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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 \textit{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 \( \text{C} = \text{C} \) 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 (\( C_2h \) 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 \( \text{C} = \text{C} \) 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,32–34 by optically-detected magnetic resonance35 (in a single crystal at 1.3 K), and recently by time-resolved RR spectroscopy.36 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.37

Görner and Schulte-Frohlinde32,33 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 monotonously 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 studies33 that for stilbene in the \( T_1 \) state an equilibrium exists between a planar trans \( (E) \) geometry and a more stable geometry that is twisted by \( 90^\circ \) at the central \( \text{C} = \text{C} \) bond (\( P \), perpendicular),

\[
\frac{k_1}{k_{-1}} = \frac{P}{Z} 
\tag{1}
\]

The equilibrium was found to be dependent on solvent polarity. On the basis of quenching by azulene, an equilibrium constant \( K_1 = k_1/k_{-1} = 4.6 \) in methanol at room temperature was determined. The value of \( K_1 \) was higher in nonpolar solvents. Saittel et al.38,39 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 \( T_1 \); \( S_0 \) 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 \( T_1 \) 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 symmetry other than aB. However, a number of bands observed at frequencies below 1000 cm^{-1} could not be assigned to aB 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 aB.

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 ROHF calculations at the 6-31G level on the other. Intensities of the aB modes (within the C2v point group) were calculated using the QCFF/PI program.

In the present paper we report time-resolved RR spectra, excited at 385 nm in glycerol at 203 K, of the following isotopomers of (E)-stilbene: C\textsubscript{6}H\textsubscript{4}HCC\textsubscript{6}H\textsubscript{5}(E-St), C\textsubscript{6}H\textsubscript{4}H\textsubscript{13}C\textsubscript{1}C\textsubscript{6}H\textsubscript{5}(E-St\textsubscript{-13C\textsubscript{1}}), C\textsubscript{6}H\textsubscript{4}DCC\textsubscript{6}H\textsubscript{5}(E-St\textsubscript{-d\textsubscript{3}}), and C\textsubscript{6}D\textsubscript{4}HCC\textsubscript{6}H\textsubscript{5}(E-St\textsubscript{-d\textsubscript{3}}) (Scheme 1). The spectra are interpreted on the basis of the theoretical calculations. For E-St and E-St\textsubscript{-d\textsubscript{3}} 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. The molecular structure of stilbene in the T1 state is discussed on the basis of the experimental and theoretical results.

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 5\pi\textsubscript{v} 5\pi\textsuperscript{*} 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\textsuperscript{48} 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\textsubscript{i}, of a given totally symmetric mode furnishes a measure of its Franck–Condon activity. B\textsubscript{i} is defined as

\[ B\textsubscript{i} = 0.172\omega\textsubscript{i}^{1/2}(x\textsubscript{i} - x\textsubscript{0})M^{1/2}L\textsubscript{i} \]  

where \omega\textsubscript{i} and L\textsubscript{i} are the ith vibrational frequency and normal-mode coordinate in the excited state, M is the matrix of atomic masses, and x\textsubscript{i} and x\textsubscript{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 ith quantum of the progression is simply given by

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

where

\[ \gamma_i = 0.5B_i^2 \]
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, we report the energies and the oscillator strengths $f$ for the lowest triplet states of (E)-stilbene, (Z)-stilbene, and (P)-stilbene (90° Twisted).

### Table 2: Structural Parameters of (E)-, (Z)-, and (P)-Stilbene in the States T1 and T10 (in Parentheses). Bond Lengths Are in Å and Angles in deg

<table>
<thead>
<tr>
<th>Sym</th>
<th>$E$ (6-31G)</th>
<th>$f$</th>
<th>6-31G</th>
<th>QCFF/PI</th>
<th>Sym</th>
<th>$E$ (6-31G)</th>
<th>$f$</th>
<th>6-31G</th>
<th>QCFF/PI</th>
<th>Sym</th>
<th>$E$ (6-31G)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>A4</td>
<td>3.905 (3.696)</td>
<td>0.006 (0.003) B</td>
<td>0.000</td>
<td>B</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>A4</td>
<td>3.905 (3.696)</td>
<td>0.006 (0.003) A</td>
<td>2.673 (2.563)</td>
<td>0.013 (0.007)</td>
<td>A</td>
<td>3.194 (3.241)</td>
<td>0.024 (0.001)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T2</td>
<td>A4</td>
<td>2.960 (2.692)</td>
<td>0.004 (-) A</td>
<td>2.981 (2.783)</td>
<td>0.002 (-)</td>
<td>A</td>
<td>3.240 (3.241)</td>
<td>0.002 (-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T3</td>
<td>A4</td>
<td>3.180 (2.854)</td>
<td>0.004 (-) A</td>
<td>3.086 (3.001)</td>
<td>0.003 (0.001)</td>
<td>A</td>
<td>3.248 (3.293)</td>
<td>0.004 (0.002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td>A4</td>
<td>3.198 (2.812)</td>
<td>0.002 (-) A</td>
<td>3.772 (3.361)</td>
<td>0.025 (-)</td>
<td>B</td>
<td>4.315 (4.099)</td>
<td>0.028 (0.035)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>T5</td>
<td>A4</td>
<td>3.232 (2.954)</td>
<td>0.002 (-) A</td>
<td>3.792 (3.373)</td>
<td>0.002 (0.001)</td>
<td>A</td>
<td>4.325 (4.126)</td>
<td>0.123 (0.164)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T6</td>
<td>A4</td>
<td>3.248 (2.978)</td>
<td>0.040 (0.047) A</td>
<td>3.822 (3.436)</td>
<td>0.066 (0.053)</td>
<td>A</td>
<td>4.393 (4.126)</td>
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<td></td>
</tr>
<tr>
<td>T7</td>
<td>A4</td>
<td>3.903 (3.696)</td>
<td>1.193 (1.137) A</td>
<td>4.209 (3.971)</td>
<td>0.490 (0.511)</td>
<td>A</td>
<td>4.884 (4.862)</td>
<td>0.528 (0.643)</td>
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<tr>
<td>T8</td>
<td>A4</td>
<td>3.934 (3.891)</td>
<td>0.000 (0.001) B</td>
<td>4.292 (4.195)</td>
<td>0.000 (-)</td>
<td>B</td>
<td>5.224 (5.102)</td>
<td></td>
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</tr>
<tr>
<td>T9</td>
<td>A4</td>
<td>4.230 (4.291)</td>
<td>0.003 (0.002) A</td>
<td>4.516 (4.292)</td>
<td>0.000 (-)</td>
<td>B</td>
<td>5.358 (5.180)</td>
<td>0.001 (-)</td>
<td></td>
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</tr>
<tr>
<td>T10</td>
<td>A4</td>
<td>4.676 (4.537)</td>
<td>0.002 (0.006) A</td>
<td>4.626 (4.537)</td>
<td>0.002 (0.006)</td>
<td>A</td>
<td>5.358 (5.181)</td>
<td></td>
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</table>

In Table 3 and Figure 1, we report the energies and the oscillator strengths $f$ for the lowest triplet states of (E)-stilbene, (Z)-stilbene, and (P)-stilbene (90° Twisted).

### B. Results

In Tables 1 and 2 we report the results of geometry optimization of S0 and T1, respectively. The calculation for the ground state, the geometry of which is well established, provides a test for the accuracy of the procedures we have used. From Table 1 it appears that both QCFF/PI and ab initio results are in good agreement with the experimental structural parameters; however, QCFF/PI tends to render the stilbene molecule planar in the trans isomer, while the ab initio calculation leads to a C1 nonplanar minimum, as it is observed experimentally. It was found by ab initio methods that the nonplanar C1 form is more stable than the planar form only by a tiny amount (0.03 kcal/mol). In Table 2 we report the structural parameters of the trans, twisted, and cis isomers in the state T1. No experimental data are available in this case. The CC bond lengths obtained by ab initio and the QCFF/PI calculations are similar, and both find the inversion of CC bond lengths in the central moiety of the molecule as the main effect of the S0 → T1 excitation. However, some differences emerge between the two sets of results: (a) while the ring CC bonds are essentially equivalent according to the ab initio calculation, the two CC bonds adjacent to the central moiety are longer than the others according to the QCFF/PI method; (b) the central moiety bonds are found longer in the ab initio than in the semiempirical calculation; (c) according to the ab initio method minima at the trans and cis geometries are found, while according to the ab initio calculation at the 6-31G level there is only one minimum on the T1 energy surface at the twisted geometry. In Table 3 and Figure 1 we report the energies and the oscillator strengths $f$ with respect to T1 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 T10, with $f = 1.14$, located at 3.70 eV above T1. Thus, T10 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, T7 and T10, have a nonnegligible oscillator strength for the transition to T1. The transition energies of both these states are larger than the transition energy of the active T10 state at the trans geometry. It follows that the T1 → T10 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-St₁-C₁, E-St₂-d₁, and E-St₉-d₁₀ in T₁ in the Planar Geometry

<table>
<thead>
<tr>
<th>Sym</th>
<th>ROHF, QCFF</th>
<th>Assign/</th>
<th>γ</th>
<th>Obs</th>
<th>ROHF, QCFF</th>
<th>γ</th>
<th>Obs</th>
<th>ROHF, QCFF</th>
<th>γ</th>
<th>Obs</th>
<th>ROHF, QCFF</th>
<th>γ</th>
<th>Obs</th>
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<tr>
<td>α₀</td>
<td>1608, 1580</td>
<td>νCC₂C₈</td>
<td>0.054</td>
<td>1573</td>
<td>1608, 1568</td>
<td>0.015</td>
<td>1563</td>
<td>1607, 1570</td>
<td>0.021</td>
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<td>1564, 1563</td>
<td>0.026</td>
<td>1557</td>
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<td>1516, 1527</td>
<td>νCC₂C₈</td>
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<td>1151</td>
<td>1508, 1520</td>
<td>0.143</td>
<td>1505</td>
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<td>1501</td>
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<tr>
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<td>1354, 1397</td>
<td>νCH (CD)</td>
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<td>1337</td>
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<td>1101</td>
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<td>1019</td>
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<td>1025, 1026</td>
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<td>0.024</td>
<td>1000</td>
<td>1027, 1025</td>
<td>0.047</td>
<td>999</td>
<td>1025, 1026</td>
<td>0.021</td>
<td>999</td>
<td>859, 829</td>
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<td>α₀</td>
<td>977, 1022</td>
<td>νCC₂C₈</td>
<td>0.050</td>
<td>966</td>
<td>970, 1018</td>
<td>0.035</td>
<td>963</td>
<td>988, 1019</td>
<td>0.041</td>
<td>978</td>
<td>945, 998</td>
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<tr>
<td>α₀</td>
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<td>νCC₂C₈</td>
<td>0.037</td>
<td>847</td>
<td>832, 887</td>
<td>0.041</td>
<td>837</td>
<td>798, 839</td>
<td>0.058</td>
<td>797</td>
<td>783, 795</td>
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<td>783</td>
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<tr>
<td>α₀</td>
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<td>νCC₂C₈</td>
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<td>650</td>
<td>632, 692</td>
<td>0.004</td>
<td>651</td>
<td>631, 689</td>
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<td>673</td>
<td>610, 671</td>
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<tr>
<td>α₀</td>
<td>625, 646</td>
<td>νCC₂C₈</td>
<td>0.000</td>
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<td>623, 644</td>
<td>0.000</td>
<td>616</td>
<td>614, 637</td>
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<td>νCC₂C₈</td>
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<td>270, 303</td>
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<td>288</td>
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<td>187, 212</td>
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<td>198</td>
<td>186, 227</td>
<td>0.037</td>
<td>198</td>
<td>179, 219</td>
<td>0.041</td>
<td>190</td>
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*The molecular geometry (C₃₈ 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 α₀ and α₀ modes are tentative possibilities; see text. *Calculated ROHF/6-31G frequencies, denotes imaginary frequencies. **The ROHF frequencies are scaled down by a factor 0.9. **Calculated QCFF/PI frequencies, **Symmetry. **Observed frequencies, **corresponding to spectra in Figure 2. **Potential energy distribution; Ph, φ = ring, e = ethylenic, τ = stretch, r = in-plane bend, w = 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, wasserrfrei reinst, Art. 4093) were used as received. Benzophenone

for (E)-stilbene and its three isotopomers in the T₁ state at the planar geometry. As mentioned above, it should be noticed that while the planar geometry is a stationary point according to QCFF/PI, it is a transition state with respect to 6-31G calculations. This is the reason for the imaginary frequencies for the α₀ mode of lowest frequency (torsion of the central CC bond).
obtained with the polarization of the probe beam perpendicular, and cell. The depolarization ratio was monitored with a Pt-100 resistance sensor. Scattered Raman light was dispersed in a single grating spectrometer and detected by a photomultiplier (RCA 1P28). The analyzing light was dispersed in a monochromator (McPherson 60) 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.

B. Methods. The time-resolved T, RR spectra were obtained as described before. In glycerol at 203 K, the triplet state of the stilbene 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 laser (Lambda Physik EMG 102E + FL 3002); the pump energy was ca. 4 mJ per pulse at the sample. The RR probe source was a Nd:YAG pumped dye laser (Quantel FL3002); the pump energy was ca. 4 mJ per pulse at the sample. Both lasers were pumped 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. Excitation was performed with a 308-nm pump pulse from an excimer laser (Lambda Physik EMG 102E). For experiments in methanol, 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 an Xe lamp (Varian VIX150UV) was 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 low temperature, i.e., in Ar-saturated glycerol solutions of ca. 0.1 mM E-St, E-St-13C2, E-St-d2, and E-St-d10, 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. The transient signal was captured and stored in a digital oscilloscope (LeCroy 9450A), and data were handled in a PDP11/23 computer.

Experimental time-resolved T, RR spectra were obtained by direct excitation in a glass, i.e., of stilbene in glycerol at 203 K as shown in Figure 2 for E-St (spectrum A), E-St-13C2 (B), E-St-d2 (C), and E-St-d10 (D). For each compound, the spectrum is constructed from three individual spectra from different frequency regions: pump wavelength, 384.5 nm; probe wavelength (A) 385.2 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 an Xe lamp (Varian VIX150UV) was 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 T1 of (A) (E)-stilbene, (B) (E)-stilbene-13C2, (C) E-stilbene-d2, and (D) (E)-stilbene-d10. Each compound, the spectrum is constructed from three individual spectra from different frequency regions: pump wavelength, 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.

The deuteriated isotopomers of (E)-stilbene were synthesized according to known procedures. Benzaldehyde was oxidized with BaMnO4 to benzaldehyde-d4. The deuterium content of the (E)-stilbenes was produced by direct excitation with a 308-nm pump pulse from an excimer laser (Lambda Physik EMG 102E). The excitation in a glass at low temperature, i.e., in Ar-saturated solutions of 0.034 M Z-St in methanol with 0.022 M benzophenone as sensitizer. The transient signal was captured and stored in a digital oscilloscope (LeCroy 9450A), and data were handled in a PDP11/23 computer.

The deuteriated isotopomers of (E)-stilbene were synthesized according to known procedures. Benzaldehyde was oxidized with BaMnO4 to benzaldehyde-d4. The deuterium content of the (E)-stilbenes was produced by direct excitation with a 308-nm pump pulse from an excimer laser (Lambda Physik EMG 102E). The excitation in a glass at low temperature, i.e., in Ar-saturated solutions of 0.034 M Z-St in methanol with 0.022 M benzophenone as sensitizer. The transient signal was captured and stored in a digital oscilloscope (LeCroy 9450A), and data were handled in a PDP11/23 computer.

Experimental time-resolved T, RR spectra were obtained by direct excitation in a glass, i.e., of stilbene in glycerol at 203 K as shown in Figure 2 for E-St (spectrum A), E-St-13C2 (B), E-St-d2 (C), and E-St-d10 (D). For each compound, the spectrum is constructed from individual spectra from different frequency regions (≈1650–1050, 1250–650 and 800–150 cm−1). The frequencies of the bands in Figure 2 are listed in Table 4 together with the most likely assignments to calculated frequencies (see discussion below). The deactivation rates of the RR bands were determined for E-St in the region 800–150 cm−1 and for...
the equilibrium geometry/geometries in the TI state and TI intersystem crossing process, (E)-stilbene finds its new minimum at the planar E geometry—the lowest triplet state. This has been explained by a shallow singlet manifold becomes sufficiently rapid to quench the intersystem crossing process completely. (For (Z)-stilbene, of the excited triplet state of stilbene, the shape of the surface 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.⁹⁹) 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 isotopomers, 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, C₂ 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 results 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 isotopomers 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, a₂ Modes. For the Raman excitation wavelength in resonance with a strongly-allowed electronic transition (T₁ → T₁₀ in the case of T₁ (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 C₂₅ 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
of E-St on the basis of frequencies (QCFF/PI and \textit{ab initio}) and \(\gamma\)-factors (QCFF/PI) calculated for totally-symmetric vibrational modes. Similar data are shown for the three isotopomers in Figures 5-7. In each figure, the theoretical spectra are compared with the observed one from Figure 2. It should be noticed that the frequencies from \textit{ab initio} calculations for the planar \(E\) form (spectra B in Figures 4-7) are not obtained at a stationary point on the PES, but at an imposed planar geometry resulting in one imaginary frequency (ethylenic torsion). In general, the agreement between theory and experiment is satisfactory, and an assignment between the theoretical and observed \(T_1\) RR spectra is reasonable for bands with strong or medium intensity in Figures 4-7. In Table 4 we list the observed frequencies for the \(T_1\) state of the four isotopomers, together with the calculated (QCFF/PI and \textit{ab initio}) frequencies of \(a_g\), \(b_g\), and \(a_u\) symmetry modes that we assign to the observed bands. We shall now discuss the assignment in some detail.

In our first report on the \(T_1\) RR spectrum of E-St, we assigned most of the observed bands to \(a_g\) normal modes of the planar \(E\) structure.\(^{10}\) 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-\(^{13}\text{C}_2\) (Figure 2B) to calculated \(a_g\) 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-\(^{13}\text{C}_2\) are small but consistent. It is evident that replacement of the central carbon atoms by \(^{13}\text{C}\) does not alter the vibrations in \(T_1\) stilbene much. Most \(a_g\) modes calculated for E-St and E-St-\(^{13}\text{C}_2\) are observed in experiment. Exceptions are the ones calculated (QCFF/PI values) at 1490 and 1183 \(\text{cm}^{-1}\) for E-St (1488 and 1175 \(\text{cm}^{-1}\) for E-St-\(^{13}\text{C}_2\)).

The vibrational pattern is changed more by deuteration, for both \(d_2\) (Figure 2C) and \(d_{10}\) substitution (Figure 2D). Again, the observed isotopic shifts are reproduced well by calculation. For E-St-\(d_2\) (Figure 6) and E-St-\(d_{10}\) (Figure 7), all calculated \(a_g\) bands are found in the experimental spectra, except for those calculated with zero intensity for E-St-\(d_2\) at 1096 \(\text{cm}^{-1}\) and for E-St-\(d_{10}\) at 829 \(\text{cm}^{-1}\) (QCFF/PI).

2. \textbf{R.\textit{R. Spectra, \(b_a\), \(b_u\), and \(a_u\) Modes.} For strictly planar E-St with \(C_{2v}\) symmetry, in the Franck-Condon approximation, \(i.e.,\) in the absence of vibronic coupling, only \(a_u\) modes are RR-active. Modes of \(b_a\), \(b_u\), or \(a_u\) symmetry can be observed only as either combinations or overtones, containing an even number of vibrational quanta. They derive their intensity from changes in frequency of the normal mode between the two resonant electronic states.\(^{60}\) As shall be seen below, the positions of most of the observed bands not assigned to \(a_g\) modes are close to calculated \(b_a\) or \(a_u\) modes, and their assignment as overtones seems therefore unlikely. However, it should also be noticed that torsional modes of very low frequency are calculated in the present work, and a fundamental frequency as low as 8 \(\text{cm}^{-1}\) has previously, in free jet experiments on ground-state stilbene, been observed to be very active and anharmonic and of very large amplitude.\(^{61}\) Hence, the observed non-totally symmetric vibrations may well be due to combinations of \(b_a\) or \(a_u\) modes involving low-frequency torsional modes.

Fundamentals of non-totally symmetric modes are in the \(C_{2v}\) point group forbidden for modes of ungerade symmetry. Modes of \(b_a\) symmetry can gain intensity only due to vibronic coupling between electronic states. If an electronic state \(T_{1g}\) is close in energy to the lower state \(T_1\) or the upper state \(T_1\) in the dominant
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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 → T₁₀ transition) of vibrational modes (aₗ symmetry only) in the planar E geometry (C₂ᵥ point group, stationary point) calculated by QCFF/PI. (B) Frequencies of vibrational modes (aₗ symmetry only) in the planar E geometry (C₂ᵥ 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 → T₁₀ transition) of vibrational modes (aₗ symmetry only) of centrally twisted stilbene-d₂ (C₂ᵥ point group, nonstationary point) calculated by QCFF/PI. (E) Frequencies of vibrational modes (aₗ symmetry only) of centrally twisted stilbene-d₂ (C₂ᵥ point group, stationary point) calculated by ROHF/6-31G level.

T₁ → T₄ transition, non-totally symmetric modes of proper symmetry may vibronically couple T₄ with T₁ or T₄. We have previously found this mechanism to be active for bₗ modes in the ground state D₀ of the benzyl radical.⁴³ The upper state T₄, active in the present experiments, has been calculated as the T₁₀ π*π* state at 3.905 eV above the T₁ state (CNDO/S). For bₗ modes to be vibronically active, they can couple either the T₁₀ state of Aₗ symmetry with a T₄ π*π* excited state of Bₗ symmetry or the T₄ state of Bₗ symmetry with a T₄ state of Aₗ symmetry. Alternatively, T₁ or T₄ - E-St may not be strictly planar. For a symmetric torsion at the Cₛ-Cₛ or Cₛ-phenyl bonds in T₁, the molecular symmetry is lowered from C₂ᵥ 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 aₗ or bₗ symmetry in C₂ᵥ may be observed in the RR spectrum. This case shall be discussed in section IVB.

The bands in Figures 2 and 4–7, which cannot be assigned to aₗ modes, are observed below 1100 cm⁻¹. Since this is the region where modes of bₗ and aₗ 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 bₗ, bₗ, and aₗ symmetry normal modes. For all isomers, the calculated frequencies of bₗ and aₗ modes are similar for many modes. We choose to concentrate on the bₗ modes, but as shall be seen below, an assignment to aₗ modes or rather their combinations may be more likely, in view of the calculated aₗ 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 bₗ and aₗ 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 bₗ 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 bₗ mode at 470 cm⁻¹ (420 cm⁻¹ in ab initio) or the aₗ band at 482 cm⁻¹ (422 cm⁻¹). This mode is described as an out-of-plane ring CCCC deformation; it is shifted little for E-St-1³C₁₂ (obs 459 cm⁻¹, calc 469 cm⁻¹) and E-St-d₁ (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 aₗ modes at 303 and 228 cm⁻¹ alone, but a contribution to the 288-cm⁻¹ band from the calculated 306-cm⁻¹ bₗ mode is possible. Likewise, the broad band observed at 704 cm⁻¹ may well have contributions from both aₗ and bₗ modes.

For E-St and E-St-1³C₁₂ all calculated modes of bₗ symmetry below 1000 cm⁻¹ have counterparts in the spectra, and the calculated bₗ modes are able to account for all the remaining observed bands.

For E-St and E-St-1³C₁₂ the highest-frequency bₗ and aₗ modes are calculated and observed close to 1050 cm⁻¹. For E-St-d₁₀, calculation predicts no bₗ or aₗ 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 aₗ symmetry. All band observed below 750 cm⁻¹, which cannot be assigned to aₗ modes, can be assigned to calculated modes of bₗ or aₗ symmetry, in particular the observed 407-cm⁻¹ band mentioned above.

For E-St-d₁₀ as well, the remaining observed bands can be assigned to calculated modes of bₗ 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 TI, 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 not found any indication of strong vibronic coupling within the manifold of \(\pi^*\) and \(\pi^*\) 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 \(b_2\) band at 36 cm\(^{-1}\) \((\tau(C = C))\) 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 isoto suppressors can be assigned to calculated vibrational modes of the planar \(E\) form of stilbene in the TI 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, \(C_3v\) 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 \(T_1 \rightarrow T_0\) 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 \(T_0 \rightarrow T_0\) transition of planar \(E\) stilbene by factors of ca. 8.5 \((T_1 \rightarrow T_0)\) 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 (ethylenic C=C 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 spectrum 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 \(C_3v\) transform into a symmetry in the \(C_3\) 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 isoto suppressors 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-\(13C_2\), and \(E\)-St-\(d_{10}\) and those below 600 cm\(^{-1}\) in \(E\)-St-\(d_{12}\). 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-\(13C_2\), those observed in \(E\)-St-\(d_{12}\) at 1562 and 958 cm\(^{-1}\), and those observed in \(E\)-St-\(d_{10}\) 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 TI 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 obviously is 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 with those of \((Z)\)-stilbene in solution at room temperature, we conclude that very similar species with respect to the torsional angle of the ethylenic C=C bond are responsible for the experimentally observed RR spectra under the different conditions. This means that we can rule out that the species observed by resonance Raman in glasses and in solution have substantially different conformation.

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. 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.
uncertainty. This is due to the fact that (i) the collection optics
shown in Figure 3 for two excitation wavelengths, namely, 381.2
intensities with decreasing excitation wavelength are not dramatic
with one notable exception: the band at 1182 cm⁻¹ seems
spectra, with 3845, 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
frequency changes were observed, and the changes in intensity
approximately a factor 2 relative to the strongest observed band
no correction was made
in tert-butyl alcohol (spectrum B). In glycerol, peaks
enhancement in Figure 3D. In the latter case, the 0-0 band of
the 0-0 band of spectrum in methanol at 203 K with 381.2-nm (0-0 band of spectrum in
the structureless spectrum in tert-butyl alcohol at room tem-
energy transfer from a sensitizer to ground-state (Z)-stilbene
the relative intensities of the bands are similar for Figures 2A
and 4.36 CP at 201 K for tert-butyl alcohol, for which the TI
absorption spectrum in methanol at 203 K may not be
that is, changes in the shape of RR spectra. This effect has been
discussed in detail for the case of weak displacements.63

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
incompletely, 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,64 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.64 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 temper-
perature. However, apart from the difference in overall intensity,
the relative intensities of the bands are similar for Figures 2A
and 3D. 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

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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 → T₂ 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 → T₂ 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 T₂. (Frequency 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 S₀ → S₁ absorption spectrum when the temperature and properties of the solvent are changed.

There is no doubt that the QCFF/PI calculations support an assignment of the observed T₁ RR and T₁ → T₂ 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 data 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 → T₂ 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 wavelengths 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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