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Molecular Structure of Stilbene in the $T_1$ State. Transient Resonance Raman Spectra of Stilbene Isotopomers and Quantum Chemical Calculations

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Time-resolved resonance Raman spectra are reported for the lowest excited triplet state of stilbene and three of its isotopomers. The spectra were obtained using a two-laser pump-and-probe arrangement under various experimental conditions. The spectrum of trans-stilbene after direct excitation in a glassy medium at low temperature (glycerol at 203 K) is compared with that of cis-stilbene under sensitized excitation in solution at room and low temperature. The dependence of resonance Raman spectra on excitation wavelength in both cases is investigated. The observed spectra and isotopic shifts are discussed and interpreted on the basis of quantum chemical molecular orbital calculations. Optimized geometries and vibrational frequencies in the $T_1$ state are calculated by a semiempirical QCFF/PI Hamiltonian and by means of ROHF ab initio methods using the 6-31G basis set. $T_1 \rightarrow T_2$ transition energies and moments are calculated using QCFF/PI and CNDO/S methods, and the triplet–triplet transition responsible for the observed $T_1 \rightarrow T_2$ absorption and resonance Raman spectra is identified as the $T_1 \rightarrow T_{10}$ transition. Corresponding resonance Raman intensities are calculated by QCFF/PI. It is concluded that trans- and cis-stilbene adopt a common equilibrium geometry in the $T_1$ state, with the ethylenic C=C bond of the ground state being weakened to a bond with essentially single-bond character in the $T_1$ state. The observed spectra in the glass are assigned to a planar geometry, implying that a relative minimum is found at a planar trans geometry ($C_2v$ point group) on the potential energy surface of the $T_1$ state. A number of observed non-totally symmetric vibrational modes are tentatively assigned to combinations of either $a_0$ or $b_0$ modes, deriving their intensities from relatively large frequency changes upon $T_1 \rightarrow T_{10}$ excitation.

I. Introduction

Stilbene (1,2-diphenylethylene) is widely used as a model in studies of C=C double-bond isomerization. The $E \leftrightarrow Z$ (trans $\leftrightarrow$ cis) photoisomerization of stilbene has been reviewed in detail. Structure and dynamics on the stilbene $S_1$ potential energy surface (PES) have been studied in a number of papers. The $S_0$ and $S_1$ states of $(E)$- and $(Z)$-stilbene have been studied by Raman and resonance Raman (RR) spectroscopies as have their anion and cation radicals. Structure and dynamics on the $T_1$ PES have been studied by time-resolved optical absorption and emission spectroscopy, by optically-detected magnetic resonance (in a single crystal at 1.3 K), and recently by time-resolved RR spectroscopy. The spectroscopic triplet energy of the $T_1$ state has been determined as 51.0 kcal/mol for $(E)$-stilbene and 55.5 kcal/mol for $(Z)$-stilbene; the relaxed triplet energy measured by photoacoustic calorimetry is 46.5 kcal/mol for $(E)$-stilbene and 42.0 kcal/mol for $(Z)$-stilbene.

Görner and Schulte-Frohlinde studied the $T_1$ state of stilbene by optical absorption methods. At room temperature, a structureless $T_1 \rightarrow T_n$ absorption spectrum, identical for $(E)$- and $(Z)$-stilbene and increasing monotonically from 400 nm down to the experimental limit of 355 nm, was observed only in the presence of a sensitizer. In Ar-saturated methanol solution at 298 K, the triplet lifetime was 62 ns for $(E)$-stilbene and 60 ns for $(Z)$-stilbene. In viscous solvents and glasses at low temperature, a structured $T_1 \rightarrow T_n$ absorption spectrum with a lifetime of $\approx 10$ ms was observed upon direct excitation of $(E)$-stilbene. In glycerol at 235 K, absorption maxima were found at 385, 366, and 350 nm; in ethanol at 98 K, maxima were found at 381, 361, and 343 nm. It was concluded from these studies that for stilbene in the $T_1$ state an equilibrium exists between a planar $trans$ geometry ($C_2v$ point group) and a more stable geometry that is twisted by $90^\circ$ at the central CC bond ($P$, perpendicular).

$$E = P \leftrightarrow Z$$

The equilibrium was found to be dependent on solvent polarity. On the basis of quenching by azulene, an equilibrium constant $K_1 = k_1/k_{-1}$ of 4.6 in methanol at room temperature was determined. The value of $K_1$ was higher in nonpolar solvents.

Saltiel et al. discussed the relative energy of the $E$, $P$, and $Z$ geometries of $T_1$ and the energy gap at the $P$ geometry between the $T_1$ and $S_0$ PES. According to their view, a minimum on the $T_1$ PES is found only at the $P$ geometry, with local maxima at the $E$ and $Z$ geometries, and the minimum on the $T_1$ PES at $90^\circ$ twist is below the maximum on the $S_0$ PES at this geometry, i.e., the potential energy surfaces cross.

We have previously reported time-resolved RR spectra of stilbene in the $T_1$ state. Room temperature RR spectra were identical for $(E)$- and $(Z)$-stilbene. This confirmed that a common
equilibrium distribution of triplet species is reached from either one of the two ground-state isomers. At 203 K and larger viscosity, the T1 RR spectrum of (E)-stilbene was qualitatively similar to the room temperature ones, but the RR bands were significantly sharper at 203 K, especially in the frequency region below 1000 cm⁻¹. At this temperature, several broad features at low frequencies separated into distinct bands and a strong band appeared at 201 cm⁻¹. This band was not observed at 293 K.

The T1 RR spectra were interpreted on the basis of preliminary calculations using a modified version of the semiempirical quantum mechanical consistent force field program (QCFF/PI). Under the assumption of a planar E structure in the T1 state, most of the observed RR bands were assigned to normal modes of a₂ symmetry. However, a number of bands observed at frequencies below 1000 cm⁻¹ could not be assigned to a₂ fundamentals. These unassigned bands included a RR band of considerable intensity at 459 cm⁻¹. The bands were tentatively assigned to overtone or combination modes or to fundamental modes of symmetry other than a₂.

To understand more completely the T1 RR spectra of stilbene, and the implications for the molecular structure of the stilbene triplet, we have continued our stilbene studies with respect to both experiment and theory. Experimentally, we have investigated isotopically substituted derivatives of stilbene, and we have obtained triplet RR spectra with different Raman excitation wavelengths and at different temperatures. On the theoretical side, we have performed more extensive quantum chemical calculations. Geometry optimizations and frequency calculations in the T1 state were carried out using the QCFF/PI Hamiltonian on the one hand and ab initio ab initio calculations using the CI procedure outlined above, with both the QCFF/PI and the CNDO/S Hamiltonians. Vibronic interactions and Herzberg–Teller-induced transition moments in the triplet manifold have been calculated according to refs 50 and 51 using the same CI and the CNDO/S Hamiltonian. No attempt has been made to study higher excited triplet states by ab initio calculations, since these have not yet been shown to be sufficiently accurate for our purpose. The evaluation of the Franck–Condon integrals is performed by associating to each totally symmetric normal mode a harmonic oscillator due to that normal mode rotation and frequency variation upon electronic transition.

To obtain time-resolved RR spectra, excited at 385 nm in glycerol at 203 K, of the following isotopomers of (E)-stilbene: C₆H₅HCCCH₂C₆H₅ (E-St), C₆H₅H⁺H⁺CHCH₂CH₂CH₂ (E-St-1C₂), C₆H₅H⁺H⁺H⁺CHCH₂CH₂ (E-St-d₁₂), and C₆H₅H⁺H⁺H⁺CHCH₂CH₂ (E-St-d₁₀) (Scheme 1). The spectra are interpreted on the basis of the theoretical calculations. For E-St and E-St-1C₂ in glycerol at 203 K, we report depolarization ratios of RR bands. For (Z)-stilbene (Z-St) in methanol with benzophenone as sensitizer, we report the T1 RR spectra at 293 and 203 K with 381.2- and 371.2-nm Raman excitation.

II. Quantum Chemical Calculations

A. Methods. Equilibrium geometries, normal coordinates, and vibrational frequencies were computed by the QCFF/PI program, upgraded as described in refs 42 and 43. All singly excited determinants (113) arising from the HOMO–LUMO reference determinant in a space of 5₄,5₅* molecular orbitals were included in the CI scheme. Calculations were also performed by the Gaussian 92 series of programs at the ROHF level employing a 6-31G atomic basis set. The vibrational frequencies obtained in this way were scaled by a common factor of 0.9. The semiempirical QCFF/PI model, despite its modest requirement of computational resources, has been shown to be quite reliable in describing conjugated and aromatic systems and hence provides an excellent first level of description. The ROHF ab initio calculation should provide a good description of the T1 state of stilbene, since this state is essentially a one-configuration state. Electronic energies and wave functions of higher triplet states were computed by the CI procedure outlined above, with both the QCFF/PI and the CNDO/S Hamiltonians. Vibronic interactions and Herzberg–Teller-induced transition moments in the triplet manifold have been calculated according to refs 50 and 51 using the same CI and the CNDO/S Hamiltonian. No attempt has been made to study higher excited triplet states by ab initio calculations, since these have not yet been shown to be sufficiently accurate for our purpose. The evaluation of the Franck–Condon integrals is performed by associating to each totally symmetric normal mode a harmonic oscillator due to that particular normal mode in the Raman spectrum. In the absence of normal-mode rotation and frequency variation upon electronic excitation, the displacement parameter, B, of a given totally symmetric mode furnishes a measure of its Franck–Condon activity. B is defined as

\[ B_i = 0.172 \omega_i^{1/2} (x_i - x_0) \lambda^{1/2} \lambda_i \]  

(2)

where \( \omega_i \) and \( \lambda_i \) are the \( i \)th vibrational frequency and normal-mode coordinate in the excited state, \( M \) is the matrix of atomic masses, and \( x_i, x_0 \) are the Cartesian coordinate vectors defining the equilibrium structure of the two electronic states involved in the transition. The Franck–Condon intensity for a transition from the vibrationless ground state to the \( i \)th quantum of the progression is simply given by

\[ F_{\omega i} = \exp(-\gamma) \gamma^\nu / \nu! \]  

(3)

where

\[ \gamma_i = 0.5 B_i^2 \]  

(4)
Oscillator strength is $T_{lo}$, with $f = 1.14$, located at 3.70 eV above absorption observed at 380 nm, corresponding to 3.26 eV. All TI. Thus, $T_{lo}$ represents the state responsible for the intense and the oscillator strengths $f$ with respect to TI of the lowest twisted geometry. In Table 3 and Figure 1.

In Table 3 and Figure 1 we report the energies and the oscillator strengths $f$ with respect to $T_1$ of the lowest excited triplets at the three most significant geometries. At the $trans$ geometry, the lowest triplet state with an appreciable oscillator strength is $T_{lo}$, with $f = 1.14$, located at 3.70 eV above $T_1$. Thus, $T_{lo}$ represents the state responsible for the intense absorption observed at 380 nm, corresponding to 3.26 eV. All the other states in this energy range possess vanishingly small oscillator strengths. A similar result is found for the $cis$ geometry. At the twisted geometry two states, $T_7$ and $T_{10}$, have a nonnegligible oscillator strength for the transition to $T_1$. The transition energies of both these states are larger than the transition energy of the active $T_{10}$ state at the $trans$ geometry. It follows that the $T_1 \rightarrow T_{10}$ absorption spectrum at the twisted geometry is predicted to be at shorter wavelength than that of the $trans$ isomer.

In Table 4 are listed calculated vibrational frequencies, assignments, and $\gamma$-factors (for totally symmetric modes only).
TABLE 4: Scaled ROHF/6-31G* and QCFF/PI* Vibrational Frequencies (cm⁻¹) and γ-Factors of the Isotopomers of trans-Stilbene E-St, E-St-C₂, E-St-d₂, and E-St-d₁₀ in the Planar Geometry

<table>
<thead>
<tr>
<th>sym²</th>
<th>E-St</th>
<th>E-St-C₂</th>
<th>E-St-d₂</th>
<th>E-St-d₁₀</th>
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<tr>
<td>ROHF, QCFF</td>
<td>assign¹</td>
<td>γ</td>
<td>obs*</td>
<td>ROHF, QCFF</td>
</tr>
<tr>
<td>a₁</td>
<td>1608, 1580</td>
<td>νC₆H₄C = νCH₂C = νCH₂C = νCH₂</td>
<td>0.054 1573</td>
<td>1608, 1568</td>
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<tr>
<td>b₁</td>
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<td>νCC</td>
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<td>0.005 1521</td>
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<tr>
<td>a₂</td>
<td>1516, 1527</td>
<td>νCC</td>
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<td>0.143 1505</td>
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<tr>
<td>b₂</td>
<td>1482, 1490</td>
<td>ωCH</td>
<td>0.008</td>
<td>1476, 1488</td>
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<tr>
<td>a₃</td>
<td>1441, 1452</td>
<td>νCC</td>
<td>0.016 1425</td>
<td>0.027 1419</td>
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<tr>
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<td>νCH (CD)</td>
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<td>0.023 1337</td>
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<tr>
<td>a₄</td>
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<td>0.041 1239</td>
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<tr>
<td>b₄</td>
<td>1198, 1183</td>
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<tr>
<td>a₅</td>
<td>1150, 1164</td>
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<td>0.008 1110</td>
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<tr>
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<td>0.026 1059</td>
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<tr>
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<td>0.021 1042</td>
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<tr>
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<td>a₇</td>
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<tr>
<td>b₇</td>
<td>846, 899</td>
<td>νCC, νCC</td>
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<td>0.031 837</td>
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<tr>
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<td>634, 695</td>
<td>νCCC</td>
<td>0.005 650</td>
<td>0.022 651</td>
</tr>
<tr>
<td>b₈</td>
<td>625, 646</td>
<td>νCCC</td>
<td>0.000 618</td>
<td>0.000 616</td>
</tr>
<tr>
<td>a₉</td>
<td>270, 303</td>
<td>νCC, νCC</td>
<td>0.014 288</td>
<td>0.014 288</td>
</tr>
<tr>
<td>b₉</td>
<td>187, 222</td>
<td>νCC, νCC</td>
<td>0.038 201</td>
<td>0.038 198</td>
</tr>
</tbody>
</table>

¹ The molecular geometry (C₃ₘ point group) for this table corresponds to a stationary point for the QCFF/PI Hamiltonian; for ROHF/6-31G* the planarity is imposed, resulting in one imaginary frequency. Assignments of b₂ and a₄ modes are tentative possibilities; see text. ² Calculated ROHF/6-31G* vibrational frequencies ω cm⁻¹; denotes imaginary frequencies. All ROHF frequencies are scaled down by a factor 0.95 calculated QCFF/PI frequencies ω cm⁻¹; corresponding to spectra in Figure 2. § Symmetry. ² Observed frequencies ω cm⁻¹; corresponding to spectra in Figure 2. Potassium fluoride energy distribution. Ph, ω = ring, ω = ethylenic, ω = stretch, r = in-plane bend, ω = out-of-plane wag, δ = in-plane skeletal deformation, τ = out-of-plane skeletal deformation.

Corresponding calculations were carried out for the Z isomer and the twisted form but are not shown here.

### III. Experiment

**A. Materials.** Methanol (Merck, p.a.) and glycerol (Merck, wasserfrei reinste, Art. 4093) were used as received. Benzophenone
(Fluka, purum) was recrystallized from methanol. (E)-stilbene (Fluka, purum, for scintillation) was found by gas chromatography (GC) to have an isomer purity of 99% (GC conditions: DB1 capillary column with He as carrier gas; temperatures: injection split 210 °C, column 185 °C, and detection 200 °C). (Z)-Stilbene (Aldrich, 97%) was purified by vacuum distillation and found by GC to have an isomer purity >99.5%.

E-St-I\(^{13}\)C, a gift from Prof. T. Gustafson, was from MSD isotopes (MS-3026, 99 atom % \(^{13}\)C). The deuteriated isotopomers of (E)-stilbene were synthesized according to known procedures.\(^{34}\) Benzoic acid was reduced with LiAlD\(_4\) to afford benzyl-d\(_2\)-alcohol. This was oxidized with BaMnO\(_4\) to benzaldehyde-d\(_4\).\(^{34}\) Benzaldehyde-d\(_2\) was synthesized by oxidation of benzyl-d\(_3\) alcohol (Merck) with pyridinium chlorochromate.\(^{35}\) Reductive self-coupling of benzaldehyde-d\(_4\) (d\(_4\)) with low-valent titanium as described by Furstner et al.\(^{36}\)\(^{37}\) yielded a mixture of (E)- and (Z)-stilbene-d\(_2\) (d\(_{10}\)), in which the E isomer was predominant. The crude material was purified by column chromatography (SiO\(_2\)), eluent ether/petroleum ether 1:5) and crystallization from ethanol. The \(^{1}H\) NMR spectra of the (E)-stilbenes thus obtained indicated complete (>95%) deuterium incorporation. For final purification the (E)-stilbenes were sublimed in vacuo (100–110 deg/15 mm) to yield white crystals.

Solutions containing solvent, (sensitizer), and stilbene were purged with Ar for more than 30 min and transferred to optical cells in a glovebox under Ar, and the cells were closed air-tight with Teflon stoppers.

B. Methods. The time-resolved T\(_{2}\) RR spectra were obtained as described before.\(^{36,57}\) In glycerol at 203 K, the triplet state of the stilbenes was produced by direct excitation with a 308-nm pump pulse from an excimer laser (Lambda Physik EMG 102E); in methanol at 293 and 203 K, the triplet state was obtained by exciting benzophenone as sensitizer with a 351-nm pump pulse from an excimer-pumped dye laser (Lambda Physik EMG 102E + FL3002); the pump energy was ca. 4 mJ/pulse at the sample. The RR probe source was a Nd:YAG pumped dye laser (Quantel), the output of which was mixed with the infrared radiation of the YAG in a nonlinear crystal. Probe wavelengths were as follows: for E-St in glycerol, 384.5, 375.0, and 369.0 nm; for Z-St in methanol, 381.2 and 371.2 nm; for E-St-I\(^{13}\)C\(_2\), E-St-d\(_2\), and E-St-d\(_{10}\) in glycerol, 385.2 nm. The probe energy was 1–2 mJ/pulse at the sample. Both lasers were pulsed at 5 Hz with pulse lengths of 10–15 ns. Pump–probe time delays were typically 40 ns for experiments in methanol and 160 ns in glycerol. Individual spectra were averaged over 1000 pulses; the triplet state RR spectra were obtained by subtraction procedures.

The sample was contained in a cylindrical Suprasil cell with 26-mm inner diameter and 6-mm inner height, placed in a spinning copper block in an insulating housing. For experiments at 203 K, the cell was cooled by a flow of cold nitrogen gas and the analyzing light pulse and measuring the transient absorption along a path at right angle to the laser beam. The sample was contained in a cylindrical cell with 2-cm path length mounted in a copper block which was cooled by a flow of cold nitrogen. The analyzing light from a Xe lamp (Varian VIX150UV) passed the cell (active area 2 x 4 mm), was then dispersed in a monochromator (McPherson Model 2035, 0.35-m focal length, grating with 1200 grooves/mm), and detected by a photomultiplier (RCA 1P28). The transient signal was captured and stored in a digital oscilloscope (LeCroy 9450A), and data were handled in a PDP11/23 computer.

C. Results. Raman experiments are reported (i) for direct excitation in a glass at a low temperature, i.e., in Ar-saturated glycerol solutions of 0.1 mM E-St, E-St-I\(^{13}\)C\(_2\), E-St-d\(_2\), and E-St-d\(_{10}\), and (ii) for sensitized excitation in the liquid state, i.e., for Ar-saturated solutions of 0.034 M Z-St in methanol with 0.022 M benzophenone as sensitizer. Subtraction techniques used in the construction of the RR spectra have been discussed in detail previously.\(^{36,57}\) Each sample cell was used to obtain spectra using (a) the probe laser only and (b) both pump and probe lasers at 40–160 ns time delay between the pump and probe laser pulses. Triplet spectra were obtained from spectra (b) after the subtraction of spectra (a), i.e., bands from solvent, (sensitizer), and ground-state stilbene have been subtracted.

Experimental time-resolved T\(_{2}\) RR spectra, obtained by direct excitation in a glass, i.e., of stilbenes in glycerol at 203 K are shown in Figure 2 for E-St (spectrum A), E-St-I\(^{13}\)C\(_2\) (B), E-St-d\(_2\) (C), and E-St-d\(_{10}\) (D). For each compound, the spectrum is constructed from individual spectra from different frequency regions: pump wavelength, 308 nm; probe wavelength (A) 384.5 nm and (B–D) 385.2 nm; pump-probe delay, 160 ns. Bands from solvent and ground-state (E)-stilbenes have been subtracted.

Time-resolved absorption measurements were performed using a pulse at 308 nm from an excimer laser as photolyzing light pulse and measuring the transient absorption along a path at right angle to the laser beam. The sample was contained in a cylindrical cell with 2-cm path length mounted in a copper block which was cooled by a flow of cold nitrogen. The analyzing light from a Xe lamp (Varian VIX150UV) passed the cell (active area 2 x 4 mm), was then dispersed in a monochromator (McPherson Model 2035, 0.35-m focal length, grating with 1200 grooves/mm), and detected by a photomultiplier (RCA 1P28). The transient signal was captured and stored in a digital oscilloscope (LeCroy 9450A), and data were handled in a PDP11/23 computer.

Figure 2. Time-resolved resonance Raman (RR) spectra in Ar-saturated glycerol solution at 203 K of the lowest excited triplet state T\(_{2}\) of (A) (E)-stilbene, (B) (E)-stilbene-I\(^{13}\)C\(_2\), (C) E-stilbene-d\(_2\), and (D) (E)-stilbene-d\(_{10}\). For each compound, the spectrum is constructed from three individual spectra from different frequency regions: pump wavelength, 308 nm; probe wavelength (A) 384.5 nm and (B–D) 385.2 nm; pump–probe delay, 160 ns. Bands from solvent and ground-state (E)-stilbenes have been subtracted.
Structure of Stilbene in the TI State

Figure 3. Time-resolved resonance Raman (RR) spectra in Ar-saturated methanol solution of 0.034 M (Z)-stilbene and 0.022 M benzophenone, of the lowest excited triplet state T1 of stilbene: temperature (A, C) 293 K and (B, D) 203 K; pump wavelength, 351 nm; probe wavelength, (A, B) 371.2 nm and (C, D) 381.2 nm; pump-probe delay, 40 ns. Bands from solvent, sensitizer, and ground-state (Z)-stilbene have been subtracted.

E-St-13C2 in the region 1650–150 cm⁻¹. All bands investigated for the two compounds were found to have ρ close to 0.3.

In Figure 3, the effects of temperature and excitation wavelength on T1 RR spectra excited under sensitized conditions in the liquid state are illustrated. Experimental T1 RR spectra of (Z)-stilbene in methanol are shown in Figure 3, A (293 K, probe wavelength 371.2 nm), B (203 K, 371.2 nm), C (293 K, 381.2 nm), and D (203 K, 381.2 nm). Again, each spectrum is constructed from three individual spectra from different frequency regions.

The dependence of RR spectra on excitation wavelength was also investigated for E-St in glycerol at 203 K. Spectra were recorded with excitation wavelengths of 384.5, 375.0, and 369.0 nm. Unfortunately, with decreasing excitation wavelength one approaches the ground-state absorption of E-St, and fluorescence is induced by the probe pulse. This limited the region of observation to >200 cm⁻¹ for 375.0-nm excitation and to >600 cm⁻¹ for 369.0-nm excitation. Changes in relative band intensities, but no changes in frequencies or new RR bands were detected in these spectra. The resulting spectra are not shown here.

IV. Discussion

In a discussion of the multidimensional potential energy surface of the excited triplet state of stilbene, the shape of the surface along torsional coordinates of the ethylenic C=–C and the C–phenyl bonds is of particular interest, because these are the main coordinates in the cis ↔ trans photoisomerization. As mentioned in the Introduction, it is well established that only at high viscosity, e.g., in glasses at low temperature, and only for (E)-stilbene, direct excitation leads to considerable population of the lowest triplet state. This has been explained by a shallow minimum at the planar E geometry on the PES of the S1 state. At high viscosity and low temperatures, the torsional motion is hindered, and efficient intersystem crossing at the planar E geometry takes place; with decreasing viscosity and increasing temperature the radiationless deactivation of the S1 state in the singlet manifold becomes sufficiently rapid to quench the intersystem crossing process completely. (For (Z)-stilbene, radiationless deactivation apparently prevents intersystem crossing even in glasses at low temperatures.20) Subsequent to the S1 → T1 intersystem crossing process, (E)-stilbene finds its new equilibrium on the T1 PES. Our present experiments deal with RR spectra obtained in this equilibrium under varying conditions such as temperature and solvent, and the question arises as to what the equilibrium geometry/geometries in the T1 state and the spectroscopic observables are. This question shall be addressed in the following on the basis of our observed RR spectra, with the discussion structured along the following lines: In sections IVA and IVB the assignment between observed and calculated RR spectra will be discussed. This involves calculated frequencies and intensities from the QCFF/PI and frequencies from the ab initio calculations. In section IVA we attempt to assign the RR spectra of the four isotomers, obtained at high viscosity and low temperature, to the planar E form in the T1 state. Arguments for and against this assignment will be discussed in detail. Alternatively, in section IVB, a possible assignment to a twisted form shall be discussed. Section IVC deals with depolarization ratios, section IVD with the effect of excitation wavelength, and section IVE with the effect of temperature and viscosity on the observed RR spectra.

A. Planar E Form, C3v Symmetry. The QCFF/PI calculations clearly indicate a planar E form to be the most stable in the T1 state. Both the planar Z and the centrally perpendicular P forms were computed approximately 2.9 kcal/mol higher. Torsion around the C–phenyl bonds resulted in a considerably higher energy. Moreover, the calculated (QCFF/PI and CNDO/S) T1 → T2 transition energies further support the spectroscopic importance of the planar E form: The T1 → T2 transition observed in the region 350–390 nm (3.54–3.18 eV) is in reasonable agreement with a transition calculated at 3.7 (QCFF/PI) and 3.9 eV (CNDO/S) with an oscillator strength around 1.1 (both methods) for the planar E form, while the corresponding transition for the P form is calculated ca. 0.9 eV higher in energy with both methods. Other observations support the existence of a stable planar form in the T1 state as well: The T1 lifetime observed in glasses at low temperature is of the order of tens of milliseconds, the T1 → T2 absorption spectrum shows vibrational fine structure, similar to that of the ground state, and a very low quantum yield of trans–cis isomerization (0.001–0.01) in glycerol at −80 °C is reported. A much shorter lifetime would be expected for a twisted equilibrium geometry, due to the small S0 – T1 energy gap.

In summary, strong evidence, independent of RR spectra, supports an assignment of the spectroscopically observed T1 state of (E)-stilbene in glasses at low temperature to a planar E geometry. This is at odds with the results of our ROHF/6-31G* ab initio calculations which predict a minimum lower by 13 kcal/mol than the planar E geometry at a geometry twisted by 90° around the ethylenic C=C bond. However, this theoretical result is at variance also with the small (4.5 kcal/mol) difference between the vertical and relaxed T1 → S0 energy gap reported above.

We shall now discuss the assignment of the experimental T1 RR spectra to the spectra calculated for the planar E form of the four isotomers of (E)-stilbene, determining the symmetry and the internal coordinates contribution to the vibrational modes that are active in the RR spectra.

1. RR Spectra, a2u Modes. For the Raman excitation wavelength in resonance with a strongly-allowed electronic transition (T1 → T10 in the case of (E)-stilbene), RR spectra are dominated by Franck–Condon scattering, and the vibrational modes observed with strongest intensity are the totally-symmetric ones. They can gain intensity by changes in equilibrium geometry between the two resonant electronic states involved in the transition or by changes in vibrational frequencies. Changes in geometry usually give the dominant contribution. Hence, we shall first attempt to assign the observed RR bands of T1 stilbene according to calculations of changes in equilibrium geometry between the states T1 and T10, projected on the totally-symmetric modes of T1. Relative intensities are expressed through the γ-factors, calculated at the planar C3v symmetry of the molecule in the T1 state.

Theoretical T1 RR spectra are constructed in the spectra A (QCFF/PI) and B (ab initio) of Figure 4 for the planar E form
E-St and E-St-I3C2 are observed in experiment. Exceptions are vibrations in Ti stilbene much. Most a, modes calculated for the ones calculated (QCFF/PI values) at 1490 and 1183 cm⁻¹ for E-St (1488 and 1175 cm⁻¹ for E-St-I3C2).

A, bands are found in the experimental spectra, except for those calculated with zero intensity for E-St-d3 at 1096 cm⁻¹ and for E-St-d10 at 829 cm⁻¹ (QCFF/PI).

The vibrational pattern is changed more by deuteration, for both d2 (Figure 6) and d10 substitution (Figure 2D). Again, the observed isotopic shifts are reproduced well by calculation. For E-St-d2 (Figure 6) and E-St-d10 (Figure 7), all calculated a, bands are found in the experimental spectra, except for those calculated with zero intensity for E-St-d2 at 1096 cm⁻¹ and for E-St-d10 at 829 cm⁻¹ (QCFF/PI).

2. RR Spectra, b, b, and a, Modes. For strictly planar E-St with C₃₄ symmetry, in the Franck-Condon approximation, i.e., in the absence of vibronic coupling, only a, modes are RR-active. Modes of b, or a, symmetry can gain intensity only due to vibronic coupling. They derive their intensity from changes in frequency of the normal mode between the two resonant electronic states.

Table 4 lists the observed frequencies for the T₁ state of the four isotopomers, together with the calculated (QCFF/PI and ab initio) frequencies of a, b, and a, symmetry modes that we assign to the observed bands. We shall now discuss the assignment in some detail.

In our first report on the T₁ RR spectrum of E-St, we assigned most of the observed bands to a, normal modes of the planar E structure. This assignment is in agreement with the results from QCFF/PI calculations in the present, more extensive, study. The assignment of observed bands of E-St-I3C₂ (Figure 2B) to calculated a, normal modes (Figure 5) is very close to that of E-St; the calculated and observed isotopic frequency shifts from E-St to E-St-I3C₂ are small but consistent. It is evident that replacement of the central carbon atoms by I3C does not alter the vibrations in T₁ stilbene much. Most a, modes calculated for E-St and E-St-I3C₂ are observed in experiment. Exceptions are the ones calculated (QCFF/PI values) at 1490 and 1183 cm⁻¹ for E-St (1488 and 1175 cm⁻¹ for E-St-I3C₂).
Figure 6. Comparison between calculated and experimental resonance Raman spectra of stilbene-d2 in the lowest excited T1 state. (A) Frequencies and intensities (γ-factors in resonance with the T1 → T0 transition) of vibrational modes (a, symmetry only) in the planar E geometry (C2h point group, stationary point) calculated by QCFF/PI. (B) Frequencies of vibrational modes (a, symmetry only) in the planar E geometry (C2h point group, imposed geometry, nonstationary point) calculated by ROHF/6-31G level. (C) Experimental RR spectrum (identical to Figure 2C). (D) Frequencies and intensities (γ-factors in resonance with the T1 → T0 transition) of vibrational modes (a, symmetry only) of centrally twisted stilbene-d2 (C2 point group, nonstationary point) calculated by QCFF/PI. (E) Frequencies of vibrational modes (a, symmetry only) of centrally twisted stilbene-d2 (C2 point group, stationary point) calculated by ROHF/6-31G level.

T1 → T0 transition, non-totally symmetric modes of proper symmetry may vibronically couple Tm with T1 or T0. We have previously found this mechanism to be active for b, modes in the ground state D0 of the benzyl radical. The upper state T, active in the present experiments, has been calculated as the T10 ππ* state at 3.905 eV above the T1 state (CNDO/S). For b, modes to be vibronically active, they can couple either the T10 state of A, symmetry with a Tππ* excited state of B, symmetry or the T1 state of B, symmetry with a Tππ* state of A, symmetry. Alternatively, T1 or T0 E-St may not be strictly planar. For a symmetric torsion at the C=C or C=C-phenyl bonds in T1, the molecular symmetry is lowered from C2h to C2 or C1, which is less likely because of a considerably higher energy, as calculated by means of the QCFF/PI method, and normal modes corresponding to a, or b, symmetry in C2 may be observed in the RR spectrum. This case shall be discussed in section 1VB.

The bands in Figures 2 and 4–7, which cannot be assigned to a, modes, are observed below 1100 cm⁻¹. Since this is the region where modes of b, and a, symmetry are found, it is reasonable to relate an assignment of the remaining bands to normal modes or combinations of these symmetries. Tentative assignments are listed in Table 4 together with a full list of calculated frequencies of b, b, and a, symmetry normal modes. For all isotopomers, the calculated frequencies of b, and a, modes are similar for many modes. We choose to concentrate on the b, modes, but as shall be seen below, an assignment to a, modes or rather their combinations may be more likely, in view of the calculated a, modes of very low frequency with substantial frequency shifts upon excitation.

On the basis of calculated frequencies only (not intensities), both QCFF/PI and ab initio, it is found that b, and a, modes are able to account for most of the yet unassigned bands. There is a remarkable qualitative agreement between calculated frequencies and the observed spectra. Indeed, most of the calculated b, modes do have counterparts in the spectra. In particular, the prominent band observed at 459 cm⁻¹ for E-St can only be assigned to the calculated b, band at 470 cm⁻¹ (420 cm⁻¹ in ab initio) or the a, band at 482 cm⁻¹ (422 cm⁻¹). This mode is described as an out-of-plane ring CCC deformation; it is shifted little for E-St-13C2 (obs 459 cm⁻¹, calc 469 cm⁻¹) and E-St-d2 (obs 445 cm⁻¹, calc 451 cm⁻¹), but very much for E-St-d10 (obs 407 cm⁻¹, calc 427 cm⁻¹), which confirms its assignment. Moreover, the relative intensity of the observed 288- and 201-cm⁻¹ bands is not predicted correctly from the a, modes at 303 and 228 cm⁻¹ alone, but a contribution to the 288-cm⁻¹ band from the calculated 306-cm⁻¹ b, mode is possible. Likewise, the broad band observed at 704 cm⁻¹ may very well have contributions from both a, and b, modes.

For E-St and E-St-13C2 all calculated modes of b, symmetry below 1000 cm⁻¹ have counterparts in the spectra, and the calculated b, modes are able to account for all the remaining observed bands. For E-St and E-St-13C2 the highest-frequency b, and a, modes are calculated and observed close to 1050 cm⁻¹. For E-St-d10, calculation predicts no b, or a, modes above 827 cm⁻¹. This large isotopic shift is reproduced in the spectra, where all observed bands above 750 cm⁻¹ can be assigned to calculated modes of a, symmetry. All band observed below 750 cm⁻¹, which cannot be assigned to a, modes, can be assigned to calculated modes of b, or a, symmetry, in particular the observed 407-cm⁻¹ band mentioned above.

For E-St-d3 as well, the remaining observed bands can be assigned to calculated modes of b, symmetry, except for the band
observed at 485 cm\(^{-1}\) and assigned to \(a_2\) symmetry. The relatively strong band observed at 561 cm\(^{-1}\) is assigned to the calculated \(b_2\) band at 603 cm\(^{-1}\).

In summary, on the basis of calculated frequencies in \(T_1\), an assignment of modes which are not of \(a_2\) parentage to \(b_2\) and \(a_2\) modes seems most likely. What then is the mechanism of enhancement? We have calculated the relevant vibronic coupling interactions and have found not any indication of strong vibronic coupling within the manifold of \(\pi\pi^*\) and \(\pi^*\pi^*\) excited triplet states, which could explain the observed spectrum. Alternatively, the observed bands which are not due to \(a_2\) modes may be assigned to combinations of \(a_2\) or \(b_2\) modes of total \(a_2\) symmetry involving one of the low-frequency modes. These combinations may derive intensity through Fermi resonance with totally symmetric modes.

For \(E\)-St, on the basis of the QCFF/PI calculations, combinations of \(a_2\) modes with the \(a_2\) band at 36 cm\(^{-1}\) (\(\gamma(CC,C)\)) yield a possible assignment. In particular, weak bands in the region below 1000 cm\(^{-1}\) may include contributions from such combinations. However, in view of the size of the molecule we have not estimated the anharmonic coupling which could give rise to the experimental observations.

In conclusion, essentially all observed RR bands from the four stilbene isotopomers can be assigned to calculated vibrational modes of the planar \(E\) form of stilbene in the \(T_1\) state, the strongest bands to \(a_2\) modes, based on Franck-Condon scattering, and weaker bands to \(b_2\) or \(a_2\) modes or their combinations. These weak bands gain their intensity from vibronic coupling or Fermi resonance.

### B. Twisted \(P\) Form, \(C_2\) Symmetry

While the combined experimental and semiempirical results seem to strongly indicate a planar triplet geometry of \(C_{2h}\) symmetry as discussed in the preceding section, \(ab\ initio\) 6-31G calculations result in a rather deep (13 kcal/mol) minimum at a twisted geometry. We therefore consider in the present section the possibility to assign the observed \(T_1\) RR spectra to twisted species, albeit, as mentioned above, the long lifetime, the vibrationally structured \(T_1\) absorption spectrum, and the calculated \(T_1\) \(\rightarrow\) \(T_0\) transition energy of 4.13---4.88 eV are arguments against this assignment.

Considerable oscillator strengths of 0.12---0.16 and 0.53---0.64 are calculated (see Table 3) by means of QCFF/PI and CNDO/S methods at the perpendicular geometry for two \(T_1\) \(\rightarrow\) \(T_0\) transitions, \(n = 7\) at 4.126 and \(n = 10\) at 4.862 eV above \(T_1\), respectively. These transitions are weaker than the \(T_1\) \(\rightarrow\) \(T_0\) transition of planar \(E\) stilbene by factors of ca. 8.5 (\(T_1\) \(\rightarrow\) \(T_2\)) and 2 (\(T_1\) \(\rightarrow\) \(T_0\)). Moreover, the used Raman excitation wavelength is significantly off-resonance with either of the two transitions of the twisted form. It should also be noted that the perpendicular form is not a stationary point on the \(T_1\) PES calculated by QCFF/PI, as one frequency (ethyleneic \(C=CC\) torsion) is calculated imaginary. The RR spectra calculated by the QCFF/PI Hamiltonian for the stronger of the two transitions (\(T_1\) \(\rightarrow\) \(T_0\)) are shown in spectra D of Figures 4--7. Additionally, frequencies calculated by \(ab\ initio\) ROHF/6-31G at the perpendicular stationary point on the \(T_1\) PES are shown in spectra E of Figures 4--7. Compared with the results for planar \(C_{2h}\) stilbene in \(T_1\), considerable changes in frequencies and intensities are calculated.

### RR Spectra

The frequencies of the totally symmetric vibrational modes of a symmetry in the twisted stationary geometry, calculated by \(ab\ initio\) methods at the ROHF/6-31G level, are shown in spectra E of Figures 4--7. The calculated spectra can readily account for all observed Raman bands. The reason for this, as opposed to the case for the planar \(C_{2h}\) point group, is that modes of \(b_2\) symmetry in \(C_2\) transform into a symmetry in the \(C_2\) point group and may become RR-active. In particular, a reasonable agreement is found in the region below 1000 cm\(^{-1}\). However, at present the reliable calculation of RR intensities at the \(ab\ initio\) level is difficult. This limits the usefulness of this approach in the interpretation of RR spectra of molecules of the size of stilbene considerably.

For the QCFF/PI calculations, spectra calculated for the \(T_1\) \(\rightarrow\) \(T_0\) transition (not shown) are in rather strong disagreement with the experimental ones while those for the \(T_1\) \(\rightarrow\) \(T_0\) transition (spectra D in Figures 4--7) which, however, is off-resonance agree somewhat better. However, the overall agreement is far worse than for the planar \(C_{2h}\) case. Although all the calculated strong bands for all four isotopomers have experimentally observed counterparts, additional observed bands of medium to strong intensity are calculated to have small intensity by theory. This is the case in particular for bands observed below 500 cm\(^{-1}\) in \(E\)-St, \(E\)-St-\(^{12}\)C\(_2\), and \(E\)-St-d\(_2\) and those below 600 cm\(^{-1}\) in \(E\)-St-d\(_2\). The reason for this could be that these bands do not derive their intensity from changes in geometry but from changes in frequency upon \(T_1\) \(\rightarrow\) \(T_0\) excitation, the spectra D in Figures 4--7 only taking into account geometry changes. However, also some intense bands observed above 800 cm\(^{-1}\) are not predicted correctly. In particular, the bands observed in \(E\)-St at 1573, 1341, 1243, 1110, 1067, and 966 cm\(^{-1}\), their analogues in \(E\)-St-\(^{12}\)C\(_2\), those observed in \(E\)-St-d\(_2\) at 1562 and 958 cm\(^{-1}\), and those observed in \(E\)-St-d\(_{18}\) at 1557, 1218, and 1095 cm\(^{-1}\) are not predicted by theory. These are bands for which reasonable agreement was found for the planar \(E\) form.

On the other hand, a remarkable agreement is seen when comparing experimental (Figures 4--7C) and calculated (Figures 4--7D, QCFF/PI) spectra in the region 500--800 cm\(^{-1}\). This may be a coincidence, but some contribution from the twisted form cannot be ruled out completely.

In summary, on the basis of calculated frequencies only, it is not possible to distinguish between planar and twisted forms of stilbene in the \(T_1\) state, as the uncertainty in calculated frequencies, no matter which method is used, is large compared with the expected differences in frequency. However, if one accepts the validity of the estimates of intensity by the semiempirical method (QCFF/PI), it becomes clear on the basis of calculated RR spectra that while the twisted form certainly may contribute to the observed spectra, it is not the spectroscopically dominant species. This is obvious in contrast to the relatively deep minimum at the twisted geometry predicted by the \(ab\ initio\) calculation. In order to explain these different results, it should be remembered that the present \(ab\ initio\) calculations are at the rather crude SCF level of theory; in principle, the calculations can be improved by using a larger basis set and a treatment of electron correlation.

From a comparison of the calculated \(T_1\) RR spectra in the planar and twisted geometries (both \(ab\ initio\) and semiempirical), it can also be concluded that substantial differences, in both frequencies and relative intensities, of RR band are expected for the two forms. For several vibrational bands, calculated changes in frequency when going from a planar to a twisted form are typically in the range 20--40 cm\(^{-1}\). As the largest observed differences in frequency are only about 5 cm\(^{-1}\), when comparing RR spectra of (\(E\))-stilbene in glasses at low temperature,36 we observe depolarization ratios of \(\rho \approx 0.3\) for all observed bands. Hence, in spite of the fact that \(b_2\) or \(a_2\) modes (in \(C_{2h}\) point group) are involved in the observed transitions, no depolarized bands are detected.

### C. Depolarization Ratios

Above, we assigned the experimental RR bands to both in-plane (\(a_2\)) and out-of-plane (\(b_2\) and \(a_2\)) vibrations. For a molecule of \(C_{2h}\) symmetry, nonresonant Raman band depolarization ratios are \(\approx 0.3\) for in-plane vibrations (\(a_2\)) and 0.75 for out-of-plane vibrations (\(b_2\)). We observe depolarization ratios of \(\rho \approx 0.3\) for all observed bands. However, in spite of the fact that \(b_2\) or \(a_2\) modes (in \(C_{2h}\) point group) are involved in the observed transitions, no depolarized bands are detected.
uncertainty. This is due to the fact that (i) the collection optics shown in Figure 3 for two excitation wavelengths, namely, 381.2 and 375.0- and 369.0-nm excitation (not shown). No absorption band. In the absence of more complete excitation the observed enhancement pattern reflects the vibrational excess at 1536 cm⁻¹ with decreasing excitation wavelength.

The question of depolarization ratios in RR scattering is a complicated one. Myers has recently shown that under a variety of conditions torsional modes can appear as polarized bands in RR scattering. However, our observations with respect to depolarization ratios support the attribution of the non-totally symmetric bands to combination bands resulting in a overall symmetry.

D. Effect of Excitation Wavelength on RR Spectra. In order to discuss the dependence of the observed RR spectra on exciting wavelength, it is useful to visualize the excitation conditions, as illustrated in Figure 8. We have remeasured the T₁ → T₂ absorption spectrum of E-St in glycerol at 202 K and plotted it (spectrum A) together with the spectrum observed by Görner and Schulte-Frohlinde under sensitized conditions at room temperature in tert-butyl alcohol (spectrum B); excitation wavelength, 353 nm; room temperature.

When considering relative intensities in the RR spectra presented in Figures 2–7, it should be mentioned that relative observed intensities are subject to rather large experimental uncertainty. This is due to the fact that (i) the collection optics for Raman light were not achromatic, (ii) no correction was made for reabsorption of the scattered light due to triplet-triplet absorption.

As mentioned above, RR spectra in glycerol were measured with 384.5, 375.0-, and 369.0-nm excitation (not shown). No frequency changes were observed, and the changes in intensity were rather small. The bands at 1243, 1000, and 917 cm⁻¹, and in particular the band at 847 cm⁻¹, increased in intensity by approximately a factor 2 relative to the strongest observed band at 1536 cm⁻¹ with decreasing excitation wavelength. In general, the observed enhancement pattern reflects the vibrational excess energy of the excitation wavelength with respect to the zero-zero absorption band. In the absence of more complete excitation spectra, no conclusions can be drawn from this.

The wavelength dependence of the T₁ RR spectra in the liquid state, i.e., in methanol at two temperatures (293 and 203 K), is shown in Figure 3 for two excitation wavelengths, namely, 381.2 and 371.2 nm. Above 800 cm⁻¹, the changes in relative Raman intensities with decreasing excitation wavelength are not dramatic with one notable exception: the band at 1182 cm⁻¹ seems considerably more intense with 381.2-nm excitation. Such a large variation in intensity over a relatively limited wavelength range of excitation is usually typical for bands deriving their intensity from vibronic coupling. The change with excitation wavelength of RR spectra due to totally symmetric vibrations has been discussed by several authors. Ultimately, it is due to the change in scattering efficiency when the exciting beam frequency moves from resonance with the 0–0 band to the 0–1 or higher bands. Even in the Franck–Condon approximation, i.e., neglecting the contribution of the Herzberg–Teller mechanism, a change in the relative intensity of totally symmetric bands is to be expected, and this depends on the displacement parameter B between the initial and the scattering state. The presence of Herzberg–Teller scattering causes interference with the allowed scattering. Such interference is of opposite sign for resonance with the 0–0 and the 0–1 bands, giving rise to asymmetric excitation profiles, that is, changes in the shape of RR spectra. This effect has been discussed in detail for the case of weak displacements.

Apart from this, the main observation upon a decrease of excitation wavelength in the liquid phase is an overall increase in resonance Raman intensity, as seen from the increasing signal-to-noise ratio. Below 800 cm⁻¹, the data from glycerol glass were incomplete, due to interfering luminescence with decreasing excitation wavelength. For (Z)-stilbene in liquid methanol, fluorescence is much weaker or absent, and therefore it was possible to detect RR spectra with shorter excitation wavelength in the low-frequency region. No new bands, overtones or combinations, were detected with the lower excitation wavelength. However, the band at 459 cm⁻¹ seems generally broader with 371.2-nm rather than 381.2-nm excitation. Again, in the absence of more detailed excitation spectra, quantitative conclusions are difficult to derive. However, the strong activity of CCCC out-of-plane modes, either as combinations or fundamentals, suggests substantial change in shape of the PES upon T₁ → T₂ excitation.

E. Effect of Temperature and Viscosity on RR Spectra. When comparing the RR spectra obtained under various conditions, one has to take into account both the effect of temperature and viscosity. While the viscosity in glycerol at 231 K is very high, 6.7 × 10⁶ cP, in methanol it ranges from 0.597 cP at 293 K to 4.36 cP at 201 K; for tert-butyl alcohol, for which the T₁ → T₂ absorption spectrum shown in Figure 8 was reported, it is 3.3 cP at 303 K. Hence, viscosity varies by ca. a factor of 7 in the temperature range of the present experiments in the liquid phase and by 6 orders of magnitude for the glycerol glass.

We shall first compare the RR spectra obtained in glycerol at 203 K with 384.5-nm (0–0 band) excitation (Figure 2A) and in methanol at 203 K with 381.2-nm (0–0 band of spectrum in ethanol at 98 K) excitation (Figure 3D). The signal-to-noise ratio is lower in Figure 3D than in Figure 2A, which can be due to a smaller concentration of triplet stilbene or to smaller RR enhancement in Figure 3D. In the latter case, the 0–0 band of the T₁ → T₂ absorption spectrum in methanol at 203 K may not be found at 381 nm. According to the viscosities given above, the absorption spectrum in methanol at 203 K probably is similar to the structureless spectrum in tert-butyl alcohol at room temperature. However, apart from the difference in overall intensity, the relative intensities of the bands are similar for Figures 2A and 2D. Only the band at 1182 cm⁻¹ is stronger in Figure 3D. It should be noted that the bands at 459, 288, and 201 cm⁻¹ are also relatively strong in the methanol 203 K spectrum.

The similarity of the spectra at 203 K in glycerol and methanol indicates that the same stilbene T₁ species are created by triplet energy transfer from a sensitizer to ground-state (Z)-stilbene and by intramolecular intersystem crossing from S₅ to T₁ in (E)-stilbene. Thus, a very similar state of relaxation of the various internal coordinates is likely to be reached by these two very different mechanisms.

The effect of temperature on the RR spectra in the liquid phase can be seen by comparing spectra A with B and spectra...
C with D (Figure 3). For 371.2-nm excitation, all bands below 1000 cm⁻¹ increase in intensity with decreasing temperature, while similar, but smaller, changes were observed below 500 cm⁻¹ for 381.2-nm excitation wavelength. It is obvious that a similar effect is less pronounced for the bands in the high-frequency region above 1000 cm⁻¹. From this it appears that temperature in particular affects the intensity and to some extent bandwidth of low-frequency vibrational modes. Unfortunately, these changes cannot be compared with changes in the absorption spectrum with temperature, as the T₁ → T₁ absorption spectrum in the liquid phase at 203 K is presently unknown. We do not in detail understand the present results; however, one may think that activity of very low-frequency anharmonic out-of-plane modes which may be active as combinations with other out-of-plane vibrations leads to a decreasing intensity and increasing bandwidth of the observed out-of-plane modes with increasing temperature.

V. Molecular Structure of T₁; Stilbene

Judging from the very different T₁ → T₁ absorption spectra of stilbene in the glass and in solution (see Figure 8), one may speculate that while the spectrum in glass is typical for a planar aromatic hydrocarbon, that in solution may have a strong contribution from a molecule in a nonplanar geometry in T₁. This view is not supported by the resonance Raman measurements reported here. In fact, if this were the case, considerable changes in RR spectra would be expected.

Alternatively, the possibility that both absorption spectra in Figure 8 belong to the same species, but the structured absorption spectrum in the glass belongs to a different transition, not observed in solution because of its weakness, was considered. We extended the absorption measurements in the glass down to 220 nm but did not observe any additional strong absorption band that could be correlated to the one observed in solution.

Hence, we attribute both absorption spectra to the same species. The disappearance of fine structure is due to inhomogeneous broadening, which is particularly strong in the T₁ state of stilbene because of the presence of a number of low-frequency modes. The broadening then arises from the population of several levels of such modes in T₁ together with frequency changes in these modes between T₁ and T₅. (For T₅ modes changes of up to 15% were calculated for the low-frequency modes.) The torsional mode around the central C–C bond is expected to be particularly active because of a very shallow minimum on the PES along this coordinate. Similar effects are observed also in the Sₐ → S₁ absorption spectrum when the temperature and properties of the solvent are changed.⁶⁵

There is no doubt that the QCFF/PI calculations support an assignment of the observed T₁; RR and T₁; T₅ absorption spectra in the glass to stilbene in a planar trans geometry. The well-resolved absorption spectrum (spectrum A in Figure 8) is typical of aromatic hydrocarbons and cannot be due to the twisted form. The long lifetime of the order of milliseconds of the T₁ state in glasses at low temperature is in agreement with this view. This interpretation is also in keeping with the usual picture of a rather flat potential energy surface along the torsional coordinate of the central C=C bond, according to which planar trans and centrally twisted geometries are almost degenerate to within 2 kcal/mol, and thus a large population of molecules is in the trans form at any temperature. Ab initio self-consistent-field calculations suggesting a twisted minimum in the T₁ state are in clear contradiction with spectroscopically observed absorption spectra in glasses at low temperature. We conclude that stilbene in low-temperature glasses adopts an essentially planar equilibrium geometry.

For the liquid phase (methanol, 293 and 203 K), optical absorption data²³ were previously interpreted to support an equilibrium between planar and twisted equilibrium forms. On the basis of the present data, as discussed above, we disagree with this view and attribute the transient triplet–triplet absorption spectrum in methanol solutions to the E planar form broadened by inhomogeneous line broadening. We suggest that, in the observed wavelength region, the T₁; T₁ absorption spectrum is dominated by the planar form while the twisted contributes most at shorter wavelengths, not accessible experimentally, due to strong absorption of ground-state stilbene. It is evident that our excitation wavelength favors observation of the planar form, and this is the one which is observed as the dominant contribution in the present T₁ resonance Raman spectra. In order to observe the twisted form by RR, lower excitation wavelengths would be required.

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