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# Femtosecond laser studies of the *cis*-stilbene photoisomerization reactions

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Femtosecond laser studies have been performed on the photoisomerization reactions of cisstilbene to obtain the most detailed understanding to date of a polyatomic isomerization reaction in a condensed phase environment. These experiments demonstrate that vibrationally hot product molecules are formed within a few hundred femtoseconds of the escape of the molecule from the  $cis^*$  region of the potential energy surface. Although the cis to trans reaction may proceed via a twisted intermediate structure, this intermediate is not intercepted on the  $\sim 150$  fs time scale. The frictional effects on the *cis* to trans reaction coordinate are found to be important and account for the anisotropy of the trans product molecules. Specific experiments presented in detail are the absorption spectrum of electronically excited *cis* molecules (*cis*<sup>\*</sup>); the anisotropy decays for *cis*<sup>\*</sup> showing motion along the reaction coordinate; the detection of the trans-stilbene product using transient fluorescence and transient absorption, confirming that the reaction generates hot product states and that the Franck-Condon modes are largely spectators in the reaction; the anisotropy (alignment) of trans product molecules illustrating the effect of friction coupling overall motion to the reaction coordinate; and a theoretical treatment of three-pulse anisotropy experiments.

## I. INTRODUCTION

Stilbene has proven to be extremely useful as a paradigm of photoisomerization. The photoreactions undergone by stilbene, *cis* and *trans*, involve rearrangements of atoms either in a geometrical isomerization process (*cis* to *trans/trans* to *cis*) or in an electronic rearrangement process to generate 4a,4b-dihydrophenanthrene (*cis* to DHP). This system therefore provides an excellent opportunity to study solvent effects on the various reaction pathways.

The photoinduced *trans* to *cis* reaction of *trans*-stilbene has been studied extensively in recent years.<sup>1-15</sup> Excitation of *trans*-stilbene between 250 and 312 nm results in an excited state population (*trans*\*) which flows over a small barrier of ~3.5 kcal/mol in alkanes<sup>4,6,10</sup> and in the isolated molecule<sup>16,17</sup> to yield ground state *cis*- and *trans*-stilbene in approximately equal amounts.<sup>3,5,18</sup> This barrier crossing process, occurring on time scales of tens to hundreds of picoseconds, has been found to be friction dependent in a manner predicted approximately by Kramers theory for the escape of a harmonically bound particle over a potential barrier.<sup>4,6,7,10,13,15,19</sup>

The isomerization reactions of electronically excited *cis*-stilbene (*cis*\*), on the other hand, occur on time scales of 0.3–2 ps even in relatively high friction liquid environments.<sup>20–27</sup> These results have been interpreted in terms of either unrestricted motion on a barrierless potential surface or motion over a very small barrier ( $\leq 1.2$  kcal/mol).<sup>22,23,26</sup>

Additionally, the *cis*\* population is partitioned between two primary reaction pathways leading to *trans*-stilbene and DHP production, respectively. This is shown schematically in Fig. 1. The fast isomerization reactions of *cis*stilbene provide the opportunity to perform detailed studies of isomerization reactions through investigations of the product molecules as well as through investigations of the excited state dynamics. Information on the reaction coordinate away from the excited state Franck–Condon region may be obtained through investigations of the rise of the product absorptions, the relative alignments of the reactant and product molecules, and the vibrational energy content of the isomerization products.<sup>22,24,25,28,29</sup>

An energy/time flow chart of some of the processes that must be investigated to develop a complete understanding of fast photochemical reactions in condensed phase environments is shown in Fig. 2. In general, the reaction begins with the precursor, in this case, *cis*-stilbene, at thermal equilibrium with the surroundings. The reaction is usually initiated at a time t=0 by a photon. The absorption of this photon leads to Franck-Condon excitation of the reactant molecule, which in this case is the cis\* isomer. The nature of the Franck-Condon absorption and the initial motion of the reactant on the excited state potential energy surface (PES) may be probed using standard resonance Raman or ultrafast pump-probe techniques. The Raman wave function will probe motion on the excited state PES that occurs on time scales less than or equal to the electronic dephasing time. If the excited electronic state is directly reactive, the Raman experiment will probe motion along the reaction coordinate. If, on the other hand, the excited electronic state persists for a substantial length of time due to a flat surface or even a minimum in the PES

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FIG. 1. A schematic drawing of the potential energy surfaces for the  $S_1$  photochemical reactions of stilbene. Approximate branching ratios and quantum yields for the important processes are indicated. In this figure, the ground- and excited-state barrier heights are drawn to scale representing the best available values, as are the relative energies of the ground states of *cis, trans*, and DHP.

along the reaction coordinate, or if there is a nonadiabatic crossing involved in the reaction, the motion probed by the Raman wave function may not divulge key aspects of the reaction coordinate.



FIG. 2. An energy/time flow chart of some of the processes which must be investigated to develop a complete understanding of isomerization reactions in solution.

Initially, the system consists of electronically and vibrationally excited reactant molecules, i.e., an ensemble of molecules possessing most or all of the excess energy placed there by the excitation photon. For cis-stilbene, this excited state persists for 0.3-2 ps, dependent on the solvent. As the molecule proceeds along the reaction path, this energy will be redistributed among the various internal and external degrees of freedom, vibrational, rotational, and translational. With small isolated molecule reactions, there are now many examples of direct measurements of energy partitioning of the excergicity of a reaction into rotational, vibrational, and translational energy contributions. Presumably in condensed phase reactions, the rotational and translational paths as well as nuclear rearrangements resulting in large geometry changes will lead initially to heating of the surroundings. This represents external friction on the reaction coordinate. The vibrational excitation of the reaction product is quite distinct from the external friction and can be examined experimentally for time scales less than the vibrational population relaxation times. In a polyatomic molecule having a sufficiently large number of modes, the internal excitation resulting from relaxation might generate a distribution of product molecules characterized by a single temperature. In this limit, the energy dissipation to internal modes may be usefully referred to as the internal friction. Therefore, for large molecules in the condensed phase, the specification of energy partitioning between internal and external energy pathways can be a useful analogy to the identification of state-to-state reaction paths in isolated molecules. The fast isomerization reactions of cis-stilbene provide an opportunity to attack this energy partitioning problem in a reasonably large molecule in condensed phase environments.

Following the isomerization of *cis*-stilbene to form product molecules, the whole system will relax on a longer time scale to the final state of products at thermal equilibrium with the surroundings. The distinction between "fast" and "slow" population relaxation of the vibrationally excited molecule is made with respect to the time scale for thermal transport to the bulk.  $T_1$  relaxation fast with respect to solvent relaxation will result in local solvent excitation, whereas  $T_1$  relaxation slow with respect to solvent relaxation will not result in local solvent excitation.

A recent study of the *cis*-stilbene to dihydrophenanthrene reaction<sup>24</sup> indicates that ground electronic state DHP is formed very quickly (with a time constant of 1.7  $\pm 0.2$  ps) from *cis*-stilbene in hexadecane excited at 312 nm. These results are consistent with the existence of an intermediate having a lifetime of  $300 \pm 200$  fs. There is no evidence for an intermediate state having a lifetime of more than a few hundred femtoseconds in the *cis* to DHP reaction. DHP appears to be formed vibrationally hot and cools on a time scale of approximately 35 ps. Anisotropy measurements of the *cis* to DHP reaction and the *cis* to *trans* reaction<sup>24,29</sup> have produced an unexpectedly low value for the initial anisotropy of DHP and an unexpectedly high value for the initial anisotropy of *trans*. These results indicate a forced reorientational motion of the transition dipole occurring during the isomerization process.

This paper presents the results of a femtosecond laser study of the *cis* to *trans* reaction of *cis*-stilbene. The experimental results presented in this paper are interpreted, along with the results of previous studies of the *cis* to DHP reaction<sup>24</sup> and *cis*<sup>\*</sup> dynamics<sup>20,22,23</sup> to provide the most detailed picture to date of a photochemical isomerization reaction in the condensed phase.

## **II. EXPERIMENT**

The subpicosecond transient absorption and anisotropy methods used here have been described in detail previously,<sup>22,24,30</sup> with the exception that the 312 nm pump pulse energy in the present experiments was  $3-7 \mu J$ . Briefly, the output of a 20 Hz Nd:YAG laser amplified colliding pulse modelocked (CPM) dye laser was split into two beams. One beam was frequency doubled in a potassium dihydrogen phosphate (KDP) crystal to provide a 312 nm excitation pulse. The polarization of this beam was rotated by a half-wave plate to obtain parallel and perpendicular pump-probe polarization geometries for anisotropy measurements.

For some experiments, other pump wavelengths were used. These additional pump wavelengths were produced by generating continuum in a 1 cm cell of H<sub>2</sub>O, amplifying a slice of the continuum at twice the desired wavelength and frequency doubling the amplified continuum pulses in a beta barium borate (BBO) or KDP crystal as described previously.<sup>24</sup> By using this method,  $\sim 2-3 \mu J$  pulses at 250 and 332 nm were obtained. When pump wavelengths other than 312 nm were used, parallel and perpendicular pump-probe polarization geometries were obtained by using either a Soleil-Babinet compensator or a mica half-wave plate in the probe beam.

The other amplified CPM beam was used to generate probe frequencies via continuum generation in  $H_2O$ . Narrow band slices with a full width at half-maximum (FWHM) of 8–12 nm of the continuum were selected by using a set of interference filters. The probe beam could be amplified and frequency doubled in KDP to obtain probe wavelengths in the ultraviolet.

The time delay was achieved by a computer controlled translation stage in one arm of the experiment. At each time delay, 15–50 laser shots were averaged for a single scan and many scans (typically eight to 48) were averaged until the signal to noise was adequate. When both the pump and the probe pulses were at 312 nm, the instrument response function, modeled as a Gaussian, was approximately 0.3 ps FWHM. When a 312 nm pump pulse was used with other probe wavelengths, the response function was 0.4–0.6 ps FWHM. When a 250 or 332 nm pump pulse was used, the response function was 0.8–1.2 ps FWHM.

Pump-probe experiments in which the fluorescence of the photochemically generated *trans* molecule was detected were carried out using two 312 nm pulses of approximately equal (4  $\mu$ J) energies. In this experiment, the first pulse excited *cis*-stilbene, which then isomerized to form ground electronic state *trans*-stilbene with a quantum yield of 0.35.<sup>31</sup> The second pulse excited the reaction product as

well. The two 312 nm pulses were obtained by frequency doubling both of the amplified CPM beams in KDP. A half-wave plate in one arm of the experiment permitted control of the relative pump and probe polarizations. These pulses were overlapped in the sample at a very small angle and the fluorescence was detected in a direction perpendicular to the direction of propagation of the pump and probe beams by using a photomultiplier tube. An interference filter centered at 350 nm was placed in front of the photomultiplier tube to select a slice of the fluorescence near the peak of trans-stilbene emission and to discriminate against both cis-stilbene fluorescence and scattered light at 312 nm. A photodiode was used to monitor the energy of one of the pulses and to discriminate against large amplitude fluctuations in laser power. Additional fluorescence detection experiments were performed as described above using two pulses of different wavelength ( $\sim 2 \mu J$  at 312 and 250 nm).

The polarization of the beams in the fluorescence experiment must be considered in detail. Because both of the pulses were approximately equal in energy, the fluorescence was at a minimum at time zero and grew in almost symmetrically on either side. When the beams were in the parallel geometry, they were propagating along the y axis, their electric field vectors were along the z axis, and the trans fluorescence was detected along the z axis. In this configuration, the signal is identical before and after time zero assuming equal pump energies. When the polarization geometry was perpendicular, one of the beams was polarized along the x axis. In this configuration, the fluorescence signal will not be symmetric because the pump and probe beams change polarization at time zero. The fluorescence signal is dependent on the polarization x or z of the probe pulse which excites the fluorescence, even for the longest possible delays between the pump and probe pulses.

Time-resolved absorption spectra of the photoisomerization products of *cis*-stilbene were obtained by using a Spex 1681 spectrograph and an intensified dual diode array (Princeton Instruments, model DIDA-512). The experimental arrangement for obtaining time-resolved spectra has been described in detail previously.<sup>24,30,32</sup> For the experiments described in this paper, UV continuum was obtained by frequency doubling a broad slice of the visible continuum in a 0.3 mm KDP crystal. A Schott BG1 filter and a quartz polarization cube were placed after the KDP crystal to pass the doubled continuum and the vertically polarized blue portion of the undoubled continuum. This provided sufficient continuum intensity over the region from 375 to 315 nm. A quartz waveplate was used to rotate the polarization of the 312 nm pump pulse to magic angle (54.7°) with respect to the vertically polarized probe pulse. Spectra were obtained by averaging ten scans of 1500 laser shots at each delay time and repeating four times for a total of 40 scans at each delay time.

The cis-stilbene (Aldrich) used in this study was purified by column chromatography so that it contained less than 0.1% trans-stilbene as detected by high pressure liquid chromatography (HPLC) (trans-stilbene was undetectable in the sample, the accuracy of the instrument sets an upper limit of 0.1%). This is an improvement in the





FIG. 3. The magic angle absorption spectrum of electronically excited *cis*-stilbene produced with a 312 nm excitation pulse. The *cis* fluorescence spectrum on an arbitrary intensity scale is also indicated in the figure.

purity of *cis*-stilbene over the previous study,<sup>22</sup> allowing more accurate measurement of anisotropies in the visible and in the UV, and of the *trans* product absorption in the 320–350 nm region. The samples were generally prepared as approximately 0.15 ml of *cis*-stilbene in 250 ml of the appropriate solvent. When a 332 nm pump pulse was used, the sample was somewhat more concentrated. For the transient absorption measurements, the sample was circulated through an S1-UV quartz cell with a path length of 0.5 or 1.0 mm. For the fluorescence experiments, the sample was circulated through a 2 mm square quartz flow cell polished on four sides.

## **III. RESULTS**

## A. The cis\* absorption spectrum

The absorption spectrum of electronically excited cisstilbene is shown in Fig. 3. The new results concern the region between 600 and 420 nm which complement spectral data reported previously.<sup>22</sup> Two relatively strong absorption peaks are observed at 15 400 and 32 000  $cm^{-1}$ (650 and 312 nm). For both of these peaks,  $\epsilon_{max} = 7000 \pm 2000 \ 1 \ mol^{-1} \ cm^{-1}$  as derived from the reported molar extinction coefficient and quantum yield for the DHP product absorption observed at a 140 ps time delay in the 420-540 nm region.<sup>24,31</sup> The 650 nm peak is consistent with the recent 500 fs spectrum of Rice and Baronavski<sup>27</sup> when it is kept in mind that their spectrum was not obtained for wavelengths longer than 720 nm. Our measurements (current and previously published<sup>22</sup>) demonstrate that this peak extends much further into the near IR. A somewhat weaker absorption peak is observed in the region around 22 200  $cm^{-1}$  (450 nm). This region is distorted in the spectrum shown in Fig. 3 due to competing cis\* gain and absorption signals. For comparison, the fluorescence spectrum of *cis*-stilbene in hexane<sup>23</sup> on an arbitrary intensity scale is also shown in Fig. 3. The net absorption signal measured and reported in this figure is actually the sum of the (negative) gain signal and the (positive) cis\* absorption signal. Thus the pure absorption peak is somewhat

FIG. 4. Magic angle transient absorption and anisotropy of *cis*-stilbene in hexadecane excited at 312 nm and probed at 650 nm. The error bars represent the standard deviation of the mean. The dashed line is a fit of the data to an exponential decay of the anisotropy (see Table I). The dotted-dashed line is the calculated anisotropy for  $r_0=0.36$  and a decay of 82 ps.

larger than indicated in the figure and the dip in the absorption between the 450 and the 312 nm peaks, which coincides with the peak of the  $cis^*$  fluorescence, is probably somewhat less pronounced in the pure absorption spectrum.

Representative anisotropy values for the  $cis^*$  absorption are also given in Fig. 3. As the measured anisotropy is always much larger than -0.2, all of the peaks observed may be attributed to transitions from the *B* state pumped at 312 nm to higher lying states of *A* symmetry. The anisotropy values obtained at 920 and 650 nm indicate the presence of at least two distinct transitions in the red and near IR portions of the spectrum. Thus the pump-probe absorption spectrum of *cis*-stilbene excited at 312 nm demonstrates the presence of at least four electronic states of *A* symmetry lying in the region between 8000 and 40 000 cm<sup>-1</sup> above the  $S_1 B$  state initially excited.

## B. Cis\* population and anisotropy decay

The strong cis\* absorption at 650 nm is not complicated by isomerization product absorptions, cis ground state bleaching signals, or cis\* fluorescence. Thus, this region provides the best opportunity to determine the cis\* lifetime and anisotropy decay. Figure 4 shows the "magic angle"  $[(I_{\parallel} + 2I_{\perp})/3]$ , where  $I_{\parallel}$  and  $I_{\perp}$  are the signals obtained using parallel and perpendicular polarization geometries, respectively] and anisotropy decays  $[r(t) = (I_{\parallel})$  $-I_{\perp}$  )/( $I_{\parallel}$  +2 $I_{\perp}$  )] obtained for *cis*\* in hexadecane by using a 312 nm pump pulse and a 650 nm probe pulse. Magic angle signals in isotropic media at low pump energies are independent of relative orientation in initially isotropic samples. The anisotropy r(t) is equal to the dipole correlation function  $0.4 \langle P_2[\mathbf{C}(0) \cdot \mathbf{C}'(t) | \rangle$ , where  $P_2$  is the second Legendre polynomial, C(0) is the transition dipole pumped by the excitation pulse, and C'(t) is the transition dipole probed at time t. Data were also obtained for cis\* in

TABLE I. Decay times of cis-stilbene transient absorption probed at 650 nm.

Solvent <sup>a</sup>	$ au_{ m iso}$ (ps)	$ au_{\rm rot} \ ({\rm ps})^{\rm b}$	<i>r</i> 0 <sup>b</sup>				
Hexane	0.99 ± 0.03	5.7 ± 2.0	$0.39 \pm 0.01$				
Hexane 330 nm pump	$1.02 \pm 0.04$	4 (+3,-1.5)	$0.39 \pm 0.03$				
Hexadecane	$1.42 \pm 0.03$ $1.50 \pm 0.03$	8.2 ± 1.6	$0.37 \pm 0.01$				
Hexadecane							
250 nm pump	$1.22 \pm 0.05$	$7 \pm 3.0$	$0.33 \pm 0.05$				
Methanol	$0.48 \pm 0.02$	¢	$0.32 \pm 0.04$				
Hexadecane Hexadecane 250 nm pump Methanol	$1.42 \pm 0.03$ $1.50 \pm 0.03$ $1.22 \pm 0.05$ $0.48 \pm 0.02$	$8.2 \pm 1.6$ $7 \pm 3.0$ <sup>c</sup>	$0.37 \pm 0.01$ $0.33 \pm 0.05$ $0.32 \pm 0.04$				

The pump wavelength is 312 nm unless otherwise specified.

<sup>b</sup>Fit assuming that  $r(t) = r_0 \exp(-t/\tau_{rot})$ . This functional form does a reasonably good job of modeling the data (see Fig. 4).

The signal to noise of the data is too poor and the lifetime of *cis*<sup>\*</sup> in methanol is too short to permit a determination of the anisotropy decay function for *cis*<sup>\*</sup>.

hexane and methanol following 312 nm excitation, cis\* in hexane following 332 nm excitation, and cis\* in hexadecane following 250 nm excitation. The decay times determined from a least squares fit to the data are summarized in Table I. The decay times obtained in hexane and hexadecane are consistent with those reported previously.<sup>22,23</sup> The lifetime reported here for *cis*-stilbene in hexadecane is somewhat shorter than that reported previously for a 650 nm probe wavelength, but consistent with that reported for a 350 nm probe wavelength; it is also consistent with Ref. 26. The difference is probably attributable to trans impurity in the previous measurement. The difference between the two measurements reported in Table I is probably also due to the difficulty in accounting for the small trans impurity signal which is still present. There is a small difference ( $\sim 300$  fs or 16%) between the decay time measured following excitation at 312 nm and that measured following excitation at 250 nm. The decay time in hexane is insensitive to an increase in the pump wavelength to 332 nm. The decay of cis\* in methanol is found to be 0.48 ps, much faster than that determined for cis-stilbene in alkanes of comparable viscosity<sup>22</sup> and only a little slower than the 0.32 ps decay of the isolated cis\* molecule.<sup>20</sup> In both of the alkane solvents, the cis\* anisotropy decay is found to be much faster than the anisotropy decay of trans-stilbene in the same solvent [indicated in Fig. 4 (see also Table I)]. This is probably due to motion along the reaction coordinate rather than a large increase in the rotational diffusion of cis- over trans-stilbene and will be discussed in greater detail below.

# C. UV transient absorption kinetics of the *cis* to *trans* and *cis* to DHP isomerization reactions

Magic angle transient absorption decay curves for samples consisting initially of *cis*-stilbene in hexadecane are shown in Fig. 5 for a pump wavelength of 312 nm and probe wavelengths of 312 and 330 nm. The anisotropy data are also shown in this figure. Similar results were obtained for *cis* in hexane and methanol. The 312 nm pump, 312 nm probe curves consist of a coherent spike at  $t_0$  on top of a net *cis*<sup>\*</sup> absorption signal which is canceled in part by a bleach-



FIG. 5. Magic angle transient absorption and anisotropy of *cis*-stilbene in hexadecane excited at 312 nm and probed at 312 and 330 nm.

ing of the ground state *cis* absorption. The *cis*<sup>\*</sup> absorption decays in  $\sim 0.5-1.5$  ps to a signal consisting of residual *cis*-stilbene bleaching, DHP absorption, and *trans*-stilbene absorption. This signal increases slightly between 2 and 10 ps in all three solvents and decays slightly with a 30 ps time constant in hexane and hexadecane to a constant value at longer times. The transient absorption signal was obtained for time delays as long as 140 ps.

The measured anisotropy starts high due to the high anisotropy of the coherent spike and decays very quickly to a low value corresponding to a weighted average of the  $cis^*$ absorption and the ground state cis bleaching signals. The anisotropy then rises to a value which is a weighted average of the DHP anisotropy, the *trans* anisotropy, and the residual cis bleaching anisotropy, and decays approximately exponentially with a rotational correlation time characteristic of *trans*-stilbene in each solvent.

For a probe wavelength of 330 nm, the *cis* bleaching signal is very small so the signals are somewhat simpler. The data obtained using 330 nm are shown on a logarithmic time scale in Fig. 6. The *cis*\* absorption signal decays with a characteristic time of 1.0 (hexane), 1.3 (hexadecane), or 0.5 ps (methanol) to a longer-lived signal corresponding to absorption by *trans*-stilbene and DHP. The decay curves obtained in alkane solvents are modeled fairly well when the data are fit to the functional form

$$I(t) = A_{c*} \exp(-t/\tau_c) + [1 - \exp(-t/\tau_c)]$$
$$\times [\Delta A \exp(-t/\tau_v) + A_{eq}], \qquad (1)$$



FIG. 6. Magic angle transient absorption of *cis*-stilbene in (a) hexadecane; (b) hexane; and (c) methanol pumped at 312 nm and probed at 330 nm. Note the logarithmic time scale.



FIG. 7. Magic angle absorption spectra of the *cis*-stilbene photoproducts produced following excitation at 312 nm.



FIG. 8. The 50 ps spectrum multiplied by a scaling factor and compared with the difference spectrum (----) calculated using the *cis* and *trans* absorption spectra measured in hexane and the DHP (----) spectrum digitized from the data in Fig. 4 of Ref. 31.

where  $\tau_c$  is the lifetime of *cis*\*,  $A_{c*}$  is the absorbance of *cis*\*,  $A_{eq}$  is the equilibrium photoproduct absorption, and  $\Delta A$  is the early time hot product absorbance. The product absorption signal decays with a characteristic time of  $\tau_v$  = 15.5 (hexane), 23.5 (hexadecane), or 17.5 ps (methanol) to a small but positive long term absorption. This longer time scale decay is attributed to the vibrational cooling of the product molecules. The data obtained in methanol exhibit a distinctly nonexponential decay and so are not modeled well by the functional form given in Eq. (1). There is no reason to suppose that the decays in alkane solvents are truly exponential either.

The anisotropy obtained at 330 nm (Fig. 5) starts at  $0.11\pm0.01$  and rises to a value which is a weighted average of the *trans*-stilbene and DHP anisotropies and decays approximately exponentially with a time constant for rotational diffusion of *trans*-stilbene characteristic of the solvent.

# D. Time-resolved absorption spectra of the photoisomerization products of *cis*-stilbene

Time-resolved absorption spectra of the photoisomerization products of *cis*-stilbene in hexane are shown in Fig. 7 for time delays of 6, 15, and 50 ps following excitation by a 312 nm pulse. These spectra are consistent with the kinetics measurements reported in the previous section and in Ref. 28, although the 6 ps spectrum shown in Fig. 12 indicates a significantly larger absorbance change at longer wavelengths than was estimated based on measurements at 320, 330, 335, and 345 nm.

The expected equilibrium ground state photoproduct absorption is compared with the 50 ps spectrum of the *cis* photoproducts in Fig. 8. The ground state spectrum shown in this figure was calculated from equilibrium spectra of *cis*-stilbene and *trans*-stilbene obtained in hexane on a stan-

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dard UV-visible spectrophotometer and the spectrum of DHP digitized from Fig. 4 of Ref. 31. The change in absorbance is given by

$$\Delta OD(\lambda) \propto \phi_{CT} \epsilon_T(\lambda) + \phi_{CD} \epsilon_D(\lambda) - (\phi_{CT} + \phi_{CD}) \epsilon_C(\lambda),$$
(2)

where the  $\phi_{CP}$ 's are the quantum yields for production of *trans*-stilbene and DHP, respectively, and the  $e(\lambda)$ 's are the molar extinction coefficients for *trans*, DHP, and *cis* as a function of wavelength.

In addition, the equilibrium spectrum of *trans*-stilbene was obtained using the femtosecond laser system used to obtain the *cis* photoproduct spectra. For this measurement, the pump pulse was blocked, the reference consisted of hexane in a 1 mm quartz cell, and the signal consisted of *trans*-stilbene dissolved in hexane in a 1 mm quartz cell. This measurement was used to calibrate the wavelength scale of the transient absorption spectrophotometer and to determine the zero baseline for this experimental apparatus.

These results demonstrate that vibrationally equilibrated (room temperature) *trans, cis,* and DHP product molecules are observed within 50 ps of the excitation of the *cis* molecule. The results shown in Fig. 8 are entirely consistent with the known extinction coefficients and reported quantum yields for the *trans*-stilbene and DHP photoproducts. However, the analysis shown in Fig. 8 is not very sensitive to the photoproduct quantum yields.

# E. Fluorescence detected *trans*-stilbene population rise and anisotropy

As discussed above, the UV absorption bands of cisand trans-stilbene and DHP are strongly overlapping, making it difficult to perform a simple transient absorption study of the cis to trans isomerization reaction such as has been performed for the cis to DHP reaction.<sup>24</sup> For each probe wavelength between 350 and 312 nm, differing amounts of trans absorption, DHP absorption, and cis bleaching must be taken into account. In order to avoid the interference of DHP absorption and cis bleaching, we have performed a fluorescence experiment as described above to detect the trans-stilbene isomerization product. A similar experiment was performed several years ago to study the cis to trans isomerization reaction in solution using 20 ps resolution,<sup>33</sup> where no time evolution was observed. The 300 fs time resolution of our instrument results in a significant improvement over the previous measurement. More recently, fluorescence detection has been used to study the cis to trans isomerization reaction of stilbene in rare gas clusters.34

The *trans*-stilbene fluorescence signal for a sample consisting initially of *cis*-stilbene in hexadecane is shown in Fig. 9 for the pump and probe polarization directions discussed previously. The rise of the fluorescence signal shown here is much slower than our instrument response function of approximately 300 fs. The fluorescence rise curves for *trans*-stilbene produced from *cis*-stilbene in hexadecane and several other solvents are compared in Fig. 10. The data in this figure are presented in the form of



FIG. 9. Time-integrated *trans* fluorescence yield curves as a function of the delay time between pumping *cis* and pumping *trans* obtained from a sample of *cis*-stilbene pumped and probed at 312 nm. Negative times in this figure only indicate the change in the designation of the two nearly identical 312 nm pulses as pump and probe. The solid curves are plotted against the upper time scale, while the dashed curves are plotted against the lower time scale. The designations ZZ, ZX, and XZ indicate the polarizations of the pump and probe beams.

"pseudomagic angle" curves obtained by adding the parallel curve to twice the perpendicular curve and dividing by three. This eliminates much *but not all* of the orientation dependence from the data. As seen in Fig. 10, the initial fluorescence rise time is not significantly dependent on whether the solvent is hexane, hexadecane, or isopropanol. However, the rise time is significantly faster in methanol.

The results shown in Figs. 9 and 10 may be fit quite well to a function of the form



FIG. 10. Pseudomagic angle fluorescence yield curves obtained in methanol (+-+-+), isopropanol  $(\cdots)$ , and hexane (---) compared with the curves obtained in hexadecane (solid line).

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$$I_{abc}(t) = \{A_1[1 - \exp(-t/\tau_1)] + A_2[1 - \exp(-t/\tau_2)]\}G_{abc}(t),$$
(3)

where  $G_{abc}(t)$  is a polarization dependent factor to be discussed later. The values of  $\tau_1$  and  $\tau_2$  which yield the best fit to the data are approximately  $\tau_1 = 6 \pm 0.5$  ps and  $\tau_2 = 20 \pm 5$  ps in hexane, hexadecane, and isopropanol and  $\tau_1 = 1.4$  ps and  $\tau_2 = 11.5$  ps in methanol. The data are not modeled well by a single exponential rise.

The use of Eq. (3) to model this data amounts to assuming that the trans\* nonradiative relaxation rate is independent of the delay time, the trans ground state absorption coefficient at 312 nm is independent of the delay time, and the formation of the trans ground state population is biexponential. However, it is not reasonable to assume that the *trans*-stilbene coming either directly from cis-stilbene or from an intermediate bottleneck state is produced vibrationally cold (see Fig. 7). The vibrational energy content of the trans-stilbene product is important because the trans\* nonradiative relaxation rate is known to be strongly dependent on temperature.<sup>4,9,10,18</sup> A more realistic model for the fluorescence rise time and a detailed discussion of the evidence for and against the presence of a bottleneck state in the cis to trans reaction pathway will be presented later in this paper.

In addition to information on the appearance of *trans*stilbene, the data shown in Fig. 9 also contain information on the average angle between the reactant *cis* (C) and product *trans* (T) transition dipole directions through its dependence on  $\langle P_2(\mathbf{C}\cdot\mathbf{T})\rangle$ . The value for this correlation function at time zero is not directly obtainable from the data, but requires a model for the fluorescence intensity as a function of delay time. Further discussion of the anisotropy measurements and the models used to interpret them are postponed until a later section.

## F. Excitation wavelength dependence of the timeresolved absorption and *trans*-stilbene fluorescence rise measurements

The UV transient absorption and trans fluorescence results presented above indicate a significant amount of vibrational excitation in the trans product molecules produced from cis-stilbene initially excited at 312 nm. In order to investigate further the partitioning of the excess energy of the cis\* to trans reaction into internal and external pathways, we have performed a series of measurements using 250 and 332 nm excitation pulses. The use of a 250 nm pump pulse introduces an extra  $8000 \text{ cm}^{-1}$ , or nearly 24% more excess energy, into the stilbene molecule. The 332 nm pump pulse introduces  $2000 \text{ cm}^{-1}$  less energy into the system. Differences or similarities between the absorption and fluorescence rise measurements obtained with this range of excitation wavelengths may help distinguish between internal and external pathways for energy disposal, and identify the relevant time scales for these processes.

Transient absorption data were obtained for *cis*stilbene in hexadecane using 250 nm pump and 650, 460, 345, 330, and 312 nm probe pulses. The data obtained at



FIG. 11. Pseudomagic angle fluorescence yield curves obtained with 312 nm (dotted line) and 250 nm pump pulses (solid line). The probe pulse was 312 nm in each case. The inset contains the 312 nm pump, 250 nm probe signal fitted to a 1.5 ps exponential rise.

650 nm were discussed above (see Table I). The data obtained at 460 nm, near the peak of the  $S_0 \rightarrow S_1$  DHP product absorption, indicate that the quantum yield for DHP production at 250 nm is essentially the same as at 312 nm. A comparison of the relative *cis\** and DHP absorption intensities indicate that the DHP quantum yield has decreased no more than 15% from its value at 312 nm.

A direct comparison of the UV transient absorption data obtained by using 312 and 250 nm excitation wavelengths indicate a slight change in the quantum yields for DHP and/or trans-stilbene formation, but no more than a  $\sim 15\%$  net decrease in photoproduct absorption. The long time behavior is remarkably similar for both pump wavelengths. The only significant difference is in the short time dynamics. Whereas the data obtained by using a 312 nm pump pulse are well fit using the functional form of Eq. (1) and a cis\* lifetime  $\tau_c$  close to the value obtained using a 650 nm probe (1.3 ps at 330 nm vs 1.4-1.5 ps at 650 nm), this is not the case for the data obtained using a 250 nm pump pulse. When these data are fit using the functional form of Eq. (1), it is necessary to use a value for  $\tau_c$  that is much less than the value obtained using a 650 nm probe pulse. For the 330 nm probe data, the value of  $\tau_c$  necessary to model the data using Eq. (1) is 0.74 ps compared with the value of 1.22 ps obtained from the 650 nm absorption kinetics. A probable explanation for the differences observed using 312 and 250 nm excitation and the implications of these results on the understanding of energy disposal in the photochemical reactions of cis-stilbene will be discussed in a later section.

The fluorescence detected *trans*-stilbene rise data obtained using a 250 nm pump pulse and a 312 nm probe pulse are shown in Fig. 11 and compared with the results obtained by using two identical 312 nm pulses. The data are not symmetric because much less *trans* fluorescence is



FIG. 12. Photoproduct absorption spectra obtained at 6 (dashed line) and 50 ps (solid line) following excitation of *cis*-stilbene at 332 nm. The dotted lines are the results obtained following excitation at 312 nm (see Fig. 7 and Ref. 56). The inset contains the 6 ps spectrum, corrected for the scattering of the 332 nm pump beam, and the calculated difference spectrum for a vibrational population distribution equivalent to a temperature of 725 K.

excited by a 250 nm probe pulse than by a 312 nm probe pulse simply due to the relative extinction coefficients of the *trans* absorption at the two wavelengths. One important conclusion to be drawn from these data is that the kinetics of the rise of the fluorescent population of *trans*stilbene product molecules excited by a 312 nm probe pulse is relatively insensitive to the wavelength used to excite the initial *cis*-stilbene reactant molecule. Note, however, that the rise of the *trans*-stilbene fluorescence excited by a 312 nm pulse following the excitation of *cis*-stilbene by a 312 nm pulse is well modeled by a single exponential with a 1.5 ps time constant.

The hot product absorption has also been investigated using a 332 nm excitation pulse. Transient absorption data was obtained for *cis*-stilbene in hexane probed at 650 and 335 nm. The 650 nm data were discussed above and summarized in Table I. The 335 nm probe data are well modeled by Eq. (1) with  $\tau_c = 1.02$  ps and  $\tau_v = 13$  ps. There is no evidence for a delay between the decay of *cis*\* and the appearance of the product absorption. The absorption spectrum of the product molecules obtained 6 and 50 ps following excitation by a 332 nm pulse are shown in Fig. 12, compared with the data obtained following excitation by a 312 nm pulse. The 6 ps spectrum appears to be much colder following excitation at 332 nm.

## IV. DISCUSSION

# A. Evidence for and against the presence of an intermediate in the *cis* to *trans* reaction excited at 312 nm

The presence of a kinetic intermediate in the *cis* $\leftrightarrow$ *trans* photoisomerization of stilbene and stilbene derivatives has long been postulated based on both experimental and theoretical considerations.<sup>35,36</sup> The nearly equal quantum yield for *cis*- and *trans*-stilbene following the excitation of either the *cis* or the *trans* isomer was the initial observation which led to the proposal that a common intermediate, called the phantom state, was reached in both the *cis* to *trans* and *trans* to *cis* reactions.<sup>35</sup> If the branching ratios listed in Fig. 1, and inferred from the measured product quantum yields, and the kinetic scheme implied by this diagram are approximately correct, it is difficult to envision a process not involving a common bottleneck state that would give rise to the observed *cis* and *trans* isomerization and recovery yields.

Several theoretical calculations have been performed to characterize this postulated intermediate state in terms of its electronic character and nuclear geometry.<sup>36-41</sup> The calculated intermediate state  $(p^*)$  is identified with the minimum in the  $S_1$  potential energy surface between the *cis* and trans geometries at or near the perpendicular geometry as sketched in Fig. 1. The results of several ab initio and semiempirical calculations have variously assigned this intermediate state as a minimum in the  ${}^{1}B$  state initially excited<sup>39-41</sup> or a minimum in a  ${}^{1}A$  state reached following internal conversion from the  ${}^{1}B$  state.  ${}^{36,37,40,41}$  This A state may be identified with either the doubly excited state that correlates with the ground state configuration of the other isomer, in which case, the minimum arises from the avoided crossing of the doubly excited A state with the ground state,  $^{36,37}$  or with another A state dominated by other electronic configurations.<sup>40,41</sup> The many calculations are at variance with each other due to the sensitivity of the calculated potential energy surfaces and electronic energies to the details of the calculation, in particular, the amount of configuration interaction included and the degree of geometric relaxation permitted.

A number of experimental studies have been performed to find concrete evidence for the existence of an intermediate state possessing a significant lifetime in the cis-trans isomerization reactions of stilbene.21,22,33,34 Although the existence of such an intermediate with a lifetime of  $10 \pm 3$  ps was indicated by using time-resolved spectroscopic techniques for "stiff" stilbene (trans-1,1'biindanylidene),<sup>42</sup> there is no direct evidence for the presence of a kinetic intermediate state in the cis-trans isomerization of unsubstituted stilbene having a significant lifetime ( $\tau \ge 1.5$  ps).<sup>34</sup> The only "delayed" signal seen in the evolution of the trans isomer is that measured by the slow fluorescence rise times. It is now considered whether this could result from the presence of a nonfluorescent intermediate structure distinct from both the cis and trans electronic structures, and whether such an interpretation is consistent with all of the experimental evidence available at this time.

The cis\* excited state absorption disappears in 0.5 ps in methanol and 0.7–1.5 ps in isopropanol, hexane, and hexadecane. The biexponential fit to the observed *trans* fluorescence rise signals gives fast components of 1.4 ps in methanol and  $\sim 6$  ps in the other three solvents. An intermediate state could account for the slow fluorescence rises obtained in all four solvents, and for the nearly identical rise times observed in hexane, hexadecane, and iso-

propanol. The internal conversion from  $p^*$  to p would be a function of the electronic properties of stilbene, and thus need not be strongly affected by the solvent or the solvent friction. However, a solvent effect on the intermediate state lifetime could arise due to solvent induced changes in the PES which increase or decrease the energy gap between pand  $p^*$ . This could account for the faster rise time observed in methanol. If  $p^*$  is identified electronically with a doubly excited state of A symmetry, the conversion from  $p^*$  to p is "forbidden" and may be relatively slow. Orlandi and coworkers have estimated the time scales to be on the order of tens to hundreds of picoseconds.<sup>43,44</sup> If  $p^*$  is identified electronically with a minimum on the singly excited B state surface, the internal conversion may be much faster, although the calculated energy gaps between p and  $p^*$  of at least 6000  $\text{cm}^{-1}$  indicate a bottleneck on the excited state surface which should possess a significant lifetime.<sup>39,41</sup>

However, all of the experimental data is not consistent with the presence of long lived intermediate, and the existence of an intermediate is not necessary to explain the observed fluorescence results. The trans-stilbene fluorescence excited by a 250 nm pulse rises on the same time scale as that found for the disappearance of the cis\* population. Thus any intermediate state must have the same fluorescence quantum yield as equilibrium trans-stilbene following excitation at 250 nm, but a substantially different quantum yield following excitation at 312 nm. This difference may be accounted for if vibrationally hot ground state trans-stilbene formation is on the same time scale as cis\* disappearance. The molecule must be formed hot, thus at early times a low yield is expected when excitation is into the  $S_1$  state owing to its dependence on excited state barrier crossing. On the other hand, the excess energy remaining in the system following isomerization may be only a small addition to the excess energy introduced into the trans molecule by exciting it at 250 nm. Thus no additional time evolution is observed when cis is pumped at 312 nm and trans is probed at 250 nm.

Additionally, the transient absorption measurements reported in this paper and in an earlier paper<sup>22</sup> do not appear to be consistent with an intermediate state possessing a significant lifetime ( $\tau \ge 0.15$  ps). An intermediate state is not necessary to fit any of the 312 nm pump transient absorption kinetics probed between 345 and 312 nm. There is no measurable delay between the disappearance of *cis*<sup>‡</sup> absorption and the appearance of product absorption. An assumption of vibrational cooling is sufficient to account for the observed long time decay components.

More conclusively, the anisotropy for the *trans* product deduced from the fluorescence measurement is the same within experimental error as the anisotropy deduced from the direct absorption measurements (see Ref. 28 and further discussion below). In addition, it is not necessary to include an intermediate state to fit the anisotropy kinetics observed in the transient absorption measurements performed at either 330 or 312 nm. The anisotropy obtained at 312 nm in hexadecane is shown in Fig. 13. The solid line in this figure was obtained by assuming three components—a coherent feature at time equal to zero having an instrument



FIG. 13. Anisotropy measurement at 312 nm following excitation of cis-stilbene in hexadecane at 312 nm. The data is fit to the model discussed in the text. The error bars represent 95% confidence levels.

limited width and an anisotropy of 0.4; an initial species A having an anisotropy of ~0.05, which decays exponentially with a characteristic time of 1.3 ps to form species B, having an anisotropy of 0.10. Species A for the data shown in Fig. 13 is a weighted average of  $cis^*$  absorption and cis bleaching and B is a weighted average of trans product absorption, DHP product absorption, and residual cis ground state bleaching. The overall orientational decay time used to fit the data shown in Fig. 13 was 80 ps, in good agreement with the literature value of  $82\pm7$  ps obtained for trans-stilbene in hexadecane.<sup>11</sup>

If an intermediate state with a lifetime between 2 and 10 ps is included in this analysis, it is found that the intermediate state absorption must have an anisotropy that is larger than the *trans* product absorption  $[r_{CI}(312 \text{ nm}) = r_{CT}(312 \text{ nm}) + 0.06].^{45}$  However, the anisotropy data obtained at 330 nm also fits well to a model consisting of two kinetically related species, where the initially produced species decays exponentially with a characteristic time of 1.3 ps to form the product species. If an intermediate state is included in the analysis of the 330 nm data, the anisotropy of the intermediate state absorption and the trans product absorption must be the same within  $\pm 0.02$ . Thus, the anisotropy data obtained in the fluorescence experiment and the transient absorption experiments is consistent with the presence of an intermediate state as discussed above only if the 330 and 312 nm pulses probe slightly different intermediate state transition dipole directions or distributions and the transition dipole probed in the intermediate state makes essentially the same angle to the initially pumped *cis* transition dipole direction as the  $S_0 \rightarrow S_1$ transition dipole of trans-stilbene does. This would not be expected if the intermediate is to be identified with a perpendicular conformation intermediate between the cis and trans geometries. Nor would such a structure have electronic spectra similar to trans-stilbene.

The conclusion most consistent with all of the avail-

able information is that vibrationally excited trans-stilbene molecules are formed on the same time scale as observed for the decay of the cis\* excited electronic state as suggested earlier.<sup>22,24,25,28,29</sup> In this model, the only bottleneck yet observed in the isomerization reaction involves the decay of population away from the cis\* nuclear conformation. Once the population escapes from the cis\* region of the excited state potential energy surface [defined as the region from which short-lived absorption (600-1000 nm) and fluorescence (340-540 nm) occur], the reaction proceeds unimpeded resulting in the appearance of the ground state product absorption on a time scale experimentally indistinguishable (with pulses of width  $\sim 150$  fs) from that for the disappearance of the cis excited state. That is, electronically identifiable, although distorted (possibly highly distorted) ground electronic state trans-stilbene is formed very quickly (in less than  $\sim 150$  fs) following the escape from the cis\* region of the excited state PES. The remainder of the dynamics observed in the experiments presented in this paper is due to vibrational relaxation of the product molecules and solvent relaxation.

# B. Calculations to model the hot trans spectrum

The vibrationally hot product spectrum measured 6 ps after the excitation of *cis*-stilbene (see Fig. 7) may be extrapolated to that at earliest times using single wavelength measurements such as those shown in Fig. 6. These measurements have been performed at 312, 320, 330, 335, 345, and 350 nm for *cis*-stilbene in hexane. This projection then represents the difference spectrum of the product molecules at the earliest times and is a measure of the vibrational energy of the product molecules. Proper interpretation of this spectrum will provide an estimate of the energy partitioning between internal and external degrees of freedom as discussed in connection with Fig. 2.

In order to interpret this spectrum in terms of the vibrational energy content of the product molecules, it is necessary to calculate the spectrum expected for various relevant thermal and/or nonthermal ground state population distributions. The resonance Raman spectra of cisand trans-stilbene have been analyzed and used in conjunction with the UV absorption spectra to obtain values for the normal coordinate displacements responsible for most of the Franck-Condon activity.46,47 Room temperature spectra calculated using these parameters along with the digitized DHP spectrum provides reasonably good agreement with the 50 ps experimental spectrum (see Fig. 14). The failure of the calculated spectrum to predict the sharp red edge of the product absorption results from the failure of the model parameters to predict the sharp red edge of the trans spectrum.47

The most straightforward place to begin to model the initial hot spectrum is to assume that during the reaction from *cis* to product, which in the case of the *cis* to *trans* reaction involves a large geometry change, all of the energy that remains in the internal (vibrational) degrees of freedom becomes distributed throughout the molecule in a Boltzmann distribution characterized by a vibrational temperature. In this case, the maximum temperature, corre-



FIG. 14. The calculated equilibrium difference spectrum compared with the 50 ps experimental spectrum. The inset contains a comparison of the calculated equilibrium *cis* and *trans* absorption spectra with the spectra measured in hexane.

sponding to all of the available energy remaining in the internal degrees of freedom, is approximately 1350 K (1225 K following excitation at 332 nm), slightly higher for *trans* and slightly lower for *cis* due to the energy difference between the *cis* and *trans* ground states.<sup>48</sup> The maximum temperature for the DHP product will be substantially lower (~1000 K). Thus, under the assumptions discussed here, the difference spectrum should correspond to the calculated spectrum for some  $T \leq 1350$  K.

A calculation of the hot spectrum has been made assuming harmonic PESs along with the displacements and frequency changes reported in Refs. 46 and 47. The calculation was performed by computing an explicit sum over states for the Franck-Condon active vibrational modes above 600 cm<sup>-1</sup> and line shape functions for low frequency modes. All cis and trans states involved in Franck-Condon active transitions and having energies less than 5000  $\rm cm^{-1}$ were retained in the sum over states. Additional states were retained to calculate the 1350 K spectrum. In addition to the Franck-Condon modes discussed in Refs. 46 and 47, the 262 cm<sup>-1</sup>  $b_{\mu}$  CCC deformation mode of *trans*-stilbene was also included in the calculation. In the current best assignment, the frequency of this vibrational mode drops from 262 to 99 cm<sup>-1</sup> in the  $S_1$  excited state.<sup>15(c)</sup> Such a frequency change will result in increased intensity on the red edge of the absorption at elevated temperatures, and thus is important to consider when modeling the product spectra shown in Fig. 7.

The calculated spectra for temperatures of 725 and 1350 K are shown in Fig. 15. The hot spectra of both *cis* and *trans* have been calculated. As we have no information on the parameters necessary for estimating the hot DHP spectrum, this small contribution has been assumed to be room temperature in Fig. 15. The effect of "hot" DHP is also incorporated into this calculation by setting the hot DHP intensity at 2.5 times that of the room temperature



FIG. 15. Comparison of the calculated 725 (---) and 1350 K  $(\cdot \cdot \cdot)$  spectra with the  $6\pm 2$  and 15 ps spectra of *trans*-stilbene; DHP (---) at 1350 K.

DHP spectrum. This estimate seemed reasonable because the explored region from 375 to 315 nm lies between the strong UV absorption and the visible absorption of DHP (see Fig. 8). The spectrum calculated for T=1350 K does not account for the shape of the observed spectrum. No equilibrium thermal distribution appears able to account for the sharp drop at ~325 nm and the hump at ~335 nm. In addition, no thermal distribution can account for the pump wavelength dependence of the 6 ps spectrum (see Fig. 12). On the other hand, the 15 ps spectrum obtained following 312 nm excitation is well represented by the calculation for T=725 K.

The shape of the initial photoproduct spectrum obtained following excitation at 312 nm suggests that the product molecules are created with significantly more excitation of modes in the range 900 to 1700  $cm^{-1}$  than would be predicted by a thermal distribution of the available energy. Population of the v=1 and v=2 levels of Franck-Condon modes in this range will allow hot band  $\Delta v = -1$  transitions to generate a hump in the spectrum. These particular vibrational levels could become populated in the initial cis-stilbene excitation process or as a result of the cis-trans isomerization. The substantial red shift of the cis-stilbene fluorescence spectrum with respect to the absorption spectrum,<sup>49</sup> along with the displacements deduced from the resonance Raman spectrum<sup>46</sup> indicates that excitation on the red edge of the absorption band (between 312 and 300 nm) will result in a distribution of electronically excited molecules with substantial population in the Franck-Condon active C-C stretching modes, ring deformation modes, and hydrogen rocking modes. If most or all of these modes are not coupled to the reaction coordinate, the population distribution placed in them by the act of photoexcitation may be largely retained in the product molecules. This model accounts for the difference between the 6 ps spectrum obtained following excitation at 312 nm and that obtained following excitation at 332 nm. The sub-



FIG. 16. Vibrational energy distributions in the 900–1700  $cm^{-1}$  Franck–Condon active modes discussed in the text.

sequent cooling of the modes would occur on their  $T_1$  time scales, expected to be in the 10 ps range.<sup>1,51</sup>

The effect of this type of a nonthermal population distribution on the hot photoproduct spectrum is readily calculated if the distribution is known. We have noted that there exists an approximate one-to-one correspondence between the Franck-Condon active modes of cis-stilbene and those of trans-stilbene. The resonance Raman spectra of the cis and trans molecules are remarkably similar in the region between 900 and 1700 cm<sup>-1.46,47</sup> This suggests that similar nuclear motions are responsible for most of the Franck-Condon activity in the cis and trans molecules. If the assumption is made that this correspondence holds for all points on the reaction path, the vibrational population distributions in the ground state product molecules may be estimated.<sup>52</sup> Population distributions calculated for excitation wavelengths of 330, 312, 307, and 302 nm are shown in Fig. 16. The primary point of interest is the relative population of the vibrational states containing one and two quanta of excitation with respect to the population of the vibrational ground state. It is exactly this sort of nonthermal distribution that is necessary to reproduce the hump observed in the experimental spectrum.

Spectra calculated using these population distributions are shown in Figs. 17 and 18. The introduction of broadening equivalent to a  $\sim$ 725 K thermal distribution in the low frequency modes in addition to the nonthermal population distribution in the 900–1700 cm<sup>-1</sup> vibrational modes



FIG. 17. A comparison of the calculated and experimental difference spectra. The calculation used the nonthermal 312 nm distribution discussed in the text. The dotted line is calculated for 300 K. The dashed line includes an estimate for the effect of hot DHP. The dotted-dotted-dashed lines are the same calculations, but using a 725 K distribution in the low frequency modes.

does a good job of reproducing both the hump and the breadth of the 6 ps spectrum. The agreement between the calculated and experimental spectra is not very sensitive to the precise temperature of the low frequency modes. The 6 ps spectrum obtained following excitation at 332 nm is in good agreement with the spectrum calculated for a 725 K



FIG. 18. A comparison of the calculated and experimental difference spectra for nonthermal distributions equivalent to 307 and 302 nm excitation. The dotted-dashed and dashed lines were calculated for distributions corresponding to 307 and 302 nm excitation. Because all of the displacements are estimates, this may be closer to the true distribution produced in the experiment following 312 nm excitation. The dotted line and dotted-dotted-dashed lines include a rough estimate for hot DHP. All of the calculations include a 725 K distribution in the low frequency modes.

population distribution. This is what would be expected based on the population distributions (see Fig. 12) shown in Fig. 16.

It should be noted that the hot DHP contribution cannot be entirely ignored. Without the inclusion of DHP in the analysis, it is not possible to reproduce the increase in the intensity of the zero-zero band at early times. The inclusion of a rough estimate for the hot DHP contribution accounts quite well for the initial intensity increase in the 315-320 nm range.

There are several conclusions that may be drawn from this analysis of the hot spectrum.

(a) Complete intramolecular vibrational redistribution is not fast with respect to the time scale of the isomerization reaction. The product molecules are formed preferentially with one or two (or more) quanta of excitation in the 900–1700 cm<sup>-1</sup> modes populated by the initial excitation process. The simulated spectra lead to the conclusion that the product molecules are formed with  $\langle E_{\rm vib} \rangle = 1900 \pm 500$ cm<sup>-1</sup> in these vibrational modes. Much of this energy is placed into these modes by the excitation pulse. The energy placed in these modes does not rapidly equilibrate with the low frequency vibrational modes and has only spectator status in the reaction.

(b) The initially formed product molecules are also formed hot in the low temperature modes coupled to the reaction coordinate. If the energy remaining in these modes is thermally distributed, it corresponds to a temperature of ~600-800 K implying that  $\langle E_{lf} \rangle = 5000-15\ 000\ \mathrm{cm}^{-1}$ .

(c) The transfer of the vibrational energy in the Franck-Condon active modes to the solvent occurs on the time scale of 10-30 ps and is moderately sensitive to the solvent.

These conclusions are consistent with two recent independent observations. A comparison of calculated and experimental absorption and emission spectra of *cis*-stilbene was performed by Todd *et al.*<sup>54</sup> This study determined that it was not possible to model both the absorption spectrum and the room temperature emission spectrum of Saltiel *et al.*<sup>49</sup> using the same potential surface if vibrational relaxation was assumed to be complete. They suggest that the room temperature emission originates from vibrationally hot molecules where the vibrational relaxation of one or more of the modes is slow with respect to the isomerization time scale. Such effects are well known for molecules having short-lived excited state.<sup>55</sup>

In a somewhat more direct experiment, Myers and coworkers<sup>56</sup> have measured the anti-Stokes resonance Raman spectrum of *trans*-stilbene produced following the excitation of *cis*-stilbene in cyclohexane at 295 nm as a function of delay between the pump and probe pulses.<sup>57</sup> The probe wavelength was 278 nm. At 5 ps, the earliest time measured, they observe a very hot spectrum and tentatively conclude that the anti-Stokes intensity arises from the v=4or 5 levels of the C=C stretching modes (1500–1650 cm<sup>-1</sup>). At 10 ps, the intensity arises from the v=3 levels. The C-H rocking region (1100–1200 cm<sup>-1</sup>) and H wagging region (950–980 cm<sup>-1</sup>) also exhibit substantial anti-Stokes intensity.

The present observations, taken in conjunction with our earlier results<sup>58</sup> and the recent work cited above,<sup>54,57</sup> serve to strengthen the view<sup>58</sup> that IVR is not rapid in this system. Rather, the amount of vibrational energy in the C=C stretching, C-H rocking, and H wagging modes of the photoproduct is directly related to the energy placed in them by the pulse used to excite cis-stilbene. This accounts completely for the insensitivity of the fluorescence detected trans appearance to the wavelength used to excite cis. The excess energy placed into the system using 250 nm excitation instead of 312 nm excitation is trapped in the Franck-Condon active modes which are decoupled from the reaction, and does not affect the energy content of the low frequency modes directly involved in the cis/trans reaction coordinate. The fluorescence experiment is sensitive to the energy content of the modes coupled to the reaction coordinate, not to the energy content of the Franck-Condon active modes.

# C. Anisotropy and intensity in the polarized fluorescence experiments

In order to model the experiments involving the fluorescence detection of *trans*-stilbene presented above, it is necessary to develop the proper formalism for describing the dependence of the fluorescence signal on the polarization, the growth of the ground state *trans* population, and the time dependent fluorescence of *trans*\*.

Equation (3) contains an anisotropy factor  $G_{abc}(t)$ which is dependent on the polarization a of the pump pulse which creates cis\*, the polarization b of the probe pulse which creates trans\*, and the polarization c of the emitted photon. G is actually a function of both t and  $\tau$ , where t is the delay between the pump and probe pulses and  $\tau$  is the delay between the probe pulse and the emission of the detected photon. The pump pulse (x or z polarized) creates a cosine-squared distribution of cis\* molecules which generate trans molecules on a time scale which may be faster than the rotational diffusion time. In the cases under consideration here, it is faster. The generated anisotropic distribution of *trans* is then excited with polarized light, either x or z polarized corresponding to the parallel and perpendicular signals. The time-integrated (over  $\tau$ ) fluorescence intensity polarized along both x and y is detected. The separation of the kinetic factors from the geometric factor  $G_{abc}$  in Eq. (3) arises from the following assumptions: (1) The isotropic absorption coefficient of trans ground state molecules is not dependent on the orientational coordinates. Changes in absorption, uncoupled from the orientational motion, resulting from changing vibrational energy content or its distribution can be considered separately as kinetic factors. (2) The trans transition dipoles responsible for absorption and subsequent emission processes by a molecule assume only one direction in the molecular frame, as if the system has only two states T and C kinetically related by Eq. (1). In reality, we could expect the trans ground state molecules to be formed far enough from the equilibrium configuration that the trans (BornOppenheimer) dipole moment could, subsequently, change both its magnitude and direction. In that case, the analysis would require the conditional probability distribution characterizing motion along the reaction coordinate. However, the experiments at the present time resolution are consistent with a two state kinetic scheme which will therefore be adopted in the following analysis: A general treatment of the anisotropy including the molecular dynamics between these two states will be discussed in a future publication. Under the assumptions given above,  $G_{abc}(t,\tau)$  is given by

$$G_{abc}(t,\tau) = \langle [\mathbf{C}(0) \cdot \mathbf{a}]^2 [\mathbf{T}(t) \cdot \mathbf{b}]^2 [\mathbf{T}(\tau) \cdot \mathbf{c}]^2 \rangle, \quad (4)$$

where  $\langle \cdots \rangle$  signifies an average over the distribution of orientations present at each time, and **C** and **T** are molecule-frame fixed transition dipoles corresponding to *cis* and *trans* structures, respectively. By converting the cosines to second Legendre polynomials,  $P_2(\cos \Theta) = [3\cos^2(\Theta) - 1]/2$ , and using the orientational averages  $\langle P_2(\cos \Theta) \rangle = 0$ ,  $\langle P_2^2(\cos \Theta) \rangle = 1/5$ , and  $\langle P_2^4(\cos \Theta) \rangle = 2/35$ , the required elements of  $G_{abc}$  (up to a multiplicative constant) are found to be<sup>59</sup>

$$G_{zzx}+G_{zzy}=1+4/5\langle P_2[\mathbf{C}(0)\cdot\mathbf{T}(t)]\rangle$$
  
-2/5 $\langle P_2[\mathbf{T}(t)\cdot\mathbf{T}(\tau)]\rangle$   
-2/5 $\langle P_2[\mathbf{C}(0)\cdot\mathbf{T}(\tau)]\rangle$   
-8/35 $\langle P_2[\mathbf{C}(0)\cdot\mathbf{T}(t)]P_2[\mathbf{T}(t)\cdot\mathbf{T}(\tau)]\rangle,$   
(5a)

$$G_{zxx} + G_{zxy} = 1 - 2/5 \langle P_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] \rangle$$
  
+ 1/5 \langle P\_2[\mathbf{T}(t) \cdot \mathbf{T}(t)] \rangle  
- 2/5 \langle P\_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] \rangle  
+ 4/35 \langle P\_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] P\_2[\mathbf{T}(t) \cdot \mathbf{T}(t)] \rangle  
(5b)

$$G_{xzx} + G_{xzy} = 1 - 2/5 \langle P_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] \rangle$$
  
-2/5 \langle P\_2[\mathbf{T}(t) \cdot \mathbf{T}(t)] \rangle  
+1/5 \langle P\_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] \rangle  
+4/35 \langle P\_2[\mathbf{C}(0) \cdot \mathbf{T}(t)] P\_2[\mathbf{T}(t) \cdot \mathbf{T}(t)] \rangle. (5c)

The correlation functions in Eqs. (5) are readily evaluated by standard methods<sup>60</sup> when only reorientation is involved. For simplicity, the assumption is made that both the *cis* and *trans* molecules rotate as spherical diffusers with the same diffusion coefficient D. The fixed angle between C and T in a molecular frame is  $\Theta_{CT}$ . The required results are

$$\langle P_2[\mathbf{C}(0)\cdot\mathbf{T}(t)]\rangle = \langle P_2[\cos\Theta_{CT}]\rangle e^{-6Dt},$$
 (6a)

$$\langle P_2[\mathbf{T}(t_1) \cdot \mathbf{T}(t_2)] \rangle = \exp[-6D(t_2 - t_1)],$$
 (6b)

$$\langle P_2[\mathbf{C}(0)\cdot\mathbf{T}(t)]P_2[\mathbf{T}(t)\cdot\mathbf{T}(\tau)]\rangle = \langle P_2[\cos\Theta_{CT}]\rangle e^{-6D\tau}.$$
(6c)

The average involving  $\Theta_{CT}$  is taken within a frame fixed in and rotating with the molecule and so involves the distribution of trans dipoles generated by the isomerization process relative to a fixed cis  $S_0 \rightarrow S_1$  dipole. The assumption of the overall motion being described by a single diffusion constant is justified by the fact that the trans molecules are formed extremely rapidly compared with normal rotational diffusion times for such molecules. In addition, the population kinetics are consistent with a two state model  $(C \rightarrow T)$ , so that the rotation of any intermediate structures is justifiably omitted from this first analysis. These considerations would suggest that only the trans rotational diffusion need be considered. In these solvents, the rotational diffusion dynamics of trans-stilbene is adequately represented by a single exponential decay.<sup>9,11,61</sup> What is not yet considered is that the isomerization process may generate rotationally hot product states which may reorient faster than expected from diffusion; these will be considered in more detail below. However, the absorption anisotropy measured at 312 nm decays with a time constant consistent with those published for trans-stilbene, indicating that such an effect is small (see Fig. 13).

For any population of excited *trans* molecules  $n_{T^*}(t,\tau)$ , the observed fluorescence signal is given by

$$S_{abc}(t) = k_r \int_0^\infty n_T^*(t,\tau) G_{abc}(t,\tau) d\tau.$$
<sup>(7)</sup>

The excitation of *cis* molecules with a population  $n_C(t')$  by the pump pulse  $I_1(t')$  yields an excited state population  $n_C (t')$  that decays to form a *trans* ground state population  $n_T(t')$ . These molecules are excited by a second pulse  $I_2(t'+t)$  after some interval t to yield the potentially fluorescent *trans*<sup>\*</sup> population  $n_T (t'+t)$ . Since we observe no coherences in the evolution of the signal induced by ~150 fs pulses, the equations of motion for these populations on this experimental time scale are assumed to be given by the following kinetic relations:

$$\dot{n}_{C^{*}}(t') = \sigma_{C}I(t')n_{C}(t') - k_{C}n_{C^{*}}(t'), \qquad (8a)$$

$$\dot{n}_{I}(t') = k_{C} n_{C*}(t') - k_{I} n_{I}(t'), \qquad (8b)$$

$$\dot{n}_T(t') = k_I n_I(t'), \tag{8c}$$

$$\dot{n}_{T*}(t') = \sigma_T(t')I_2(t'+t)n_T(t') - k(t')n_{T*}(t'), \quad (8d)$$

where  $\sigma_c$  and  $\sigma_T(t')$  are the absorption cross sections for *cis*- and *trans*-stilbene, respectively,  $k(t') = k_i(t') + k_r$  is the decay rate of *trans*<sup>\*</sup> due to isomerization  $(k_i)$  and radiative decay  $(k_r)$ ,  $k_c$  is the decay rate of *cis*<sup>\*</sup>, and  $k_I$  is the decay rate of any intermediate between *cis*<sup>\*</sup> and *trans*. The absorption cross section for *trans* at any wavelength and the *trans*<sup>\*</sup> isomerization rate may both be time dependent due to vibrational cooling of the *trans* product molecules (see Figs. 5–7). If there were no intermediate state influencing the kinetics of the reaction, Eq. (8b) could be omitted from the kinetic scheme and Eq. (8c) replaced by  $\dot{n}_T(t') = k_C n_{C^*}(t')$ . The simple biexponential rise of the fluorescence signal would not be expected if an intermediate were involved.

In the small conversion limit, assuming for the moment delta function pulses for  $I_2(t'+t)$  and I'(t'), the excited state *trans* population is found to be

$$n_{T*}(t,\tau) = \sigma_T(t,\tau) n_T(t,\tau) \exp\left[-\int_0^\tau k(x+t)dx\right].$$
(9a)

With no intermediate state,

$$=k_C n_C \sigma_C \sigma_T(t,\tau) \left(1-e^{-k_C t}\right) \exp\left[-\int_0^\tau k(x+t) dx\right].$$
(9b)

Using Eqs. (5), (7), and (9) equations for modeling the experimentally measured *trans* product fluorescence signal may be obtained

$$S_{\parallel}(t) = S_{zzx}(t) + S_{zzy}(t),$$
 (10a)

$$S_{\perp}(t) = S_{zxx}(t) + S_{zxy}(t),$$
 (10b)

$$S'_{\perp}(t) = S_{xzx}(t) + S_{xzy}(t).$$
 (10c)

By analogy with transient absorption and ordinary timeresolved fluorescence experiments, a "pseudomagic angle" signal and an anisotropy function may be defined

$$S'_{T}(t) = [S_{\parallel}(t) + 2S'_{\perp}(t)]/3,$$
 (11a)

$$r'(t) = [S_{\parallel}(t) - S'_{\perp}(\tau)] / [S_{\parallel}(t) + 2S'_{\perp}(\tau)].$$
(11b)

However,  $S'_T(t)$  is not entirely independent of the angular reorientation and randomization of the initially anisotropic distribution of *trans*<sup>\*</sup>, and r(t) is not independent of the population kinetics.<sup>59</sup> In the quantitative analysis of the present data, the fact that the excitation and probing pulses  $I_1(t')$  and  $I_2(t')$  are not actually delta functions in time was incorporated.

In order to calculate the fluorescence signals, let

$$F(t) = k_r \int_0^\infty \exp\left[-\int_0^\tau k_i(x+t)dx - k_r\tau\right]d\tau, \quad (12a)$$
$$H(t) = k_r \int_0^\infty \exp\left[-\int_0^\tau k_i(x+t)dx - k_r\tau - \tau/\tau_R\right]d\tau, \quad (12b)$$

where  $\tau_R = 6D^{-1}$  is the time constant for rotational diffusion of *trans*. Then using Eqs. (6), (7), and (10)-(12), we have

$$S_{\parallel}(t) = K\sigma_{T}(t)(1 - e^{-k_{c}t})[F(t) + 2r_{0}e^{-t/\tau_{R}}F(t) - 0.4H(t) - r_{0}e^{-t/\tau_{R}}H(t) - 4/7r_{0}e^{-t/\tau_{R}}H(t)],$$
(13a)

$$S_{\perp}(t) = K\sigma_{T}(t)(1 - e^{-k_{c}t})[F(t) - r_{0}e^{-t/\tau_{R}}F(t) + 0.2H(t) - r_{0}e^{-t/\tau_{R}}H(t) + 2/7r_{0}e^{-t/\tau_{R}}H(t)], \quad (13b)$$

$$S'_{\perp}(t) = K\sigma_{T}(t) (1 - e^{-k_{c}t}) [F(t) - r_{0}e^{-t/\tau_{R}}F(t) - 0.4H(t) + 0.5r_{0}e^{-t/\tau_{R}}H(t) + 2/7r_{0}e^{-t/\tau_{R}}H(t)], \quad (13c)$$

and

$$S_T(t) = K\sigma_T(t) (1 - e^{-k_c t}) [F(t) - r_0 e^{-t/\tau_R} H(t)], \quad (14a)$$

$$S_T(t) = K\sigma_T(t) (1 - e^{-k_c t}) [F(t) - 0.4H(t)], \quad (14b)$$

$$r(t) = [r_0 e^{-t/\tau_R} [F(t) - 4/7H(t)] - 0.2H(t)]/$$

$$[F(t) - r_0 e^{-t/\tau_R} H(t)]$$
(15a)

$$[F(t) - F_0 e^{-t} H(t)], \qquad (13a)$$

$$r'(t) = r_0 e^{-t/\tau_R} [F(t) - 11/14H(t)] / [F(t) - 2/5H(t)],$$
(15b)

where  $r_0 = r_{CT}(0) = 0.4 \langle P_2[\cos \Theta_{CT}] \rangle$  and K is a constant.

The biexponential fit to the data given by Eq. (3) amounts to assuming that  $k_i(t)$  is independent of time, that the rise of the *trans*-stilbene population in Eq. (9) is biexponential, and that the *trans* absorption cross section is time independent.

# D. Comparison of a model for the fluorescence with experiment

A simple model for  $k_i(t)$  has been used to analyze *trans* fluorescence yield measurements previously<sup>28</sup>

$$k_i(t) = B_s \exp[-E_a/k_b T(t)],$$
 (16)

$$T(t) = (T_m - T_{eq}) \exp(-t/\tau_v) + T_{eq}.$$
 (17)

The Arrhenius form for  $k_i(t)$  has been used extensively to model the isomerization for  $trans^{*4,6,10,12,13}$  and has been found to be effective for alkanes, but not as reliable for alcohols.<sup>5,8,12</sup> The barrier height in alkanes is ~3.5–4 kcal/ mol.<sup>4,6,10</sup> The pre-exponential factor  $B_s$  is determined from the decay of  $trans^*$  fluorescence or transient absorption at constant temperature. Modeling the temperature decay as an exponential [Eq. (17)] while somewhat artificial, has a basis in Newtonian cooling where the heat flux through a surface is proportional to the temperature difference. For low frequency modes ( $v < kT_{eq}$ ) with a Boltzmann population distribution  $\langle E \rangle = kT$  per mode, an exponential decay of the energy implies an exponential decay of the temperature.

The comparison of this model with one measurement of the fluorescence yield in hexadecane resulted in best fit parameters of  $T_m = 725$  K and  $\tau_v = 14$  ps.<sup>28</sup> In the present paper, we have performed two measurements each in hexadecane and hexane, and one each in methanol and isopropanol. In addition, a much better signal to noise ratio was obtained for the signal from *trans* in hexadecane.

The initial set of calculations used a trans<sup>\*</sup> barrier height of 3.5 kcal/mol and values of  $B_s=2.16$  and 4.74 ps<sup>-1</sup> for hexadecane and hexane, respectively, with  $T_{eq}$ =293 K.<sup>10</sup> Fits of this model to the data are shown in Figs. 19 and 20. Only the "positive" time signal  $S_T(t)$  has been considered, as these data are independent of the value of  $r_0$ [Eq. 14(b)]. The trans absorption cross section  $\sigma_T(t)$  is assumed to be constant. This is a reasonable approximation, although it is not exact [see Fig. 5(a)]. For hexane, the fitting parameters are  $T_m=600\pm50$  K and  $\tau_v=11$  $\pm 1.0$  ps; for hexadecane, the parameters are  $T_m=675\pm50$ K and  $\tau_v=13.5\pm1.0$  ps. As shown in the figure, it is pos-



FIG. 19. Pseudomagic angle fluorescence yield curves  $S'_T$  in hexane, compared with calculation performed using  $(T_m=600 \text{ K}, \tau_v=11 \text{ ps})$ ,  $(T_m=625 \text{ K}, \tau_v=10.5 \text{ ps})$ , and  $(T_m=650 \text{ K}, \tau_v=10 \text{ ps})$ .

sible to find a value of  $\tau_v$  that fits the data for a range of values of  $T_m$ . However, it is not possible to find a reasonable fit for all values of  $T_m$ . For hexadecane and hexane, respectively, the temperature range over which reasonable fits may be found are approximately  $600 \leqslant T_m \leqslant 750$  K and  $550 \leqslant T_m \leqslant 700$  K. Note in Fig. 20 that the data set represented by the +'s defines a much sharper dependence of  $S_T^{(\prime)}(t)$  on t at very early time than the data set represented by the  $\bigcirc$ 's does. As a result of the improved determination of the early time behavior of  $S_T^{(\prime)}(t)$  in the present study, the calculation is found to represent the entire curve. The unexplained early time deviations discussed in Ref. 28 are not present. Given an estimate for  $r_0$ , as discussed below,



FIG. 20. Pseudomagic angle fluorescence yield curves  $S'_T$  in hexadecane, compared with a calculation performed using  $(T_m=650 \text{ K}, \tau_v=14 \text{ ps})$ ,  $(T_m=675 \text{ K}, \tau_v=13.5 \text{ ps})$ , and  $(T_m=700 \text{ K}, \tau_v=13 \text{ ps})$ .

the parameters given above also do a reasonable job of modeling the behavior of the "negative" time data  $S_T(t)$ .

The above calculations use a value for  $E_a$  of 3.5 kcal/ mol. This is supported by much of the previous work on *trans* isomerization in alkane solvents,<sup>4,6</sup> although somewhat larger values are sometimes proposed, especially for longer chain alkanes. The barrier height may be as large as  $4.1 \pm 0.3$  kcal/mol in hexadecane.<sup>10</sup> The fluorescence yield as a function of time has been calculated using a barrier height of 4.0 kcal/mol. The quality of the fit is found to be much more sensitive to the parameters ( $T_m$  and  $\tau_v$ ) than when a barrier height of 3.5 kcal/mol is used. The best fit is found for  $T_m = 575$  K,  $\tau_v = 15$  ps in hexadecane and  $T_m = 525$  K,  $\tau_v = 12.5$  ps in hexane. The range for acceptable fits is  $\pm 25$  K.

The data obtained in methanol and 2-propanol are more difficult to model. There is much discussion in the literature as to the barrier height in alcohol solvents.<sup>5,6,8,12,15(a)</sup> In general, it is found that isoviscosity plots in alcohols of varying chain lengths yield barrier heights that decrease with increasing chain length.<sup>8,12</sup> Based on these studies, we have estimated an effective barrier height of 2.7 kcal/mol in 2-propanol to calculate the fluorescence yield as a function of time. The best fit parameters are found to be  $T_m = 600$  K and  $\tau_v = 10$  ps. These parameters are consistent with those obtained in alkane solvents, but must be viewed with a bit more skepticism due to the inability of equilibrium measurements to define a barrier height in alcohols. In the work of Kim, Courtney, and Fleming,<sup>12</sup> the effective barrier height in C<sub>1</sub>-C<sub>2</sub> alcohols was found to be  $\sim$  3.5 kcal/mol. A fit of the methanol data using this barrier height yields  $T_m = 525 \pm 25$  K and  $\tau_v = 5.5 \pm 0.5$  ps. It has also been postulated that the barrier height in alcohols is very small, less than  $\sim 1 \text{ kcal}/$ mol.<sup>5,6,8,15(c)</sup> It is not possible to fit the alcohol data to the model discussed above with a barrier height <1.5 kcal/ mol and  $T_m \leq 1350$  K.

The conclusion that may be drawn from the above analysis is that the product molecules are formed vibrationally excited in modes connected to the *cis/trans* reaction coordinate. A vibrational temperature of  $\sim 650$  K will adequately account for the fluorescence yield curves obtained in hexane and hexadecane. This is consistent with the temperature range deduced from the analysis of the hot absorption spectrum.

#### E. Reactant to product anisotropy measurements

Using the parameters determined above for the best fit to the  $S'_T(t)$  data, it is possible to extract a value of  $r_0$  from a comparison of the experimental r'(t) and r(t) data with calculated curves. This is shown in Fig. 21. It is clear from these data that  $0.10 < r_0 < 0.30$ , although the model does not fit the decay of the anisotropy particularly well in general. The best value from a compilation of all of the data is  $r_0=0.20\pm0.05$ . This value is slightly less than but encompasses that deduced from the first reported hexadecane measurements.<sup>29</sup>

A quantitative analysis of the magic angle transient



FIG. 21. Fluorescence anisotropy measurements: (a) r(t) in hexane; (b) r'(t) in hexane; (c) r(t) in hexadecane; and (d) r'(t) in hexadecane. From top to bottom,  $r_0=0.30$ , 0.26, 0.20, 0.14, and 0.10.

absorption data and the anisotropy data obtained at 312 and 330 nm in hexadecane will also yield an estimate for  $r_0 = r_{CT}(0)$ . The data obtained in hexadecane are chosen for this analysis for two reasons: First, the data are more accurate (see Figs. 5 and 13), especially at 330 nm where the hot product spectrum persists longer than it does in hexane. Second, the longer overall reorientation times for stilbene and DHP in hexadecane result in relatively small errors due to projecting the observed data back to t=0under the assumption [only very approximately correct (see below)] that all species decay with the same overall reorientational decay time.

As mentioned previously, the observed anisotropy at 312 and 330 nm is a weighted average of the values for the cis\* absorption, ground state cis bleaching, DHP absorption, and *trans* absorption signals. The anisotropy of a multiple component system such as this is given by

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{T}(t)}$$
$$= A_{1}(t)r_{1}(t) + A_{2}(t)r_{2}(t) + A_{3}(t)r_{3}(t) + \cdots,$$
(18)

where  $I_{\parallel}(t)$  and  $I_{\perp}(t)$  are the total measured signals for parallel and perpendicular polarization geometries, respectively,  $I_T(t) = I_{\parallel}(t) + 2I_{\perp}(t)$ , and  $A_n(t) = I_n(t)/I_T(t)$ , where  $I_n(t)$  is the total signal due to the *n*th component and  $r_n(t)$  is the anisotropy due to the *n*th component. Under the assumption that all components have approximately the same overall reorientation time  $\tau_R$  and that the decay of the anisotropy due to reorientation may be modeled as a single exponential, Eq. (18) reduces to the following for the anisotropy curves shown in Figs. 5 and 13:

$$r(t) = [A_{c*}(t)r_{c*}(0) + A_{cb}(t)r_{cb}(0) + A_D(t)r_{CD}(0) + A_T(t)r_{CT}(0)]\exp(-t/\tau_R),$$
(19)

where  $A_{c*}$ ,  $A_{cb}$ ,  $A_{D}$ , and  $A_{T}$  are the fractional absorbance

signals due to *cis*\*, *cis* bleaching, DHP, and *trans*, respectively, and  $r_{c*}$ ,  $r_{cb}$ ,  $r_{CD}$ , and  $r_{CT}$  are the anisotropies of these signals.

The curves in Fig. 5, were fit under the constraints obtained from the measured quantum yields and relative molar extinction coefficients for cis, trans, and DHP. The quantum yields of trans and DHP produced from cisstilbene excited at 313 nm are 0.35 and 0.10, respectively.<sup>26</sup> The relative extinction coefficients are  $\epsilon_D(312 \text{ nm})$  $\approx \epsilon_T$ (312 nm),  $\epsilon_C$ (312 nm) $\approx 0.20 \epsilon_T$ (312 nm),  $\epsilon_D$ (330 nm)  $\approx 0.35 \epsilon_T (330 \text{ nm})$ , and  $\epsilon_C (330 \text{ nm}) \approx 0.12 \epsilon_T (330 \text{ nm})$ nm). The relative extinction coefficients of cis and trans were obtained from their absorption spectra. The relative extinction coefficients of trans and DHP were estimated from the spectrum of DHP published in Ref. 31. As this spectrum was obtained in a mixed methyl-cyclohexane/ isohexane solvent, there may be a slight solvent shift in the hexadecane spectrum relative to the published spectrum. Such an effect would lower  $\epsilon_D(312 \text{ nm})$  relative to  $\epsilon_T(312 \text{ nm})$ nm) and may raise or lower  $\epsilon_D(330 \text{ nm})$  relative to  $\epsilon_T(330 \text{ nm})$ nm). Given the above quantities, for long delay times, after the vibrational cooling occurs,  $A_D(312 \text{ nm}) = 0.29A_T(312 \text{ nm})$ nm) and  $A_{cb}(312 \text{ nm}) = -0.26A_T(312 \text{ nm})$ .

Additional constraints are obtained from the known value for  $r_{cb}(0) = 0.40$  and the calculated value of  $r_{CD}(0) = -0.20$ . Calculations of the electronic structure of DHP predict that the  $S_0 \rightarrow S_2$  transition dipole lies along the  $C_2$  axis of the molecule.<sup>62,63</sup> Given a reaction coordinate that does not rotate the direction of the  $C_2$  axis in space, and the fact that the  $S_0 \rightarrow S_1$  transition dipole of *cis*-stilbene lies approximately parallel to the ethylene bond, perpendicular to the  $C_2$  axis, <sup>24,64</sup>  $r_{CD}(0)$  for ultraviolet probe wavelengths will certainly be negative and will probably fall very close to the limiting value of -0.20 expected for perpendicular transitions.

This analysis of the anisotropy obtained at 312 nm yields a value of  $r_{CT}(0) = 0.23$ . If  $\epsilon_D(312 \text{ nm}) = 0.50\epsilon_T(312 \text{ nm})$ , which would require a very large solvent shift for the DHP spectrum, then  $r_{CT}(0) = 0.20$ . The same analysis of the anisotropy obtained at 330 nm yields a value of  $r_{CT}(0)$  between 0.18 and 0.24, the exact value being dependent on the magnitude of the vibrational cooling component assigned to the DHP signal. If it is assumed that there is no DHP contribution at all to the 330 nm data,  $r_{CT}(0) = 0.16$ —this is the minimum possible value.

From the above analysis, we may conclude unequivocally that  $0.16 \le r_{CT}(0) \le 0.24$ . The data shown in Fig. 5 are not consistent with values falling outside this range. This range is entirely consistent with the value deduced from the fluorescence measurements where there is no interference from other photoproducts. Thus we may safely conclude that  $r_{CT}(0) = 0.20 \pm 0.04$  and use this value in an analysis of alignment in the *cis* to *trans* reaction of electronically excited *cis*-stilbene.

# F. The anisotropy of *cis*\* and motion along the reaction coordinate

Thus far in this discussion, the position has been taken that the *cis* to *trans* reaction may be considered a two state system kinetically related by Eqs. (8) without an intermediate. The assumption that the time spent on the reaction path is short compared with the lifetime of  $cis^*$  is implicit in such an analysis. This assumption is well supported by the experimental data as discussed at length in Sec. IV A above. However, it is clear, even in the absence of a distinct intermediate, that the time on the reaction pathway is not infinitesimally short. That is, *trans* is not produced instantaneously from *cis*<sup>\*</sup>. The only data from experiments at ~150 fs time resolution that signal the ultrafast motion along the reaction coordinate is the anisotropy of the *cis*<sup>\*</sup> signal as probed at 650 nm.

The anisotropy of  $cis^*$  probed at 650 K was found to decay much faster than *trans* in the same solvents. This decay, especially in hexadecane, is much too fast to be attributed simply to the rotational diffusion of *cis*. For *cis*, *trans*, and DHP approximated as asymmetric ellipsoids, the rotational diffusion coefficients may be calculated in the two limits of slip and stick boundary conditions. The  $S_1 \leftarrow S_0$  transitions of *cis*, *trans*, and DHP are polarized within a few degrees of the long axis of the molecule. Therefore, in the following we will assume they are polarized along the longest principal axis of the ellipsoid. Then the anisotropy decay is given by

$$r(t) = 0.3(2/3 + G)\exp[-(6D - 2\Delta)t] + 0.3(2/3 - G)$$
$$\times \exp[-(6D + 2\Delta)t], \qquad (20a)$$

where

$$D = (D_1 + D_2 + D_3)/3, \tag{20b}$$

$$\Delta = (D_1^2 + D_2^2 + D_3^2 - D_1 D_2 - D_1 D_3 - D_2 D_3)^{1/2}, \quad (20c)$$

and

$$G = (D_1 - D) / \Delta. \tag{20d}$$

The rotational diffusion coefficients  $D_i$  are given by

$$D_i = kT/\eta V \lambda_i \,, \tag{20e}$$

where  $\eta$  is the viscosity in centipoise, V is the volume of the ellipsoid  $(4\pi abc/3)$ , k is the Boltzmann constant, T is the temperature in degrees Kelvin, and  $\lambda_i$  is a friction coefficient. The friction coefficients may be considered in two limits. In the limit of slip boundary conditions, the friction coefficients have been tabulated by Youngren and Acrivos for a range of ellipsoid parameters.<sup>65(a)</sup> The values in Ref. 65(a) were calculated using a definition of  $\lambda_i$ =Torque/ $\eta\pi a^3\omega$ , where a is the longest semiaxis and must be corrected<sup>65(b)</sup> for use in Eq. (20e), where the definition is  $\lambda_i$ =Torque/ $\eta V\omega$ . The values in Table II were obtained by interpolation using the published table of values in Ref. 65 and applying the correction factor  $3a^2/4bc$ .

In the limit of stick boundary conditions, the friction coefficients are given by the following:<sup>66</sup>

$$\lambda_1 = 4(b^3 + c^2) / [(b^2Q + c^2R)abc],$$
 (21a)

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	<u></u>	j b		<b>A</b> <sub>1</sub>	$ au_1{}^{d}$	A2	$ au_2^d$
	a,b,c (Å)	slip	stick	[Top (slip), bottom (stick boundary conditions)]			
	5.85	0.530	5.850	0.0044	6.73	0.356	14.4
DHP	4.2	2.419	8.055				
	2.65	0.754	8.652	0.002	71.8	0.398	92.4
Cis	5.7	0.138	5.212	0.001	2.36	0.399	10.9
	3.9	1.296	7.398				
	3.25	0.665	7.685	0.0005	71.5	0.3995	92.9
Trans	6.85	1.574	5.762	0.021	14.0	0.379	33.2
	3.5	8.475	13.787				
	1.75	2.884	13.322	0.0001	51.4	0.3999	97.7
TWIST	6.7	0	5.124			0.4	15.3
	4.2	0.918	7.465				
	4.2	0.918	7.465			0.4	124

TABLE II. Parameters for the calculation of stick and slip rotational diffusion constants.\*

Calculation as described in the text, considering *cis, trans*, and DHP as asymmetric ellipsoids having the axes lengths listed above. The volume of the ellipsoid is  $(4/3)\pi abc$ .

<sup>b</sup>Slip friction parameters interpolated from the numerical calculation of Youngren and Acrivos (Ref. 65) and corrected for the true volume of the ellipsoid.

Stick friction parameters calculated as described in the text.

<sup>d</sup>Rotational diffusion times in ps/cp at 298 K.

$$\lambda_2 = 4(c^2 + a^2) / [(c^2 R + a^2 P) abc], \qquad (21b)$$

$$\lambda_3 = 4(a^2 + b^2) / [(a^2 P + b^2 Q)abc], \qquad (21c)$$

where



1000\*[VISCOSITY/TEMPERATURE]

FIG. 22. Rotational diffusion of DHP and stilbene. The open symbols are data obtained for trans-stilbene from the literature {(circles) alkane solvents [data from S. H. Courtney, S. K. Kim, S. Canonica and G. R. Fleming, J. Chem. Soc. Faraday Trans. 2 82, 2065 (1986)]}; (triangles) alkane solvents (Ref. 11), and (squares) alcohols (Ref. 62). The solid symbols represent data obtained in the current investigations [(circles) DHP from Refs. 24 and 29] {the value used for hexadecane solvent is an average of those reported in Refs. 24 and 29 along with an additional measurement of 70 ps; the values vary so much because of the small magnitude of the DHP absorption [(triangles) cis data as reported in Table I]}. The solid lines are the major components calculated for slip and stick boundary conditions as discussed in the text and in Table II [(solid line) cis; (dashed line) DHP; (dotted-dashed line) trans]. The transstilbene data in alkane solvents is reasonably well approximated by slip boundary conditions, however, detailed studies have shown that the solvent dependence is not really this simple (Refs. 9 and 11). Note that while DHP also falls close to the slip limit, cis is much faster than the slip calculation predicts.

$$P = \int_0^\infty (a^2 + s)^{-1} [(a^2 + s)(b^2 + s)(c^2 + s)]^{1/2} ds,$$
(22a)

$$Q = \int_0^\infty (b^2 + s)^{-1} [(a^2 + s)(b^2 + s)(c^2 + s)]^{1/2} ds,$$
(22b)

$$R = \int_0^\infty (c^2 + s)^{-1} [(a^2 + s)(b^2 + s)(c^2 + s)]^{1/2} ds.$$
(22c)

The values of these friction coefficients for the ellipsoids used to approximate *cis, trans*, and DHP are given in Table II.

The data and calculations are summarized in Fig. 22. Only the slow components of the calculated biexponential anisotropy decays are shown as these dominate the results. *Trans* and DHP in alkane solvents are in fairly good agreement with the values calculated for slip boundary conditions. The experimental value for  $cis^*$  in hexadecane, on the other hand, is much faster than the slip calculation predicts. Clearly, the fast anisotropy decay of  $cis^*$  in hexadecane (and presumably in the other solvents) is related to motion on the reaction coordinate rather than to the rotational diffusion of cis.

Two mechanisms for the fast anisotropy decay of *cis*\* are considered. First, the decay may be due to very fast rotational diffusion of stilbene in a compact, more spherical, intermediate structure. Second, the decay may be due to a reorientation of the transition dipole due to motion of the stilbene nuclei on the excited state potential energy surface. It is important to make a distinction between these two mechanisms because the first will result in a broad distribution of product transition dipole directions, while the second will result in a much narrower distribution.

The first mechanism would require an intermediate state with a much more spherical shape than expected for the cis isomer. For example, rotation of the phenyl rings from 43° towards a geometry where they are perpendicular to the ethylenic C-C bond will result in a much more compact and spherical structure where the slip diffusion times are very fast. However, such an intermediate is not consistent with the initial motion postulated on the basis of resonance Raman experiments<sup>46</sup> or with an intermediate having a 90° twisted geometry. The initial dynamics proposed by Myers and Mathies involves motion of the ethylenic carbons and hydrogens and torsion of the phenyl rings toward a more planar DHP-like geometry. This type of a motion is also in agreement with the deductions of Petek et al.<sup>67</sup> This motion will result in a more asymmetric shape and a longer rotational diffusion time which approaches that calculated for DHP. A 90° twisted geometry results in a more elongated structure which, when approximated as a prolate ellipsoid (see Table II) and assuming long axis polarized transitions, also results in longer rather than shorter rotational diffusion times. In light of the above discussion, it appears that the fast anisotropy decay of cis\* is due to motion on the excited state potential energy surface rather than rotational diffusion.

The magnitude of the rotation of the transition dipole may be estimated under the approximation that the size and shape of the molecule is constant and that the decay of the anisotropy due to rotational diffusion is single exponential and independent of the orientation of the transition dipole. For stilbene, these conditions may be met by assuming a prolate spheroid which rotates in space around one of the short axes under the influence of the excited state potential energy surface with the transition dipole direction and the long axis of the spheroid always coincident. In this case, r(t) may be approximated by

$$r(t) = r_0(t) \exp(-t/\tau_{\text{diffusion}}), \qquad (23)$$

where  $r_0(t)$  is the change in the anisotropy due only to the rotation of the spheroid and thus the probed transition dipole as a function of time on the reaction coordinate. Under these assumptions, the transition dipole rotates 8° or 9° ( $\tau_{\text{diffusion}} = 36-82 \text{ ps}$ ) in hexadecane and 7°±3° ( $\tau_{\text{diffusion}} =$ 7-16 ps) in hexane within the 1/e lifetime of the excited state. The uncertainty is greater in hexane because the exact value of the diffusional contribution is far more important. This is consistent with the rotation angle (10° if  $\tau_{\text{diffusion}} = 25 \text{ ps}$ ) estimated in the same manner from the data of Todd *et al.* for *cis*-stilbene in isopropanol.<sup>23</sup>

# G. Analysis of reactant to product alignment in the photoreactions of *cis*-stilbene

In the above discussion, we have found an initial anisotropy for *trans*-stilbene formed from *cis*-stilbene of 0.20  $\pm$ 0.04. Previous studies have determined that the initial anisotropy for DHP formed from *cis*-stilbene is 0.17  $\pm 0.03$ .<sup>24,29</sup> These numbers provide information on the average reactant to product alignment in the photoisomerization reactions of *cis*-stilbene

$$r(0) = (2/5) \langle P_2(\cos\Theta) \rangle.$$
(24)

If the products are formed in a narrow Gaussian-like distribution of relative alignments, these anisotropy values may be converted to average angles in a straightforward manner. For the anisotropies given above,  $\langle \Theta \rangle_{CT} = 35^{\circ} \pm 4^{\circ}$ and  $\langle \Theta \rangle_{CD} = 38^{\circ} \pm 3^{\circ}$ . These angles provide a constraint which must be satisfied when considering the feasibility of proposed reaction coordinates.

The most frequently proposed reaction coordinate for the cis to trans reaction involves torsion about the central double bond through a 90° twisted (or perpendicular) intermediate. For the cis to DHP reaction, the most straightforward reaction coordinate involves rotation of the phenyl rings to a more nearly planar geometry followed by electronic rearrangement to form a bond between 4a and 4b positions on the phenyl rings. In an isolated molecule, such reaction coordinates must involve a rotation of the molecule about the  $C_2$  symmetry axis (in the following, this is defined as the y axis) in order to conserve angular momentum. Linear momentum is conserved by requiring the center of mass to remain fixed. The rotation produced by the reaction coordinate may be estimated by assuming a piecewise linear reaction coordinate. For a linear reaction coordinate, the conservation of angular momentum is guaranteed if<sup>68</sup>

$$0 = \sum_{i} m_i \left( \mathbf{R}_i^{(r)} \times \mathbf{R}_i^{(p)} \right), \tag{25}$$

where the summation is over the *i* atoms with masses  $m_i$  in the molecule. The coordinates  $\mathbf{R}_i^{(r/p)}$  are the Cartesian coordinates of the atoms of the reactants/products with the origin at the center of mass. Thus the conservation of angular momentum defines the precise orientation of the product molecule with respect to the reactant molecule. More complicated reaction coordinates may be approximated by calculating the coordinates at specified intervals and assuming linear reaction coordinates connecting these intervals. This will be referred to as a piecewise linear reaction coordinate. Torque-free calculations of this sort were recently reported by Michl and co-workers.<sup>69</sup>

Two model systems have been considered to calculate the rotation of the molecule about the symmetry axis. The first model consists of two phenyl rings in a planar *cis* configuration about a somewhat elongated central carboncarbon bond. The y axis is defined as the  $C_2$  symmetry axis, The x axis is defined by the initial direction of the ethylenic double bond and the z axis is out of the plane of the molecule. The hydrogen atoms are omitted from the calculation. The rings are then rotated in 10° increments to the planar *trans* configuration and Eq. (25) is made to hold for each incremental step by rotating the direction of the ethylene bond in the xz plane. Figure 23(a) shows the rotation as a function of an ethylenic torsion angle and compares the result with that obtained for a reaction coordinate consisting of two linear steps and consisting of



FIG. 23. Rotation of the stilbene molecule around the Y axis required to conserve angular momentum assuming piecewise linear reaction coordinates. (a) Y-axis rotation produced by moving from a planar *cis* structure to a planar *trans* structure. The circles are the values calculated for 10° incremental linear steps in the reaction coordinate. The squares are the values calculated in a two linear reaction steps  $cis \rightarrow 90^\circ$  twisted  $\rightarrow$  *trans*. The + is calculated for a one step linear reaction coordinate. The triangles are the values calculated for a two step *cis* to *trans* reaction using realistic coordinates. (b) Y-axis rotation produced by moving from 45° phenyl torsion angles to a planar *cis* structure. The circles are calculated for 5° incremental linear steps in the reaction coordinate. The square was calculated for a one step linear reaction using realistic coordinates. (b) *Y*-axis rotation produced by moving from 45° phenyl torsion angles to a planar *cis* structure. The circles are calculated for 5° incremental linear steps in the reaction coordinate. The triangle is the value obtained for a single step *cis* to DHP reaction using realistic coordinates.

one linear step. The error introduced by assuming one or two steps is only a few degrees. The overall effect is a rotation of  $-38.4^{\circ}$  around the y axis.

The other motion that must be considered is the rotation of the phenyl rings from between 30° and 50° to a more nearly planar geometry. A calculation performed by starting with a model *cis* molecule, where the phenyl rings are twisted by 45°, is shown in Fig. 23(b). The rings are rotated to a planar geometry in 5° increments. This results in an overall rotation around the y axis of  $-5^\circ$ . Using a one step linear reaction coordinate predicts a rotation of  $-4.6^\circ$ .

The predicted values for a two step reaction through a twisted intermediate to form *trans* stilbene and a one step reaction to form DHP are also shown in Fig. 23. These



FIG. 24. A comparison of the experimentally determined angle between the pumped and probed transition dipoles for the cis to trans reaction with those expected in the absence of friction and in the presence of a very large friction. In the absence of any knowledge of the problem, the measured anisotropy provides information only on  $\langle \cos^2\Theta_{CT} \rangle$ . However, for fast reactions such as those of cis-stilbene, it is reasonable to assume a fairly narrow Gaussian-like distribution of final product orientations. In this case, the anisotropy measurement provides  $\langle |\Theta_{CT}| \rangle$ . Additional constraints may be found in the physics of the reaction. The reaction will conserve the direction of the  $C_2$  axis in space because (at least for the reaction coordinates discussed) no angular momentum would be generated around the x or z axes to force a rotation. The only mechanism for rotation is the slow rotational diffusion of the molecule. Thus  $\langle |\Theta_{CT}| \rangle$ defines not a cone, but an angle in the xz plane. In addition, it is unreasonable to assume that the reaction from cis to trans occurs with the rings passing through each other. The steric effects that cause cis-stilbene to have an 8° ethylenic torsion and a 45° phenyl ring rotation at the ground state equilibrium geometry will cause the torsion to occur in a defined direction. This, combined with a knowledge of the transition dipole directions, produces the measured angle displayed in this figure. Note how the rotation  $\delta\phi$  allows the isomerism from cis<sup>\*</sup> with its ethylene bond parallel to x to occur by minimizing the volume of solvent swept out during the motion.

points were calculated for more realistic coordinates for reactants and products. The *cis* and *trans* coordinates were obtained from gas electron diffraction data.<sup>70,71</sup> The 90° twisted structure was estimated using the optimized geometry calculated by Troe and Weitzel.<sup>41</sup> The coordinates for DHP were obtained from calculations.<sup>63</sup> Once again, the hydrogen atoms were omitted from the calculation. These calculations indicate a rotation of  $-37^{\circ}$  for the *cis* to *trans* reaction and a rotation of  $-4.5^{\circ}$  for the *cis* to DHP reaction.

The next step is to consider what happens when a surrounding solvent is introduced into the problem. Although there must still be a conservation of angular momentum in the overall system, the system is no longer an isolated molecule. Intuitively it appears as if the solvent should decrease the overall rotation of the molecule since the friction causes energy transfer to the solvent motions resulting in a final angle somewhat smaller than given above. If the frictional torque due to rotation around the yaxis is very large, the molecule will open up without any rotation; however, since the friction on the torsion and the friction on the rotation are related, the reaction will occur very slowly. *Clearly another view of the reaction coordinate*  is needed when the motion occurs in a frictional environment.

# H. SOLUTION PHASE REACTION COORDINATES-

Barrier crossing and barrierless motions that result in conformational changes may involve complicated nuclear motions of the molecule when viewed in the laboratory frame even though the molecule frame based motion is relatively simple. Obviously such effects must be incorporated in the interpretation of frictionally controlled processes even though the effects of motions derived from the internal potential on overall translations and rotations play little role in gas phase processes. In that case, the conservation laws for linear and angular momenta determine that the overall motions precisely compensate for any momentum changes that result from the internal forces. The situation is quite different in condensed phase, where the reaction coordinate must be determined by *both* the internal and overall motions.

The basic principles needed to understand the reaction coordinate appropriate to isomerization of stilbene are implicit in previous studies of rotational diffusion of flexible chains,<sup>72</sup> atom transfer reaction in solution,<sup>73</sup> and most specifically in recent work by Moro on the frictional coupling of internal and external motions.<sup>74</sup> The key point for the present discussion is that the overall motions that occur in solution phase reactions are derived from diffusion equations and not from the conservation of angular momentum. In effect, this conservation is accommodated by considering the reaction coordinates as pathways of minimum friction. As long as the angular momentum correlation function decays rapidly enough, say in comparison with the orientational correlation function, the diffusion approach will be adequate. Since the angular momentum correlations decay on the time scale of collisions and isomerization reactions are often slower than this, the present view should represent a useful starting point. In the cases where relatively large volumes are being moved under the influence of the internal potential, it is likely that a diffusive model is valid.

The overall motions which are uncoupled to the potential based dynamics in a gas are coupled in a solution as a result of friction. For the case of isomerization, this is readily seen by considering the isomerization of an ABBA molecule about the B-B axis from a cis ( $\theta = 0$ ) to a trans  $(\theta = \pi)$  configuration. The internal potential exerts a force on the A atoms tending to open the dihedral angle. As a consequence of there being a solvent present, these motions are opposed by a frictional force. The moments of these frictional forces about the center of mass are not conservative, so the whole system is caused to rotate about its y axis. This rotation of the whole system minimizes the friction on the motion through the reaction coordinate and therefore must be taken into account as part of the reaction coordinate. The effect just described is not expected to be small when the internal and external motions involve hydrodynamic volumes of comparable magnitudes. Although, as pointed out by Moro,<sup>74</sup> they would be negligible if rotation of a small group (say methyl) attached to a large group were being considered.

As indicated above, the effect of frictional coupling of the internal and overall motion must be considered as part of the reaction coordinate in isomerism processes. This is because about the same volume of solvent is involved in both motions. The effect of overall motion is to reduce friction for motion across the potential surface. There appear to be two obvious ways to deal with this problem. In the first, the friction associated with each atom in the motion could be considered along with constraints from the internal potential and the relative positions of the atoms at each point in the motion. In the second, qualitative approach, a Langevin equation for motion in the reactive coordinate can be coupled, by frictional forces, to the Langevin equation for overall motion. Thus for the internal motion on a surface  $V(\theta)$ , the motion is governed by

$$\ddot{\theta} = -\beta_i \dot{\theta} + V'(\theta) / I_i - \gamma_{ie} \dot{\phi}, \qquad (26)$$

where  $\phi$  represents the overall angular velocity, and  $I_i$  and  $\beta_i$  are the internal motion moment of inertia and angular friction. Since there is no potential associated with overall motion, the Langevin equation is approximately

$$\ddot{\phi} = -\beta_e \dot{\phi} - \gamma_{ei} \dot{\theta}, \qquad (27)$$

where  $I_e(\phi)$  is the overall moment of inertia implicit in  $\beta_e$ , and  $\gamma$  is the angular frictional coupling between the motions. That is,  $\gamma$  provides for a retarding force on the overall motion proportional to how quickly the system is undergoing the internal motion. In general, the moment of inertia of the whole system changes as the internal motion proceeds. For the case that these changes are neglected and the overall motion is more overdamped than the internal motion, we may set  $\ddot{\phi}=0$  and obtain the motion through the reactive coordinate as

$$\ddot{\theta} = -\beta_i (1 - \alpha^2) \dot{\theta} + V'(\theta) / I_i \,. \tag{28}$$

In most cases of isomerism, this motion would also be overdamped with  $\alpha^2 = \gamma_{ie} \gamma_{ei} / \beta \beta_e \approx \gamma^2 / \beta_i^2$ . Thus it is seen that the friction on the reactive passage is *reduced* by the factor  $(1 - \alpha^2)$  is a result of the coupling to the overall motion. Equation (27) implies that a rotation of the overall system by  $\alpha \,\delta \Phi$  should occur as a result of a reactive motion  $\delta \theta$ . Such coupling should have profound effects on the anisotropy experiments that excite the *cis* structure and probe the *trans*. Indeed, in order to explain these observations by this simple approximation, the factor  $\alpha$  would require to have the value

$$\alpha = (\delta\theta)^{-1} \left\{ \theta_{CT} - \cos^{-1} \left[ \pm \left( \frac{1+5r}{3} \right)^{1/2} \right] \right\} = 0.26, \quad (29)$$

where  $\theta_{CT}$  is the angle between *cis* and *trans* transition dipoles when there is no overall motion and *r* is the measured anisotropy extrapolated to earliest times. Thus the friction along the reaction path is reduced by 7% as a result of incorporating about 25° of overall motion, according to this analysis. As shown above, the overall motion is 38° in the absence of friction due to the compensation of the angular momentum along the reaction path, so the + sign in Eq. (29) must be the more correct one to use.

In the context of this discussion, it is also interesting to consider the  $\sim 8^{\circ}$  rotation of the cis\* transition dipole direction deduced in the previous section during the 1/e lifetime of the excited state. If, as predicted by theory, the transition dipole direction remains approximately parallel to the ethylenic double bond for small torsion angles, an 8° rotation may be brought about by a  $\sim 22^{\circ}$  ethylenic torsion, or the combination of a 45° rotation of the phenyl rings toward a more planar geometry and a  $\sim 12^{\circ}$  ethylenic torsion. A somewhat smaller torsion angle will account for the observed anisotropy decay if the transition dipole follows the longest axis of the molecule. Thus the fast decay of the cis\* anisotropy is again seen to be consistent with motion occurring along the reaction coordinate, at least the cis to trans reaction coordinate, during the lifetime of the cis excited state.

The 37° angle deduced for the *cis* to DHP reaction is much harder to account for. A reaction coordinate consisting of a simple rotation of the phenyl rings followed by an electronic realignment should result in a high degree of alignment between the reactant and product. For  $S_0 \leftarrow S_1$ transition dipoles deduced from simple calculations, and the *y*-axis rotation deduced above  $\langle |\Theta_{CD}| \rangle = 5^\circ \pm 5^\circ$ . This range of angles results in a very high predicted anisotropy  $r_{CD}(0) = 0.39 \pm 0.01$ . There are several possible explanations for the discrepancy between these two results.

The visible absorption of DHP could consist of transitions to more than one electronic state, although this is contrary to the prediction of simple pi-orbital calculations. Calculations predict an x polarized transition at 24 000  $cm^{-1}$  (-2° in the xz plane), two y polarized transitions at 35 000 cm<sup>-1</sup>, and an x polarized transition at 45 000 cm<sup>-1</sup>  $(-6^{\circ} \text{ in the } xz \text{ plane.}^{63} \text{ The observed anisotropy could be}$ accounted for if one of the y polarized transitions actually lies at a somewhat lower energy. This possibility needs to be explored experimentally and theoretically. Resonance Raman depolarization ratios of the totally symmetric vibrational bands of DHP as a function of wavelength may expose the presence of overlapping transitions polarized in different directions.<sup>75,76</sup> In addition, more accurate measurements of  $r_{CD}(0)$  as a function of wavelength should uncover the presence of more than one state.<sup>77</sup>

Assuming, as appears likely, that the visible absorption consists of one electronic transition polarized in approximately the direction predicted by pi-orbital calculations, the low experimental anisotropy indicates that the reaction coordinate for the *cis* to DHP reaction is more complicated than a phenyl ring rotation and an electronic rearrangement. Although a simple reaction coordinate is aesthetically pleasing, it may not be correct. In particular, there have been several theoretical calculations exploring the possible role of hydrogen migration coordinates in the isomerization reactions of polyenes.<sup>78</sup> Isotopic substitution studies that are underway of both the reactants and the products at ultrafast time resolution will help to explore the reaction coordinate in more detail.

## **VI. SUMMARY AND CONCLUSIONS**

The experimental results and discussion presented in this paper provide the most detailed picture to date of a photochemical isomerization reaction in the condensed phase. The *cis* to *trans* reaction proceeds very quickly, occurring in at most a few hundred femtoseconds following the decay of the *cis* excited state. The most likely form of the potential surface is a shallow slope toward opening the ethylenic torsion angle and rotating the phenyl rings followed by an ultrafast nonadiabatic transition to a PES with a much steeper slope for isomerization. The resonance Raman measurements and the *cis*<sup>\*</sup> absorption and fluorescence anistropy measurements probe motion along the initial PES.

The energy partitioning in this reaction can be estimated from the approximate energy content of the product molecules. Two experiments were performed to analyze the energy content of the *trans* product. The time-resolved absorption experiments demonstrated that IVR is not ultrafast in stilbene. The energy placed in the Franck–Condon active modes by the excitation pulse (332, 312, or 250 nm) remains in those modes until long after the reaction is complete. These modes have only spectator status in the reaction, and thus, this energy plays no role. Following excitation at 312 nm, on average  $\sim 1900 \pm 500 \text{ cm}^{-1}$  remains trapped in the Franck–Condon active modes.

The integrated fluorescence yield experiments demonstrated that the molecule was formed hot in the low frequency modes directly coupled to the *cis/trans* reaction coordinate, but not hot enough to account for all or even most of the excess energy placed into the molecule by the excitation photon. Assuming a Boltzmann distribution of the energy in these modes, the energy content corresponds to a temperature of ~600-800 K or  $\langle E_{lf} \rangle = 5000-15000$ cm<sup>-1</sup>. The large range in the average energy is due to the uncertainty in the temperature estimate and the uncertainty in how many modes this energy distribution is spread over.

Excitation of  $cis^*$  at 312 nm placed  $E/h=c/\lambda + \Delta H/h=32\ 050+1600\ cm^{-1}=33\ 650\ cm^{-1}$  into the system. In the above analysis, we have found that ~7000-17\ 000\ cm^{-1}\ or\ 20\%-50\% of this amount can be accounted for as internal excitation of the vibrational degrees of freedom. Of this amount, 5000-15\ 000\ cm^{-1}\ (15\%-45\%) of the total) is probably distributed by the reaction as a result of the internal friction on the reaction coordinate. At least 50% of the initial energy is not accounted for and has likely been transferred to the surrounding solvent through external friction on the reaction coordinate.

The importance of these frictional effects are highlighted by our failure to observe a *trans* fluorescence signal following the excitation of *cis*-stilbene vapor.<sup>79</sup> Because there is no external friction on the reaction coordinate in this case, all of the energy remains in internal degrees of freedom. The *trans* molecule is produced with much more energy in the low frequency modes and thus, when *trans* is excited to *trans*<sup>\*</sup>, the molecules escape over the barrier very quickly, reducing the *trans* fluorescence quantum yield to near zero. The anisotropy measurements again demonstrate that frictional effects are important. The conservation of angular momentum is distributed over the stilbene molecule and the surroundings through the interaction of the stilbene molecule with the surroundings during the reaction (the external friction on the reaction coordinate). This effect accounts quite well for the initial anisotropy found in the *trans* photoproduct absorption and illustrated in Fig. 24.

The DHP anisotropy is much harder to account for and must imply either the presence of two or more electronic transitions in the visible absorption band or a much more complicated reaction coordinate than a simple phenyl ring torsion toward a more planar geometry followed by electronic rearrangement to form DHP. This conundrum will require further efforts, both experimental and theoretical, before a reasonable solution is proposed.

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 $\langle E_{\rm RT}\rangle + \Delta H + hc/\lambda = \sum hv_i [\exp(hv_i/k_BT) - 1]^{-1},$ 

where  $\langle E_{\rm RT} \rangle$  is the average vibrational energy at room temperature,  $\Delta H$  is the energy difference between the *cis*-stilbene minimum and the relevant product minimum, and  $hc/\lambda$  is the photon energy. The vibrational frequencies for the 72 vibrational degrees of freedom were obtained from the calculation of Warshel (Ref. 50). This estimate of the temperature is insensitive to the exact values of the vibrational frequencies.

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time, a phenomenon not observed in other solvents where there is no suggestion of a wavelength dependent  $cis^*$  lifetime. However, measurements made in our laboratory failed to confirm the wavelength dependence in cyclohexane. The  $cis^*$  lifetime was found to be  $1.42\pm0.03$  ps. Although this is somewhat longer than would be predicted by the viscosity of cyclohexane, there is no evidence for unusually fast vibrational relaxation or other atypical behavior in cyclohexane.

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$$= \frac{1}{27} \left\{ 1 + \frac{4}{5} P_2(a \cdot b) P_2(C \cdot T) e^{-6Dt} + \frac{4}{5} P_2(a \cdot c) \right.$$
$$\left. \times P_2(C \cdot V) e^{-6D\tau} + \frac{4}{5} P_2(c \cdot b) P_2(T \cdot V) e^{-6D(\tau - t)} \right.$$
$$\left. + \frac{16}{35} Q_2(a,b,c) Q_2(C,T,V) e^{-6D\tau} \right],$$

where **a**, **b**, and **c** are any two unit vectors in the laboratory fixed frame having the significance discussed in the text and where  $Q_2(\hat{x},\hat{y},\hat{z})$  is given as

 $Q_2(\hat{x},\hat{y},\hat{z}) = 1 - \frac{1}{2}[(x \cdot y)^2 + (y \cdot z)^2 + (z \cdot x)^2] + \frac{9}{2}[(x \cdot y)(y \cdot z)(z \cdot x)].$ Note that in the special case that V = T,  $P_2(C \cdot V) = P_2(\cos \Theta_{CT})$ , this reduces to the expressions used in the text. The conditions under which

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