The exchange polarization model of photoisomerization: A rationale for profound solvent effects on photoisomerization of trans-stilbene and all-trans retinal

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Abstract

The exchange model of photoisomerization proposed recently by us for S_1 trans-stilbene is further examined and confirmed with a set of new data on trans-stilbene-d_{10}. The model is then generalized (termed the exchange polarization model) in order to account for the known photoisomerization behaviors of all-trans retinal in polar and non-polar solvents. This new model gives a clear picture of how the isomerization reaction proceeds in the excited electronic state. It leads to a working hypothesis for controlling the photoisomerization pathways of polyenes.

Keywords: Time-resolved Raman; Photoisomerization; Stilbene; Retinal

1. Introduction

In a series of picosecond time-resolved Raman spectroscopic investigations of trans-stilbene in the lowest excited singlet state (hereafter abbreviated as S_1 tSB), we showed that the C=C stretch Raman bandwidth is markedly solvent dependent and that this bandwidth has a linear relationship with the rate of photoisomerization both in alkanes [1] and in alcohols [2]. We explained this rather unexpected relationship by introducing a new exchange model that assumes very rapid hoppings of excited tSB between the S_1 state and another nearby electronic state (called the Z state for simplicity). According to this model, the isomerization of S_1 trans-stilbene is described as a process composed of a solvent-induced diabatic hopping from the S_1 to the Z potential surface and a subsequent adiabatic evolution on the Z potential surface to the perpendicular configuration (Fig. 1). As is shown in the following, the C=C stretch Raman bandwidth is proportional to the forward hopping rate W_1 in the exchange model. The isomerization rate is proportional to W_1 multiplied with the branching ratio $W_2/(W_2 + W_3)$ between the back hopping (rate W_2) and the evolution on the Z surface (rate W_3). A linear relationship is thus expected to hold between the solvent dependent C=C stretch Raman bandwidth and the rate of isomerization, if the branching ratio remains constant. A likely candidate for the Z state in this
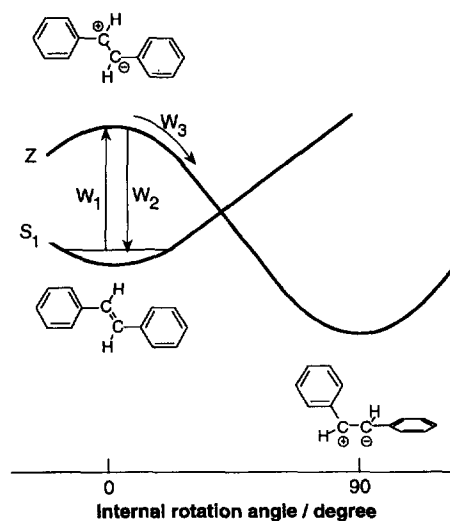
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Fig. 1. The exchange model of vibrational dephasing and photoisomerization of S_1 trans-stilbene.

model is a zwitterionic state having an energy minimum at the perpendicular configuration [3,4]. Such a state is also believed to take part in the excited-state photoprocess of tetraphenylethylene [5].

In the present paper, we first study a set of new data for S_1 trans-stilbene-d_{10} (tSB-d_{10}) that give further support to the exchange model. This reinforcement has been deemed necessary because of the unfortunate band overlapping in the S_1 tSB Raman spectrum; the lower frequency side of the C=C
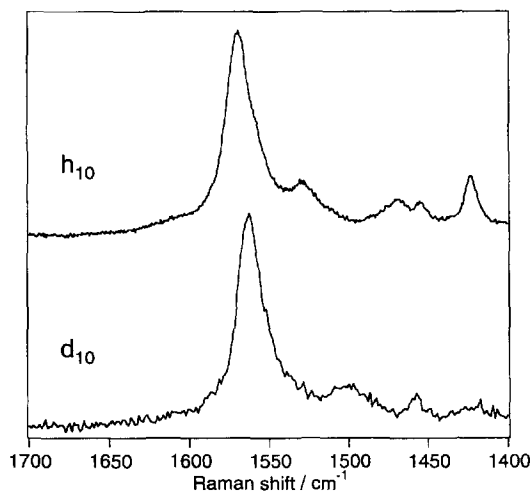
Fig. 2. Raman spectra of S_1 trans-stilbene-h_{10} (upper) and of S_1 trans-stilbene-d_{10} (lower) in hexane.

stretch band is partially overlapped with a phenyl-ring band. On account of this band overlapping, only the higher frequency side of the C=C stretch band was available for the fitting analysis and, as a result, some uncertainties remained in our previous investigations [1,2]. Upon the deuteration of the ring hydrogens, the phenyl-ring mode shifts down to a lower frequency and leaves the C=C stretch band isolated (Fig. 2). The band-shape analysis is therefore better performed for S_1 tSB-d_{10} than for S_1 tSB.

We then try to generalize the exchange model so that it is applicable to molecules other than tSB. This is a more speculative but nevertheless a more attractive part of the present work, because the generalized model, termed the exchange polarization model, gives scope for manipulating the photoisomerization pathways of conjugated polyenes. It is shown that the exchange polarization model explains very well the profound solvent effects known for the photoisomerization of all-trans retinal.

2. Experimental

The transform-limited picosecond time-resolved Raman spectrometer has been described elsewhere [6]. It is capable of giving time-resolved Raman spectra with 2.2 ps time resolution and 3.5 cm^{-1} wavenumber resolution. This optimized time and wavenumber resolution has enabled us to determine accurate Raman band shapes of S_1 tSB after the vibrational cooling process [7] is over (50 ps after the photoexcitation).

The sample of tSB-d_{10} was synthesized according to the literature [8] from benzaldehyde-d_5 and purified by column chromatography. The solvents used in the Raman measurements were commercially obtained (HPLC or Special Reagent Grade) and used as received.

3. The exchange model of vibrational dephasing and photoisomerization of S_1 trans-stilbene

According to the exchange model of vibrational dephasing in S_1 tSB [1,2], the frequency of the C=C stretch vibration

hops to and fro between the two distinct values ω_1 (in the S_1 state) and ω_2 (in the Z state) with the forward ($\omega_1 \to \omega_2$) hopping rate W_1 and the backward ($\omega_2 \to \omega_1$) hopping rate W_2. The position and the shape of the C=C stretch Raman band reflect this exchange dynamics. In a slow modulation limit in which $W_1 < W_2$, $\delta\omega$, where $\delta\omega = \omega_1 - \omega_2$, the band shape is approximated by a Lorentzian with a shift of the peak position $\Delta\Omega$ and an increase of the bandwidth $\Delta\Gamma$ given as follows [9].

$$\Delta\Omega = W_1 W_2 \delta\omega / (\delta\omega^2 + W_2^2) \quad (1)$$

$$\Delta\Gamma = 2W_1 \delta\omega^2 / (\delta\omega^2 + W_2^2) \quad (2)$$

Here, the shift of the peak position $\Delta\Omega$ is taken from the unperturbed frequency ω_1. The increase of the bandwidth $\Delta\Gamma$ represents an extra bandwidth caused by the exchange dephasing that is observed in addition to the other widths including the instrumental width. In the following, we discuss the solvent-dependent changes (and not the values themselves) of the peak position and the bandwidth so that we can extract information on the relationship between $\Delta\Omega$ and $\Delta\Gamma$ without knowing their origins.

Fig. 3 shows the relationship between the observed changes of the peak position and the bandwidth of the C=C stretch Raman band with changing the solvent from hexane to dodecane. The peak positions and the bandwidths were determined with the Lorentzian fitting of the whole C=C stretch Raman band. The plot in Fig. 3 shows a clear linear relationship between the peak position and the bandwidth and hence the same relationship between $\Delta\Omega$ and $\Delta\Gamma$. This linear relationship, which was also obtained for tSB-h_{10} in the previous investigations [1,2], can be explained in terms of Eqs. 1 and 2. By dividing Eq. (1) by Eq. (2), we obtain:

$$\Delta\Omega / \Delta\Gamma = W_2 / 2\delta\omega \quad (3)$$

where $\delta\omega$ is the frequency difference between the S_1 and Z states and is not solvent dependent. Therefore if W_2 is solvent independent, $\Delta\Omega$ is expected to change linearly with $\Delta\Gamma$ and this is actually observed in Fig. 3. In other words, the exper-
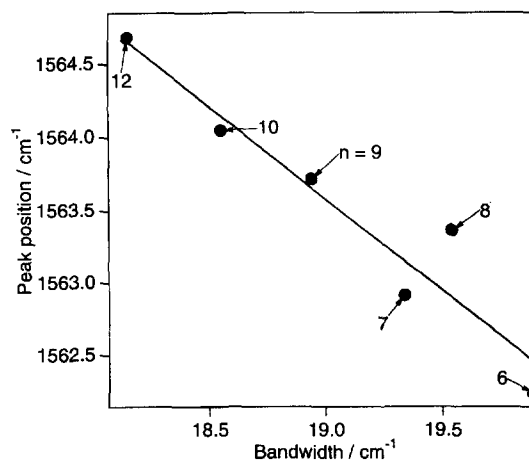

Fig. 3. The relationship between the peak position and the bandwidth of the C=C stretch Raman band of S_1 trans-stilbene-d_{10} in six different alkanes, hexane ($n = 6$) to dodecane ($n = 12$).
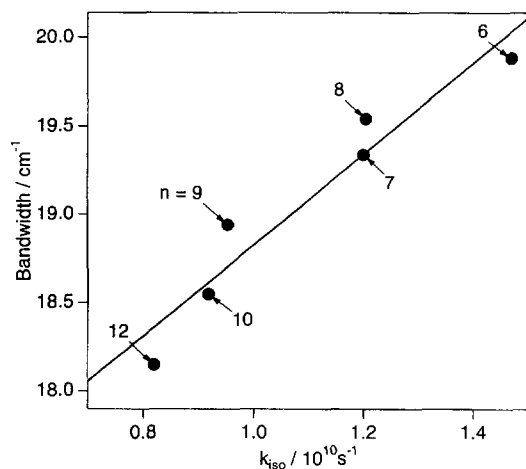
Fig. 4. The relationship between the rate of isomerization and the width of the C=C stretch Raman band of S_1 trans-stilbene-d_{10} in six different alkanes, hexane ($n = 6$) to dodecane ($n = 12$).

imental linear relationship between $\Delta\Omega$ and $\Delta\Gamma$ suggests that W_2 can be considered solvent independent in the framework of the present exchange model.

If W_2 is solvent independent, $\Delta\Gamma$ in Eq. (2) is proportional to W_1. This means that the width of the C=C stretch Raman band changes with the solvent with a linear relationship with (solvent-dependent) W_1. The rate of isomerization $k_{iso} = W_1 W_2 / (W_2 + W_3)$ is also proportional to W_1, if W_3 is solvent independent. It is most likely that the rate W_3 of the evolution on the Z potential surface is intrinsic to tSB and is not strongly dependent on the solvent. If W_3 is assumed to be solvent independent, the exchange model then predicts a linear relationship between the change of the bandwidth $\Delta\Gamma$ and the rate of isomerization. The experimental results shown in Fig. 4 indicate that this linear relationship holds between the C=C stretch bandwidth and the rate of isomerization of S_1 tSB.

Thus, the solvent-dependent changes of the peak position and the bandwidth of the C=C stretch Raman band of S_1 tSB-d_{10} are well explained, as well as those for tSB-h_{10} in our previous investigations [1,2], by using the exchange model. The linear relationship between the width of the C=C stretch Raman band and the rate of isomerization is also satisfactorily interpreted. The slope in the plot in Fig. 4 ($(2.6 \pm 0.4) \times 10^{-10}$) agrees with that for tSB-h_{10} ($(2.8 \pm 0.4) \times 10^{-10}$) within experimental uncertainties, showing that the correlation between the C=C stretch Raman bandwidth and the rate of isomerization is not accidental. This fact gives further support for the exchange model of vibrational dephasing in S_1 tSB and its correlation with the photoisomerization.

It is noted that the time-dependent Raman spectral changes of S_1 tSB reported by us [1] and other groups [10,11] are also well explained by the exchange model, as was already reported in our previous paper [2].

Table 1
Quantum yields of photoisomerization of all-trans retinal by direct irradiation

Solvent	Product			
	13-cis	11-cis	9-cis	7-cis
3-Methylpentane [a]	0.10	–	0.015	–
Hexane [b]	0.10	–	0.02	–
Ethanol [a]	0.22	0.090	0.020	~0.003

[a] $10^{-4} - 10^{-5}$ mol dm^{-3} aerated solution at 298 K [12]. [b] 2×10^{-4} mol dm^{-3} aerated solution at 296 K [13].

4. The exchange polarization model and photoisomerization of all-trans retinal

The exchange model for S_1 tSB can be viewed as a time-domain picture of the solvent-induced polarization of a double bond in an electronically excited singlet state. This picture leads to a generalization of the exchange model called the "exchange polarization model" which is described below. In the exchange polarization model, the solvent-induced polarization is considered as the solvent-induced time-domain exchange between a non-polar or less polar singlet excited state (the S_1 state in the case of trans-stilbene) and a nearby polarized singlet excited state (the Z state). As the polarized state is closer in energy to the non-polar state, the solvent-induced exchange occurs more frequently and the hopping rate to the polarized state becomes higher. If we take an average over a time scale longer than the inverse of the exchange rates, this higher hopping rate corresponds to a more polarized average structure of the double bond. A higher hopping rate to the polarized structure means a higher efficiency of isomerization in the exchange model (Fig. 1). We then come to a thought that a double bond that is more exchange-polarizable in the excited state, for which a nearby polarized state is available for exchange hoppings, is more liable to photoisomerization.

It is known that the photoisomerization of all-trans retinal is highly selective in non-polar hydrocarbon solutions [12,13]. The primary photoproduct is the 13-cis isomer with a small amount of the secondary product 9-cis, and the other cis isomers, 11-cis and 7-cis, are never formed (Table 1). Our recent time-resolved infrared study has shown that the isomerization of all-trans retinal takes place in the excited singlet manifold and not in the excited triplet manifold [14]. This selectivity of the photoisomerization pathways of all-trans-retinal can be explained in terms of the exchange polarization model with an idea of the hyperconjugation effect. The 13,14 and 9,10 double bonds of retinal are distinguishable from the 11,12 and 7,8 double bonds by the existence of a methyl group attached to the 13 and 9 positions.
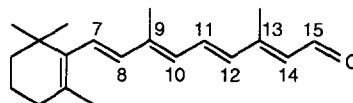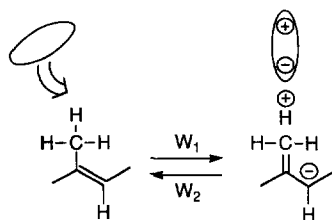
Fig. 5. The exchange polarization model with hyperconjugation of the photoisomerization of all-trans retinal.

If we assume a solvent-induced hyperconjugation effect on the methyl groups at the 13 and 9 positions, in which an inductive interaction between the solvent and the methyl group polarizes the double bonds through hyperconjugation, the exchange polarization model is applicable to the singlet excited state of all-trans-retinal (Fig. 5). It then predicts that the 13,14 and 9,10 double bonds are more liable to isomerization than the 11,12 and 7,8 double bonds for which no hyperconjugation is available. This prediction accords very well with the experimental observation that the 13-cis and 9-cis isomers are selectively formed by the photoisomerization of all-trans retinal. There is another piece of information that supports the present consideration. For the 13-desmethyl analogue of retinal, in which the methyl group at the 13 position is replaced with a hydrogen, the primary photoisomerization product is the 9-cis isomer and not the 13-cis [15]. This result suggests that the existence of a methyl group affects the photoisomerization pathway.

In a polar solvent, ethanol, the photoisomerization of all-trans-retinal is more efficient but is less selective. The total quantum yield of photoisomerization increases from 0.12 to 0.33 on going from hexane to ethanol, and both the 11-cis and the 7-cis isomers are formed in ethanol (Table 1). The exchange polarization model accounts for these trends as well. The solvent polarity should enhance the exchange polarization of S_1 all-trans-retinal by lowering the energy of the polar state and hence increase the efficiency of photoisomerization. The hydrogen-bonding interaction of the carbonyl group may also play a role in actuating the exchange polarization (Fig. 6). It is highly likely that the probability of having this hydrogen-bonding-induced polarization decreases on going from 1 to 5, because more electron migrations have to be involved for longer distances of charge separation. The exchange polarization model of photoisomerization then predicts that the quantum yield decreases in the order of 13-cis, 11-cis, 9-cis, and 7-cis. The observed quantum yields in Table 1 exactly show this trend. The same is true for methanol for which relative quantum yields are reported as 60:30:10:1 for 13-cis:11-cis:9-cis:7-cis [16].

The exchange polarization model has been introduced, based on the exchange model for S_1 tSB, in order to account for the photoisomerization behaviors of all-trans retinal. This model is yet to be substantiated by further experimental verifications. The advantage of this model lies in the fact that it gives a clear picture of how the isomerization reaction pro-
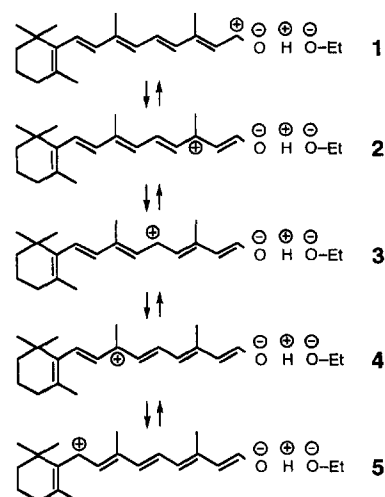

Fig. 6. The hydrogen-bonding-induced exchange polarization of all-trans retinal

ceeds. It is readily acceptable by organic chemists who are familiar with drawing the polarized structure of the reactive intermediates for predicting the reaction pathways and products. Furthermore, the exchange polarization model leads to a working hypothesis for controlling the photoisomerization pathways of polyenes. Introducing an inductive group to a double bond (chemical control) or placing a charge/dipole moment in the vicinity of a double bond (physical control) may selectively accelerate the photoisomerization that takes place around this particular double bond. It is highly likely that both the chemical and physical controls are adopted by nature in bacteriorhodopsin in which the all-trans-retynylidene chromophore photoisomerizes uniquely and efficiently to the 13-cis form.

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