

Photochemical isomerization in the absence of a potential barrier

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Abstract. Different time resolved spectroscopic techniques have been used to investigate the photophysics of the isomerization reaction of 1,1'-diethyl-4,4'-cyanin. The molecule is characterized by a very short excited state lifetime, linear viscosity dependence over a wide viscosity range and no or negative temperature dependence of the reaction rate. The wavelength dependence of the ground state recovery experiment reported earlier (Åkesson *et al* 1986, *Chem. Phys. Lett.* **126** 385) has been shown to be the result of dependence mainly on the analyzing light. We believe that this molecule can be a representative of the barrierless reaction type ($E_0 < 0$) and that the probe wavelength dependence in the GSR experiment is due to the fact that different spectroscopic techniques may probe different physical events in the case of barrierless reactions, and suggest that it is a result of stimulated emission in combination with the resolution of the movement of the population on the excited state surface.

Keywords. Photochemical isomerization; 1,1'-diethyl-4,4'-cyanine; barrierless reactions; time resolved spectroscopy.

1. Introduction

The isomerization reaction of triphenyl methane molecules (TPM) have been considered as typical representatives of the barrierless reaction type ($E_0 < 0$) (Bagchi 1987). In this type of reaction the reactive motion is a twisting of a bulky group through the solvent, and the rate of the reaction is mainly determined by the viscosity of the solvent. From the available experimental results it can, however, be concluded that the photophysics and relaxation dynamics of these molecules are complex. It is therefore desirable to find an alternative to TPM molecules in the study of barrierless reactions.

We have identified the cyanine molecule 1,1'-diethyl-4,4'-cyanine to be a representative of the $E_0 < 0$ case (figure 1). This is based on the very short lifetime in the excited state, the linear viscosity dependence and the observed negative temperature dependence of the reaction rate (figures 2, 3) (Åkesson *et al* 1986). The negative temperature dependence cannot by itself be viewed as evidence for an $E_0 < 0$ case, but comparison between this molecule and similar molecules having a low E_0 gives a more reliable identification of this molecule as a barrierless one.

In order to understand the photophysics of this molecule we have investigated the excited state lifetime with different spectroscopic techniques: two-wavelength pump and probe experiments, excited state absorption decay measurements, pump and probe experiment with subpicosecond pulses and time resolved fluorescence.

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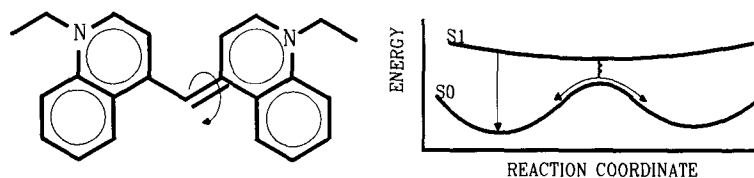


Figure 1. The “barrierless” molecule 1,1'-diethyl-4,4'-cyanine and a schematic picture of the ground state and excited state potential surface.

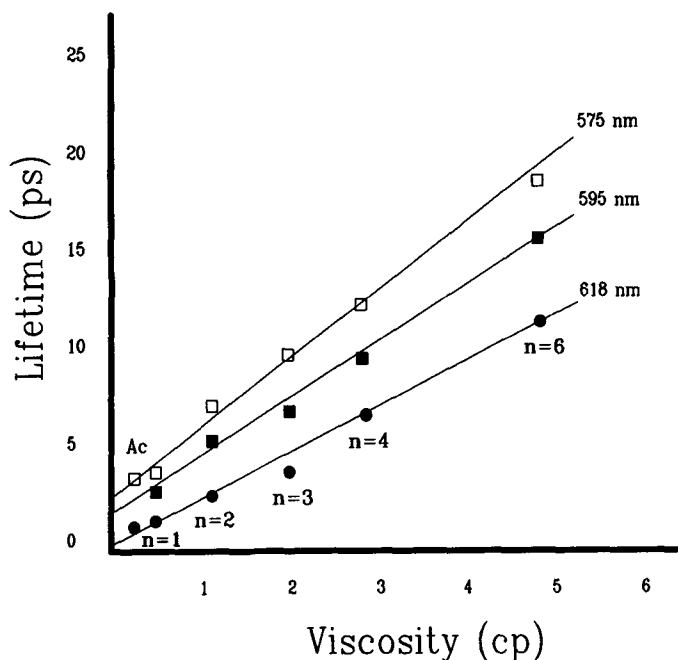


Figure 2. The viscosity dependence of the reaction rate, studied at three different pump and probe wavelengths with sub-picosecond pulses. Solvents are mostly *n*-alcohols except for acetone (AC).

The most general theory of barrierless reactions is the BFO theory (Bagchi *et al* 1983), where the decay of the population on the excited state surface is described by a modified Smoluchowski equation.

$$\frac{\partial P(x, t)}{\partial t} = A(\partial^2 / \partial x^2)[P(x, t)] + B(\partial / \partial x)xP(x, t) - k_{nr}S(x)P(x, t) - k_r P(x, t),$$

where k_{nr} is the radiationless relaxation rate from the excited state surface and $S(X)$ is the sink function representing the probability for radiationless relaxation as a function of reaction coordinate (intramolecular twisting).

The theory treats two different cases of the non-radiative relaxation from the excited state. In one case the relaxation occurs in a very narrow region where the excited state potential surface has its minimum, called a “pinhole sink function”. The other case is a position dependent sink function, where the probability for non-radiative relaxation varies with the intramolecular twisting angle by a Gaussian or a Lorentzian

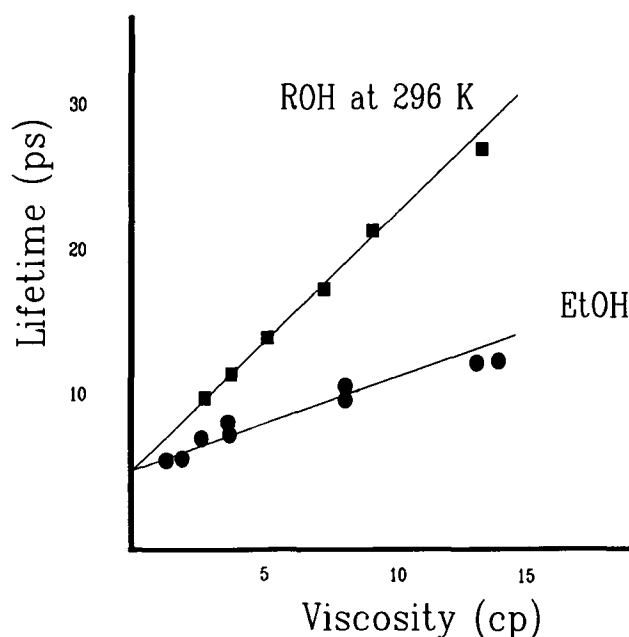


Figure 3. The negative temperature dependence indicates that the molecule can be a representative of the barrierless type. ROH = different *n*-alcohols at room temperature; EtOH = ethanol at different temperatures.

function. In the first case, the solution of the Smoluchowski equation predicts a linear viscosity dependence of the reaction rate due to the fact that the non-radiative relaxation rate depends on how fast the population reaches the sink. For the position dependent sink, the viscosity dependence is expected to be nonlinear. Both the pinhole and the position dependent sink cases predict non-exponential decay functions, especially in the pinhole case. The BFO theory also predicts an excitation wavelength dependence of the reaction rate.

Since experiments reveal a linear viscosity dependence over a wide viscosity region (Åkesson *et al* 1986), the pinhole sink function seems to be a reasonable representation of the radiationless decay.

2. Experimental results

A wavelength dependence of the reaction rate has earlier been reported in a pump and probe experiment (Åkesson *et al* 1986). With separately tuned excitation and probe wavelength we have further investigated this wavelength dependence and found that it is mainly the analyzing light that influences the observed lifetime. With the actual time resolution we cannot observe any of the predicted excitation wavelength dependence on the relaxation rate. Over the studied wavelength region, the isomerization lifetime varied with, approximately, a factor of 2 in the two solvents studies (decanol and hexanol). In the shorter wavelength region (560–590 nm) we observed the longer lifetime, around 20 ps for the HexOH solution and 35 ps for the DecOH solution. Figure 4 shows the results of measurements of the ground state absorption

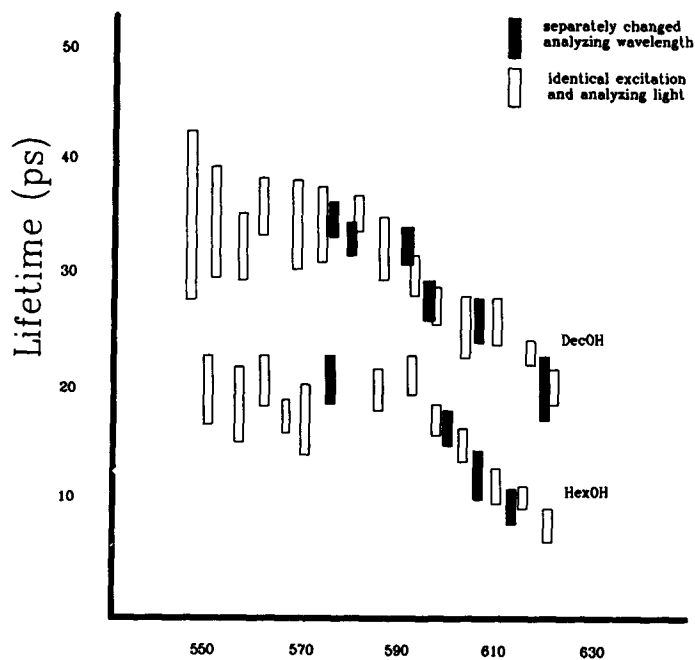


Figure 4. The wavelength dependence of the relaxation rate, measured with pump and probe technique. The observed lifetimes depend on the analyzing wavelength.

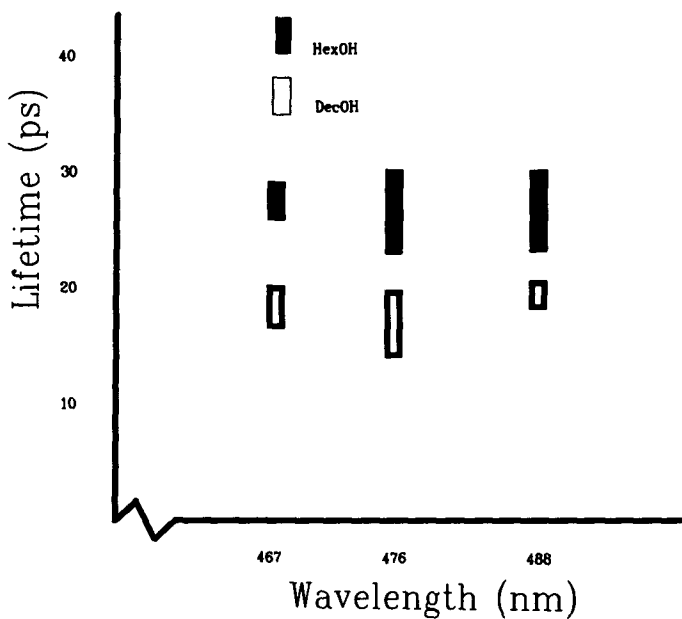


Figure 5. Results of ESA measurements at three different probe wavelengths. The observed lifetimes are in good agreement with the along lifetimes, observed with GSR technique in the blue part of the absorption spectrum.

recovery with identical excitation and probe wavelength and those with independently tuned analyzing light.

The two-wavelength technique also allowed us to measure the excited state decay rate (ESA), probing at 488, 476 and 467 nm, where we found a lifetime which is in good agreement with the lifetime measured with the GSR technique in the blue part of the absorption band (560–590 nm) (see figure 5). In order to further investigate the photophysics of this molecule we measured the fluorescence intensity as a function of time, and found rather complicated behaviour with multiexponential decays and a wavelength dependence of the fluorescence lifetime. The emission was studied in the wavelength region 560 to 750 nm, and the results are displayed in figure 6. The observed decays are all dominated by a fast decay (10–30 ps) which represents more than 90% of the total fluorescence intensity. Due to the fact that the measured lifetimes are close to the time resolution, we do not find it meaningful to extract more than one picosecond lifetime from the observed decays, although the wavelength dependence of the decay displayed in figure 6 may suggest the presence of two picosecond lifetimes with a slightly different spectra. Pump and probe experiments with subpicosecond pulses (~ 400 fs) revealed that the shorter GSR lifetime measured in the red part of the absorption band can be resolved in at least two different lifetimes with one of them being very short (~ 4 and 8 ps, respectively, for the two solvents). Both the shorter and the longer lifetimes clearly depends on the wavelength used in the GSR experiment, and decreases with longer wavelength.

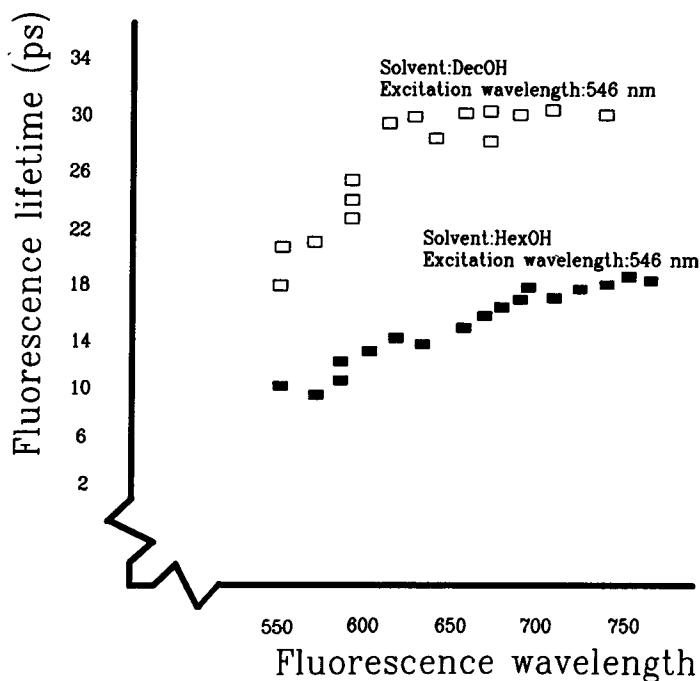


Figure 6. The fluorescence lifetime depends on the emission wavelength, and the longer lifetimes are in agreement with the ESA measurements.

3. Conclusions

In some respect there seem to be satisfactory agreement between theory and experiment, but the excitation wavelength dependence on the relaxation rate has not been experimentally verified, and even more interesting is that the theory cannot explain the analyzing wavelength dependence found for this type of molecules.

We believe that this wavelength dependence in the GSR measurements is due to a combination of stimulated emission and ground state absorption recovery, and the reason for this will follow from the discussion below.

Since there is no high barrier in the excited state for the reactive motion, there is no clear separation of timescales between the reactive motion in the excited state and motions on the rest of the potential surface. Therefore, according to Bagchi *et al* (1989), physical events on the excited state surface can be probed in different ways with different spectroscopic methods. GSR measurements estimate the total recovery times of the initially excited molecules, and contain in general contributions from both excited- and ground-state processes. The fact that GSR and ESA lifetimes agree within experimental error show that the ground-state processes are very fast (sub-ps) and that GSR and ESA measurements provide a measure of the lifetime of the excited-state population.

The wavelength dependence of the fluorescence lifetimes is best explained as an effect of the relaxation along the reaction coordinate; only for long fluorescence wavelength ($\lambda > 650$ nm) is the fluorescence decay reflecting the decay of the excited state population at the point of the sink. For shorter wavelengths the fluorescence decay to a large extent reflects the relaxation through a narrow region of coordinate space, which results in decay components much shorter than that representing decay from the sink.

When GSR measurements are performed at wavelengths overlapping with the fluorescence spectra of the molecule, the measured signal will inevitably contain some contribution from stimulated emission. In the GSR measurement this will show up as a bleaching, and for a "normal" molecule, having a wavelength independent fluorescence lifetime which represents the decay-time of the excited state, this does not disturb the measured GSR lifetimes. However, in the case of barrierless relaxation we have just concluded that the fluorescence decay measured within a narrow wavelength region will contain very fast non-exponential components due to the transient relaxation along the reaction coordinate.

Thus, when GSR measurements on barrierless molecules pick up some contribution from stimulated emission, the observed decays will become non-exponential and contain decay components faster than those measured in the blue part of the spectrum. This explains the probe-wavelength dependence of the relaxation rate displayed in figures 2 and 4. With the better time-resolution offered by the 400 fs pulses we can also show that the contribution from stimulated emission is non-exponential, as predicted by theory.

References

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