photoisomerisation rate coefficients of *trans*-stilbene in compressed liquid and supercritical *n*-pentane versus solvent viscosity at 298 K (■), 340 K (□), 390 K (●), and 450 K (○)

experiments, one finds an excellent linear correlation between k and $1/\eta$ in *n*-alkanes and *n*-alkanols with a solvent-specific slope. Again, an equivalent friction dependence of fast excited state barrier-crossing processes in other molecules like *cis*-stilbene, tetraphenylethylene, and *trans*-1-[1-indanylidene]-indane (“stiff” stilbene) [22–24] is convincing evidence that this behavior seems to be rather the rule than an exception. The time scale of motion along the reaction path extends from several hundred picoseconds in DPB to a couple of hundred femtoseconds in *cis*-stilbene and, still, there is no evidence that the frequency dependence of the friction coefficient plays a significant role. As the entirely similar reaction of *trans*-stilbene in solution occurs typically in a time range between 30 to 300 ps, we conclude that also in this case it is the zero frequency friction that affects the photoisomerisation dynamics, such that β is adequately represented by the macroscopic solvent viscosity. Therefore, the surprising observation that the pressure dependence of k_{iso} for *trans*-stilbene in single liquid *n*-alkanes gives $k_{\text{iso}} \propto \eta^{-\alpha}$ with $\alpha \approx \frac{1}{2}$, as shown in Fig. 3 for *n*-pentane solution, does not indicate a breakdown of the simple friction model in the Smoluchowski limit, as the interpretations (i) and (iii) would suggest.

What then could be the reason? Considering the slopes α of the different $k_{\text{iso}}(\eta)$ -isotherms for *trans*-stilbene in Fig. 3, which are about -0.3 , one has to realise that this, because of the form of $\eta(\rho, T)$, effectively means that the activation energy at constant density ρ decreases with increasing viscosity. This observation is in contrast to that for DPB in *n*-hexane shown in Fig. 2, where the isotherms are parallel with slope -1 . From a detailed analysis of such data [10] one can extract an effective barrier height $E_{0,\text{sol}}$ that decreases linearly with increasing density of the solvent. The order of magnitude of this barrier shift effect is

illustrated in Table 1 by comparing values of $E_{0,\text{sol}}$ for *trans*-stilbene in different solvents. It is interesting to note that in compressed liquid *n*-propanol one almost reaches the regime of barrierless dynamics [14]. This is also evident in the room temperature $k(\eta)$ -isotherm measured in *n*-butanol (Fig. 4), which turns into a linear k vs. $1/\eta$ dependence at higher pressures, indicating that there is no further decrease of the effective barrier height. It has to be stressed again that this unexpected dependence of the reaction rate on solvent viscosity apparently has to be connected with specific properties of the S_1 -PES of *trans*-stilbene, because corresponding measurements for, e.g., DPB or TPE in *n*-alkanes and *n*-alkanols do not exhibit this variation of the apparent activation energy with viscosity.

Table 1 Effective barrier heights $E_{0,\text{sol}}$ for *trans*-stilbene photoisomerisation in the S_1 -state under different experimental conditions

Condition	$E_0/\text{kJ mol}^{-1}$
Jet-cooled isolated molecule (E_0)	15.0
Jet-cooled 1:1-complex with <i>n</i> -hexane	12
Supercritical ethane at $\rho_r \approx 0.2$	8
<i>n</i> -pentane at $\rho_r = 2.62$	6.4
<i>n</i> -pentane at $\rho_r = 3.43$	5.2
<i>n</i> -propanol at $\rho_r = 2.92$	3.9
<i>n</i> -propanol at $\rho_r = 3.72$	1.3

The dependence of k_{iso} on viscosity becomes even more puzzling when the time scale of motion along the reaction coordinate becomes comparable to that of solvent dipole re-orientation around the changing charge distribution within the reacting molecule – in addition to mechanical one also has to consider dielectric friction. Fig. 5 illustrates this

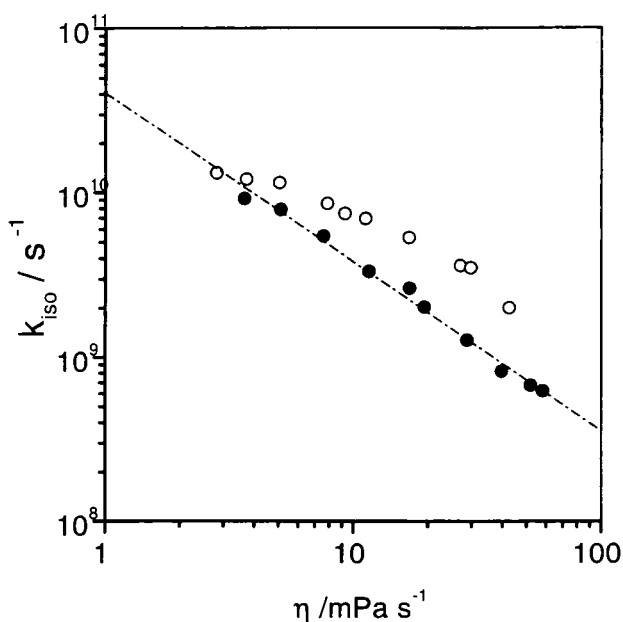


Fig. 4
Photoisomerisation rate coefficients in compressed liquid *n*-butanol at 298 K versus solvent viscosity for DPB (●) and *trans*-stilbene (○). The dashed line corresponds to $k_{\text{iso}} \propto 1/\eta$

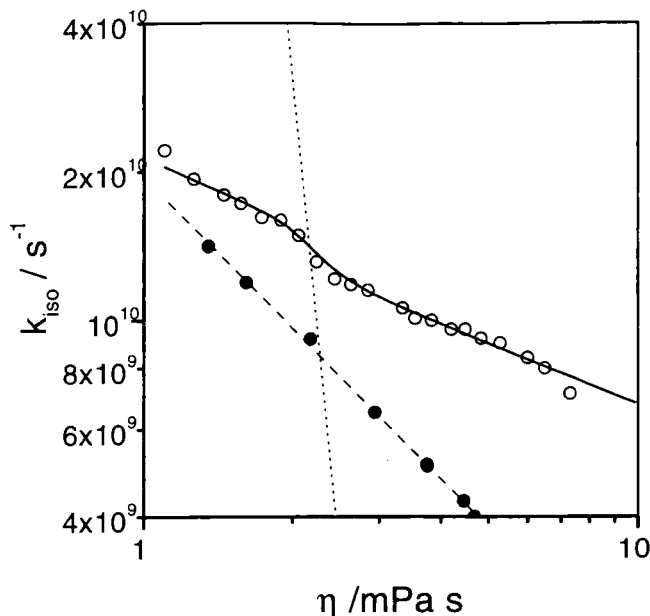


Fig. 5
Photoisomerisation rate coefficients in compressed liquid ethanol at 298 K versus solvent viscosity for DPB (●) and *trans*-stilbene (○). The dashed line corresponds to $k_{\text{iso}} \propto 1/\eta$. The full line corresponds to a model fit using a time-dependent photoisomerisation barrier along the path. The dotted line indicates the variation of local dielectric relaxation required by the model to fit the data (see text)

point for the photoisomerisation of *trans*-stilbene in ethanol at room temperature. The $k(\eta)$ -curve exhibits a turning point which is caused by a crossover of competing solvation and reaction time scales: as the viscosity increases, the dielectric relaxation time of the solvent increases more rapidly than the typical time necessary for barrier crossing [14]. Gradually, the solvation dynamics starts to freeze out on the time scale of reactive motion, the polar barrier is no longer decreased by solvent dipole reorientation, and the rate coefficient drops more rapidly with increasing viscosity. As soon as the solvent dipoles are completely “frozen”, we have the same situation as in a nonpolar solvent, i.e. only the electronic polarisability of the solvent leads to a further decrease of the barrier with increasing solvent density.

In a simplistic way, one can translate this qualitative picture into a kinetic model by introducing a time-dependent barrier height $E_{0,\text{sol}}(t)$:

$$E_{0,\text{sol}} = E_0 + B \cdot \rho_r + B_P \cdot \rho_r \left[1 - \exp\left(-\frac{t}{\tau_D}\right) \right] \quad (2)$$

where B characterises the “static” solvent shift arising from the fast components of the solvent dielectric response (mostly the electronic polarisability) and B_P the corresponding contribution from the slower orientational relaxation of the solvent dipoles in the solvation shell. Both B and B_P are negative and reduce the barrier height with respect to its value E_0 in the isolated molecule. ρ_r is the reduced density of the solvent and τ_D its dielectric relaxation time. This expression obviously leads to a time-dependent rate coefficient $k(t)$:

$$k_{\text{iso}}(t) = k^* \cdot \exp\left(\frac{B_P \cdot \rho_r [1 - \exp(t/\tau_D)]}{RT}\right) \quad (3)$$

where k^* denotes the rate coefficient for barrier crossing along the reaction path in the orientationally nonrelaxed solvent environment. By integrating this expression one can calculate decay curves at different viscosities and extract from these approximate first order decay times that may be compared with the experimental values.

However, if one fits this model to the observed inflection point in the viscosity dependence, one finds that the dielectric relaxation time has to be proportional to the tenth power of the viscosity, i.e. $\tau_D \sim \eta^{10}$ at least! With this assumption we obtain a viscosity dependence of k corresponding to the full line in Fig. 6. Such a rapid change of τ_D with η would imply that certain parts of the frequency spectrum of the solvent dielectric response, which are specifically probed by the barrier-crossing process in the photoisomerisation of *trans*-stilbene, freeze out almost instantaneously at a viscosity near to 2.2 mPa s at 298 K in ethanol – at least in the vicinity of the solvated molecule. Whether such an assumption is realistic, could be tested by MD simulations and measurements of the pressure dependence of the high frequency part (in the Giga- to Terahertz range!) of the response spectrum in liquid alcohol solutions.

The analysis in terms of this simple kinetic barrier shift model shows that a modification of the Smoluchowski model with a density dependent-barrier height suffices to

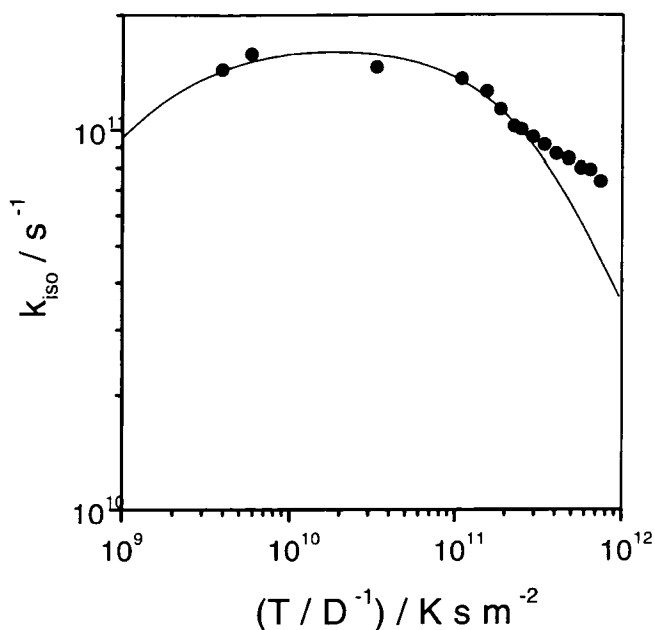


Fig. 6 Photoisomerisation rate coefficient of *trans*-stilbene in compressed supercritical *n*-pentane versus inverse self-diffusion coefficient of the solvent. The full line corresponds to a model fit of Eq. (4) to the data using $E_{0, \text{sol}} = 630 \text{ cm}^{-1}$

describe the observed $k(\eta)$ -dependence including the transition to the barrierless limit. In a more sophisticated and conceptually more satisfactory approach, one could try alternatively to model the dynamics of the reaction as a motion of the system on an at least two-dimensional free energy surface with different dynamic friction along the two degrees of freedom. However, on the basis of kinetic data on the viscosity dependence of the rate coefficient alone, and at the present state of the art of quantum chemical calculations of excited state surfaces of such large molecules, it is not possible to specify such a surface in a reasonable way. This also applies to the interpretation by other dynamic models as, e.g., attributing the observed $k(\eta)$ -dependence for *trans*-stilbene in ethanol to non-equilibrium solvation along the reaction path. Theoretically this situation can be described in terms of a time-dependent dielectric friction coefficient [25]. Fitting the parameters of a corresponding model of the measured rate coefficients, however, also remains arbitrary without detailed knowledge of the PES for the reaction [14].

Therefore, at the present state of our knowledge, it seems adequate to use the *ad hoc* empirical model of solvent-induced PES modifications that have to be tested both by experiments over a wide range of conditions and by MD simulations using tractable model potentials. Additional direct evidence for such solvent effects comes from the recent observation of different wave packet dynamics on the excited PES of *cis*-stilbene in different solvents [26].

One has to keep in mind, however, that another challenging problem is still connected with the friction β that enters

into the rate expression Eq. (1) and its exact relation to the solvent viscosity η . The pressure-dependent measurements of different systems and their analysis leave no doubt that there exists a linear relationship between them, but the constant of proportionality is strongly solvent and solute dependent and is not fully understood. The coupling between internal and overall motion will enter here as well as the particular minimum friction path that the system can find under the given physical conditions. It seems, however, that *trans*-stilbene and other molecules of similar size and complexity are not the proper choice for investigating this question in detail to separate the many interrelated factors.

3. Kramers Turnover Regime and Unimolecular Fall-Off Range

Continually decreasing the friction acting on the barrier crossing process will eventually lead into a regime where the photoisomerisation is controlled by the intramolecular dynamics – no barrier recrossing will occur and the thermal rate coefficient k_{iso} should approach the transition state limit or, equivalently, the high pressure limit of the unimolecular reaction rate. The transition from the diffusive Smoluchowski limit to the high pressure limit was originally described theoretically by Kramers [27] and is known as the Kramers turnover. The Kramers model and its extension, the Grote-Hynes model [28], have been discussed endlessly [6, 29], and there have been many attempts to observe the turnover experimentally. So far, in liquid solution evidence for the turnover has only been found for the thermal boat-chair isomerisation of cyclohexane in compressed CS_2 , where the rate coefficient shows a maximum when the pressure is varied [30]. In contrast, for the photoisomerisation of *trans*-stilbene or DPB it was found at very low viscosities in supercritical solvents like ethane, CO_2 , SF_6 [8, 10, 20, 31] or, recently, *n*-pentane [11], as shown in Fig. 9. If one connects one-dimensional Kramers theory to multi-dimensional unimolecular rate theory which describes the fall-off range from the low pressure regime, where $k_{\text{iso}} = k_0 \rho$, to the high pressure limit, where $k_{\text{iso}} = k_\infty$, one arrives at a simple expression which correctly describes the variation of the rate coefficient from the low density gas phase to the compressed fluid solution if one takes the density dependence of the photoisomerisation barrier into account [8]:

$$k_{\text{iso}} = \frac{k_0 \cdot \rho \cdot k_\infty}{k_0 \cdot \rho + k_\infty} \cdot \left\{ \left[\frac{\beta^2}{4\omega_B^2} + 1 \right]^{1/2} - \frac{\beta}{2\omega_B} \right\}^{-1} \quad (4)$$

A prerequisite for using this formula is, of course, an adequate model of the reacting molecule and collisional energy transfer to calculate k_∞ and $k_0 \rho$ from statistical theories. With the strong collision assumption the rate of energy transfer is basically given by the collision frequency at the respective solvent density (bath gas pressure). The molecular model usually consists of a set of harmonic frequencies for the reactant well and the transition state ob-

tained from quantum chemical calculations and comparison with measurements of the isolated molecule, if such data are available. This is a crucial part of the problem that will be discussed in the next section. For the moment we just suppose that we have a suitable set of frequencies. We then have to use the density-dependent barrier height $E_{0,\text{sol}}$ for *trans*-stilbene, and the isolated molecule barrier height E_0 for DPB, if we want to describe the observed Kramers' turnover, in accordance with the observations in the compressed liquid phase.

The question then is, how this behavior eventually can be linked to that of the isolated molecule. For this purpose one has to measure the photoisomerisation rate at low solvent densities in the gas phase at pressures between about 1 kPa and 1 MPa. Of particular interest is the variation of the barrier height at these low densities, so one extracts k_∞ from the initial part of the measured fluorescence decays [32]. Corresponding results are shown in Fig. 7 for methane, ethane, and *n*-propane solvents as a function of the polarisability of the solvent environment. The starting point at zero pressure corresponds to a thermal ensemble of *trans*-stilbene under collision-free conditions. There are two surprising points to note: (i) k_∞ starts to increase already at very low gas pressures, i.e. the photoisomerisation barrier is already lowered in very low density environment, and (ii) k_∞ finally reaches a plateau value which depends on the particular solvent used. The latter will be an important point in the discussion of the applicability of statistical rate theories in the next section. The observation of an appreciable effect on $E_{0,\text{sol}}$ at very low densities is not yet understood in detail. One probably has to find a way of correctly

taking into account the fact that the local density of solvent around a *trans*-stilbene is higher than the mean density, a fact that is known from investigations of solvent shifts of electronic spectra in supercritical solvents.

4. Photoisomerisation in Jet-Cooled Molecules and Complexes

As much of the above interpretation rests on our understanding of the intramolecular dynamics, measuring the dependence of the barrier-crossing rate on internal energy is crucial for testing molecular models and determining accurately the barrier height E_0 to photoisomerisation in the isolated molecule. From the excitation energy dependence of fluorescence lifetimes of jet-cooled molecules one obtained E_0 and microcanonical rate coefficients $k(E)$ for *trans*-stilbene [33, 34] and DPB [35–37] which could be fitted satisfactorily by RRKM models [38, 39] for both molecules. However, while for DPB the calculated k_∞ agreed closely to k_{iso} as measured in low viscosity solvents [39], k_∞ was almost an order of magnitude smaller than the experimental value for *trans*-stilbene [38]. In terms of the solvent effects discussed above that is no surprise: it would simply reflect the fact that $E_0 > E_{0,\text{sol}}$ for *trans*-stilbene, and $E_0 \approx E_{0,\text{sol}}$ for DPB. But there could be also other reasons behind this huge discrepancy in the case of *trans*-stilbene photoisomerisation. It has been suggested that the degree of IVR may not be the same in both cases [40]: IVR might be incomplete in the isolated molecule and more closely approach a statistical distribution over all vibrational modes in solution due to collision-enhanced relaxation. However, even in solution IVR does not seem to be complete on the time scale of photoisomerisation [26, 41]. Alternatively, if the PES was diabatic in isolated stilbene, the solvent might slow down the passage through the crossing region leading to an enhancement of the reaction rate [42].

Without a reliable PES for the reaction, one cannot reach a final decision with respect to any of these possibilities. As recently stressed by Gershinsky and Pollak [43], a different model for stilbene than the one used at present [44] might change the picture entirely, removing the discrepancy between the rate in solution and in isolated stilbene. But still, a few points emerge from the pressure-dependent studies that support the view that solvent-induced changes of the PES specifically in *trans*-stilbene are responsible for the rate enhancement in solution. Firstly, the effect starts to show at such low densities that it would be difficult to imagine that the solvent would slow down the passage through a potential crossing point on a diabatic PES. Secondly, the effect is specific in the sense that the final plateau of the rate coefficient reached in low viscosity environment depends on the solvent used. If IVR enhancement was the cause behind this effect, the rates should at some pressure eventually become equal in *all* solvents. This clearly is not the case as, e.g., in helium there is no measurable effect on the rate coefficient at all [45]!

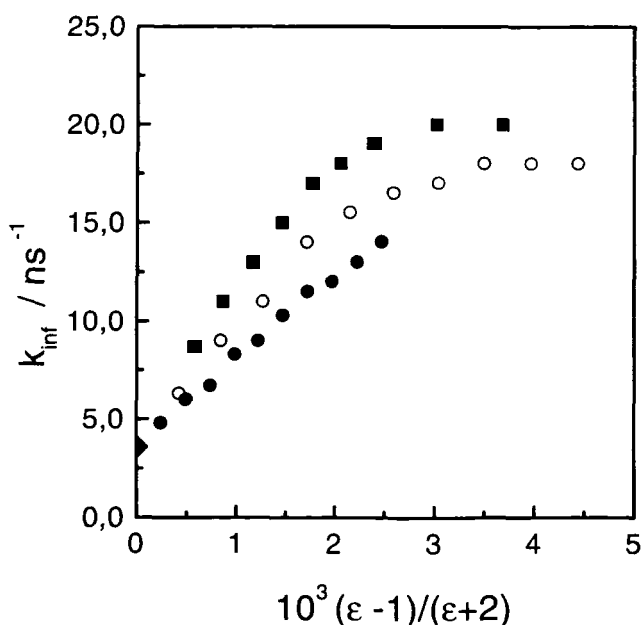


Fig. 7 Solvent polarity dependence of the high pressure limit of the photoisomerisation rate coefficient in methane (●), ethane (○), and *n*-propane (■) at 330 K. The pressure ranges from about 0.01 to 1 MPa. The rate coefficient obtained in a thermal ensemble under collision-free conditions under the vapour pressure of *trans*-stilbene is also included (◆)

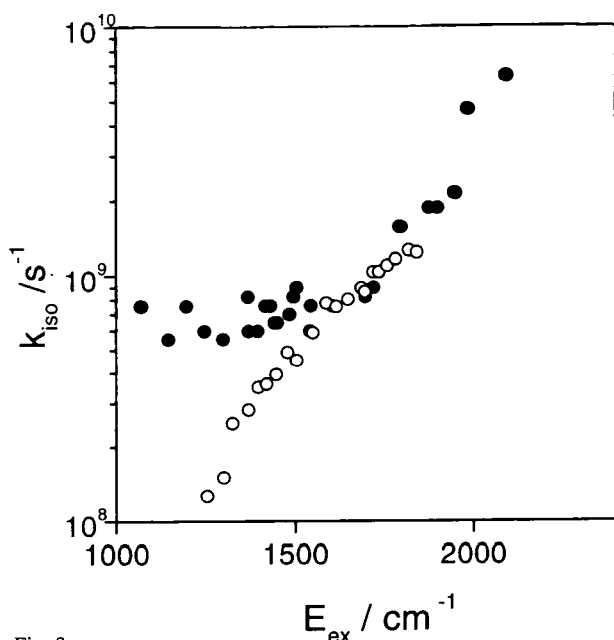


Fig. 8
Excess energy dependence of radiationless decay rate coefficients measured in a jet-cooled stilbene/hexane mixture. (●): 1:1 complex of *trans*-stilbene with *n*-hexane. (○): isolated *trans*-stilbene

Already the presence of a single molecule can have a dramatic effect on the photoisomerisation dynamics as experiments on jet-cooled *trans*-stilbene:*n*-hexane complexes have shown [46, 47]. Fig. 8 shows the enhancement of the microcanonical reaction rate and the lowering of the photoisomerisation barrier in 1:1-complexes. On the basis of such experiments alone, however, one cannot distinguish between the different explanations that have been suggested. The lowering of the threshold visible in Fig. 8 could also be understood in terms of enhanced IVR within the complex due to the presence of additional low frequency van der Waals modes [48]. Again, for DPB no corresponding effect could be found [49]. A quite different example shown in Fig. 9 may illustrate how dramatic such single

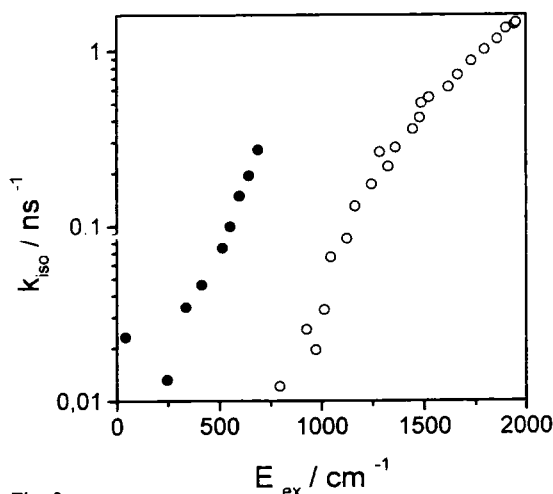


Fig. 9
Excess energy dependence of radiationless decay rate coefficients of jet-cooled DCS (○) and its 1:1 complex with acetonitrile (●)

solvent molecule effects in jet-cooled complexes can be: the microcanonical barrier-crossing rate of the isolated substituted compound *N,N*-dimethylaminocyanostilbene (DCS) is accelerated by more than one order of magnitude at the same internal energy upon complexation with a single acetonitrile molecule [50]. This can only be explained by a significant change in the characteristics of the PES, probably due to intramolecular charge transfer interactions.

5. Conclusions

The friction β in the large amplitude photoisomerisation reactions we have studied is proportional to macroscopic solvent viscosity η , and the original Kramers theory is sufficient to describe the effect of friction in the range from intermediate to strong damping, i.e. from low viscosity fluid to compressed high viscosity liquid solution. We may connect this one-dimensional model to multidimensional unimolecular rate theory to obtain a representation of the density dependence of the rate coefficient down to the thermal collisionless regime. The details of the friction, however, are not fully understood, as the proportionality between β and η is solvent dependent.

The apparent failure of this approach in the case of *trans*-stilbene can be traced to modifications of the excited state PES by the solvent. Although this interpretation is not unique, at present, it seems to be the only one that is consistent over the entire range of physical conditions studied, starting at the jet-cooled isolated molecule and solvent cluster and ending in compressed liquid solution at very high viscosities. This is appealing, but, of course, one could envisage that a combination of different processes could also give a satisfactory representation. It has become apparent that detailed information about the PES is urgently needed to provide safer ground for a profound understanding of the photoisomerisation dynamics. On the other hand, there is a wealth of experimental information that has to be accounted for, not leaving much room for entirely new models.

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