Theoretical Study of the Lowest $^1\text{Bu}$ States of trans-Stilbene

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The results of a theoretical study of the ground state, $^1\text{A}_g$, and of the lowest $^1\text{Bu}$ states of trans-stilbene are presented. The vertical and adiabatic excitation energies of the lowest $^1\text{Bu}$ states have been computed using multiconfigurational SCF theory, followed by second-order perturbation theory. It is shown that the two lowest excited states are separated by a small energy gap in the Franck–Condon region. They are the $^1\text{Bu}_1$ characterized by the HOMO–LUMO single excitation substantially localized on the ethylenic moiety, and the $^2\text{Bu}_2$ formed by a combination of one electron excitations localized mainly on the benzene rings. The most intense transition is found to be the lowest in energy when the interaction between different states is included at the level of second-order perturbation theory. The vibronic structure of emission and absorption spectra of the two lowest $^1\text{Bu}$ states have been determined within the Franck–Condon approximation. The spectrum calculated for the $^1\text{Bu}_2$ state agrees with the experimental spectrum, while the low intensity band computed for the $^2\text{Bu}_2$ state has no experimental counterpart. It is concluded that this band is buried in the strong $^1\text{Bu}_1$ absorption and therefore not observed.

1. Introduction

Stilbene and stilbene-type molecules have attracted a widespread interest of both theoretical and experimental chemists for more than 60 years because they are prototype molecules for the study of electronic excited state deactivation and of the mechanism of photoreactivity. The modeling of the photoisomerization is easier than other photoprocesses because its reaction coordinate, the torsion around the central CC bond leading to trans–cis isomerization, is well defined. Thus, the trans–cis photoisomerization of stilbene has been extensively studied both experimentally and theoretically.

According to the commonly accepted picture, the mechanism of cis–trans photoisomerization of trans-stilbene (TS) is based on the following concepts:

- The $S_1$ state, belonging to the $B_u$ representation of the $C_{2v}$ point group, is to a large extent characterized by the HOMO–LUMO excitation. As indicated by quantum yield and lifetime of fluorescence spectra and by intensity of the lowest energy absorption band, it has large transition oscillator strength.
- Its HOMO–LUMO character leads, as in ethylene, to a flat potential energy surface and this makes isomerization feasible in the $S_1$ excited state in accordance with the Woodward–Hoffmann rules.
- The doubly excited HOMO, HOMO–LUMO, LUMO singlet state, of $A_g$ symmetry, observed in the two-photon spectroscopy, may become the lowest excited state at the twisted geometry and favor the photoisomerization.
- The decay from the $S_1$ state to the ground state and the photoisomerization process may be enhanced by a conical intersection between $S_0$ and $S_1$.

A quantitative assessment of the ordering of the lowest electronic states and of the shapes of their potential energy surfaces and thus of the contributions of these mechanisms to the decay of $S_1$ is still lacking. An important step in this direction is provided by a recent paper by Molina et al., in which a quantum chemical study of the vertical transitions of the low-lying excited states of TS, using multiconfigurational wave functions (CASSCF) and second order perturbation theory (CASPT2), is reported. The results of this study were in general in good agreement with experimental data. In particular, they have been useful for the assignment of the two-photon spectra of TS recently investigated by Hohlneicher et al.

However, surprisingly, the electronic state associated to the lowest intense transition, described mainly by a one-electron promotion of HOMO–LUMO type, with an oscillator strength of 0.7 (denoted hereafter as $^1\text{Bu}(\text{HL})$), was found to correspond to the $^2\text{Bu}_2$ state. Its calculated energy, at 4.07 eV, is in good agreement with the experimental measure, which is around 4.0 eV. The $^1\text{Bu}_2$ state was found at lower energy, 3.77 eV above the ground state, with an oscillator strength of 0.04. It is of the $L_0$ benzenic type and is described mainly by a combination of the singly excited configurations HOMO–(LUMO+1) and (HOMO–1)–LUMO (denoted hereafter as $\text{Bu}(-)$).

The prediction of a weak transition $^1\text{Bu}$ below the allowed HOMO–LUMO state is in disagreement with experimental evidence and also with earlier theoretical studies, which possibly benefited from errors cancellation. The authors discussed this discrepancy, noting that the amount of the vertical separation between the two lowest $^1\text{Bu}$ states, 0.3 eV, is of the same order of magnitude as the accuracy of the computational methods used. Furthermore, they suggest that the ordering of two states may depend on the molecular geometry and this was proposed also in a recent study by Hohlneicher et al. The issue is of some importance, not only for its implications on the dynamics of the trans–cis photoisomerization process, but also from the methodological point of view, that is with reference to the accuracy and reliability of the CASSCF/CASPT2 approach in the case of two close-lying electronic states. When
states are so close as here, this method becomes quite uncertain and the interactions between the states at the correlated level might change their ordering. Recently, in 1998, the CASPT2 method was extended to include such effects. This resulted in the multi-state (MS) CASPT2 approach, which includes the interaction between the different states at the level of second order perturbation theory. It has shown to be able to treat such interactions successfully in a number of applications.

The present work reexamines the ordering of the lowest excited states of TS, using this more advanced technique. We have performed the calculations using an enlarged active space, which includes all 14 $\pi$-orbitals with 14 active electrons, while Molina et al.,\textsuperscript{16} used a 10/12 active space. The typical $C=\equiv C$ central bond distance ($C_1-C_1$ in Figure 1) was optimized pointwise at the MS−CASPT2 level of theory, and for each geometry several $1B_u$ excited states were computed.

However, more important for the analysis of the absorption and fluorescence spectra is the possibility we have today of computing not only the vertical excitation energies, but also the geometry of the excited states and harmonic frequencies at the CASSCF level of theory. This gives us the possibility to model the Franck−Condon spectra, which allows a detailed discussion of the character of the two $1B_u$ states with respect to their geometry and the shape of the energy surface around the equilibrium geometry. Comparison to the observed spectra becomes more meaningful. One should remember that the vertical excitation energy is a theoretical concept and can be estimated by experiment only qualitatively. With the Franck−Condon spectra available, a direct comparison of the 0−0 transitions and the vibronic progressions becomes possible. We have recently published such an analysis for the two-photon allowed excitation to the $2A_g$ state.\textsuperscript{25} Here we shall do the same for the two lowest state of $1B_u$ symmetry.

2. Computational Details

Complete Active Space (CAS) SCF\textsuperscript{21} calculations have been performed and the dynamic electron correlation was added using multiconfigurational second-order perturbation theory. MS−CASPT2,\textsuperscript{22−24} The MOLCAS-5 quantum chemistry program\textsuperscript{26} was used.

The active space choice is a crucial step in a CASSCF calculation. The stilbene molecule with its 14 valence $\pi$ MO’s and 14 $\pi$ electrons is a challenging case. In this study, the dependence of the geometry on the active space choice has been investigated for the ground state. We explored several possibilities going from a minimal choice of 10 active electrons in 10 active $\pi$ MO’s (10/10), up to the largest calculation including all the 14 active electrons in the 14 active valence $\pi$ MO’s (14/14). As intermediate cases, we performed the calculation with 10 active electrons in 12 active $\pi$ MO’s (10/12), as already performed by Molina et al.,\textsuperscript{16} and 12 active electrons in 12 active orbitals (12/12). All these calculations were performed in $C_{2h}$ symmetry (planar molecule). By placing the molecule in the xy plane, the $\pi$ orbitals belong to the $a_u$ and $b_g$ irreducible representations of $C_{2h}$. In the 14/14 calculation, for example, the active space is composed by 0.0.7.7, active orbitals in the four irreducible representations $a_u$, $b_u$, $a_g$, and $b_g$, respectively.

Generally contracted basis sets of atomic natural orbital (ANO) type were used with the contraction scheme 3s2p1d on C and 2s1p on H.\textsuperscript{27} The geometry of the ground state and two excited $1B_u$ states were optimized at the CASSCF level by computing analytical first derivatives.\textsuperscript{2} The ethylenic $C=\equiv C$ bond was reoptimized pointwise at the 14/14 CASPT2 level of theory. The geometry of the ground state was also optimized using density functional theory (DFT), with the B3LYP exchange-correlation functional, and a 6-31G* basis set. The program Gaussian98 was employed.

The 10/12-CASSCF harmonic frequencies (10/12 frequency calculation at the 10/12 optimized geometry) for the $1A_g$ and $1B_u$ states were computed using analytical second derivatives. It was not feasible to perform such calculations using a larger active space.

The multistate option (MS) of the CASPT2 method was used to study the $1B_u$ states. This is a new feature of MOLCAS-5 that allows to perform CASPT2 calculations for a number of the selected roots from a state average CASSCF calculation (in this case three $B_u$ states). An effective Hamiltonian constructed by second-order perturbation theory is diagonalized to obtain the final MS−CASPT2 energies.\textsuperscript{24}

The method was used to compute excitation energies at the optimized geometries and also at intermediate points where the ethylenic $C_1-C_1$ distance was varied pointwise together with the ethylene−phenyl ($C_1-C_3$) distance (see Figure 1 for the numbering of the atoms). CASPT2 calculations were performed for the ground state at the same points. In this way it was possible to study the ordering of the $1B_u$ states as a function of the most important geometry parameters. The oscillator strengths have been obtained using the “mixed” reference functions that are obtained from the MS-CASPT2 calculation. To compare our results with the experimental data of Hohlneicher et al.,\textsuperscript{11} the vibronic spectra of the two $1B_u$ states were computed according to the Franck−Condon mechanism. Harmonic force fields at the equilibrium geometries were computed analytically using the 10/12 CASSCF wave functions. For the $B_u$ states, a common set of force constants was used, obtained from the 10/12 CASSCF wave function. The intensities were estimated from Franck−Condon factors, and a spectrum was constructed from Lorentzian line profiles. The profile of the computed spectrum depends strongly on the amount of displacement of the equilibrium nuclear coordinates along vibration modes and on vibrational frequencies of the final state and therefore gives a sensitive measure of the accuracy of the geometry of the excited state. The calculations of Franck−Condon factors were performed with a recent program, capable of treating states with several excited vibrational quanta in a large number of modes.\textsuperscript{29}

3. Results and Discussion

3.1. Geometries and Relative Energies. In Table 1 the ground-state equilibrium geometries obtained at the CASSCF level with different active spaces are presented. The central $C_1-C_1$ bond length obtained with the 10/12 active space is the same as the 14/14 value, while the 10/10 and 12/12 calculations give a slightly shorter $C_1-C_1$ bond. The 14/14 CASPT2 $C_1-C_1$ bond length is 1.363 Å. This value is slightly longer than the 14/14 CASSCF result, and it is also longer than the experimentally accepted value, which is between 1.33 and 1.35 Å.\textsuperscript{30−32} The latter value is most likely correct, because this bond should be longer than in ethylene, due to conjugation with the phenyl rings. It appears that CASSCF with all $\pi$-orbitals active gives accurate
The optimized geometry of 2°B state with the 14/14 active space shows a longer central C1–C1 bond, 1.505 Å, and a shorter C1–C2 bond, 1.419 Å. Clearly, the excitation to this state affects substantially the central moiety of TS.

The analysis of the 14/14 wave function of the 1°B state at its equilibrium geometry shows that this state has a strong multiconfigurational character, with a small weight of the HOMO–LUMO configuration and a modest oscillator strength (<0.05). This state does not correspond to the ionic 1°B state responsible for the lowest, strong band in the absorption spectrum. Actually, as we shall see below, the state dominated by the HOMO–LUMO configuration, with large oscillator strength, is the second at this optimized geometry.

With the 10/12 active space, the wave function of the 1°B state at the optimized geometry shows a larger HOMO–LUMO character and a sizable oscillator strength (ca. 0.3). This state thus resembles more the B3°(HL) state, which is the lowest by experiment. Clearly, the ordering of the three close lying excited states depends on the molecular geometry, on the active space used, and on the amount of correlation included. The reordering of the different states for different geometries makes it very difficult to optimize the geometry of the HOMO–LUMO state with the 14/14 active space.

Therefore, we decided to perform single point calculations at the (state average) CASSCF, CASPT2, and MS-CASPT2 levels of theory for the three lowest B° states with a 14/14 active space at the following CASSCF optimized geometries (angstrom):

<table>
<thead>
<tr>
<th>geometry</th>
<th>R(C1–C1)</th>
<th>R(C1–C2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°A(14/14)</td>
<td>G1</td>
<td>1.350</td>
</tr>
<tr>
<td>1°B(14/14)</td>
<td>G2</td>
<td>1.383</td>
</tr>
<tr>
<td>1°B(10/12)</td>
<td>G3</td>
<td>1.409</td>
</tr>
<tr>
<td>intermediate geometry</td>
<td>G34</td>
<td>1.441</td>
</tr>
<tr>
<td>2°B(14/14)</td>
<td>G4</td>
<td>1.505</td>
</tr>
</tbody>
</table>

The geometries are those reported in Table 1 (G1), and Table 2 (G2, G3, and G4). One additional intermediate geometry was added to the list of optimized geometries, (G34), in which the geometric parameters for the central moiety were taken from an average of G3 and G4 geometries while the ring structure was taken from G4 geometry. We have then constructed the potential energy curves for the three lowest B° states as a function of the C1–C1’ bond distance.

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**TABLE 1**: Geometry of the 1°A° State at the CASSCF Level, with Different Active Spaces

<table>
<thead>
<tr>
<th></th>
<th>10/12</th>
<th>12/12</th>
<th>14/14</th>
<th>B3LYP</th>
<th>exptf</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(C1–C1)</td>
<td>1.391</td>
<td>1.397</td>
<td>1.402</td>
<td>1.395</td>
<td>1.391</td>
</tr>
<tr>
<td>r(C1–C2)</td>
<td>1.399</td>
<td>1.399</td>
<td>1.400</td>
<td>1.395</td>
<td>1.391</td>
</tr>
<tr>
<td>r(C1–C3)</td>
<td>1.392</td>
<td>1.378</td>
<td>1.395</td>
<td>1.395</td>
<td>1.381</td>
</tr>
<tr>
<td>r(C2–C3)</td>
<td>1.402</td>
<td>1.402</td>
<td>1.402</td>
<td>1.399</td>
<td>1.383</td>
</tr>
<tr>
<td>r(C2–C4)</td>
<td>1.406</td>
<td>1.406</td>
<td>1.408</td>
<td>1.409</td>
<td>1.397</td>
</tr>
<tr>
<td>R(C1–C2)</td>
<td>1.391</td>
<td>1.389</td>
<td>1.394</td>
<td>1.394</td>
<td>1.381</td>
</tr>
<tr>
<td>A</td>
<td>126.9</td>
<td>126.6</td>
<td>126.8</td>
<td>126.7</td>
<td>126.4</td>
</tr>
<tr>
<td>B</td>
<td>118.4</td>
<td>118.6</td>
<td>118.4</td>
<td>118.5</td>
<td>119.0</td>
</tr>
<tr>
<td>C</td>
<td>123.5</td>
<td>123.5</td>
<td>123.6</td>
<td>123.6</td>
<td>123.2</td>
</tr>
</tbody>
</table>

**TABLE 2**: 1°B° and 2°B° Geometry with Different Active Spaces

<table>
<thead>
<tr>
<th></th>
<th>10/12</th>
<th>12/12</th>
<th>14/14</th>
<th>B3LYP</th>
<th>exptf</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(C1–C1)</td>
<td>1.409</td>
<td>1.362</td>
<td>1.383</td>
<td>1.505</td>
<td></td>
</tr>
<tr>
<td>r(C1–C2)</td>
<td>1.414</td>
<td>1.454</td>
<td>1.435</td>
<td>1.419</td>
<td></td>
</tr>
<tr>
<td>r(C1–C3)</td>
<td>1.439</td>
<td>1.428</td>
<td>1.434</td>
<td>1.443</td>
<td></td>
</tr>
<tr>
<td>r(C1–C4)</td>
<td>1.408</td>
<td>1.415</td>
<td>1.414</td>
<td>1.379</td>
<td></td>
</tr>
<tr>
<td>r(C1–C5)</td>
<td>1.377</td>
<td>1.413</td>
<td>1.410</td>
<td>1.437</td>
<td></td>
</tr>
<tr>
<td>r(C1–C6)</td>
<td>1.413</td>
<td>1.414</td>
<td>1.413</td>
<td>1.428</td>
<td></td>
</tr>
<tr>
<td>r(C1–C7)</td>
<td>1.414</td>
<td>1.417</td>
<td>1.417</td>
<td>1.379</td>
<td></td>
</tr>
<tr>
<td>R(C1–C2)</td>
<td>125.6</td>
<td>126.7</td>
<td>126.8</td>
<td>127.2</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2.731</td>
<td>2.733</td>
<td>2.717</td>
<td>2.714</td>
<td>2.611</td>
</tr>
<tr>
<td>B</td>
<td>0.263</td>
<td>0.261</td>
<td>0.261</td>
<td>0.261</td>
<td>0.263</td>
</tr>
<tr>
<td>C</td>
<td>0.240</td>
<td>0.238</td>
<td>0.238</td>
<td>0.238</td>
<td>0.241</td>
</tr>
</tbody>
</table>
The computed vertical excitation energies (oscillator strength) for the three 1B_u states are 4.03 (0.01), 4.04 (0.81), and 5.73 (0.01) at the MS-CASPT2 level. In the next section we shall discuss the vibrational structure for the emission and absorption spectra of the two lowest 1B_u states, to show that their different character is reflected also in the Franck-Condon envelop of the two electronic transitions. Here we only notice that the vertical energy for the S1 has been experimentally found to lie in the energy range 4.0–4.2 eV.2

The MS–CASPT2 energy curves of the three 1B_u states as a function of the C1−C3 distance are shown in Figure 2. The intense state is always the lowest and its minimum energy is found for R (C1−C3) equal to ca. 1.41 Å, which is a geometry close to G3. We see a clear difference between this state and the weakly allowed state. In the strongly allowed state the elongation of the CC double bond is more pronounced, from 1.35 to 1.41 Å, while the phenyl bond has shortened from 1.47 to 1.41 Å. The excitation in the intense 1B_u state is largely localized in the ethylene fragment. As a consequence we decided to use the G3 equilibrium geometry in the calculation of the Franck-Condon structure. The result of that calculation provides further evidence that the G3 geometry corresponds well to the geometry of the strong 1B_u state (see below).

The computed adiabatic excitation energies for the lowest 1B_u state is 3.30 eV. This value is lower than the experimental value around 3.8 eV.11 Thus, the MS-CASPT2 treatment appears to overestimate the interaction between the three states.

3.2. Vibrationally Resolved Absorption and Fluorescence Spectra for the 1B_u(HL) and 1B_u(−) States. The 10/12 harmonic frequencies for the 1A_g and 1B_u states, with their assignments, are presented in Tables 5–8. The corresponding force field has been used for the calculation of the vibrationally resolved electronic spectra. The CASSCF frequencies are overall ca. 10% higher than the experimental frequencies. This is due to the use of a harmonic force field, but also to the missing correlation effects in the CASSCF approach. At the CASSCF level, analytic force constants are troublesome when the investigated state interacts with other states. This seems to happen here for the 1B_u state, where at least some vibrational modes of b_u symmetry are affected (see for example the harmonic frequency of ν_55, which is 2490 cm⁻¹). The large IR intensities computed for some vibrational modes also suggest some nonphysical interactions with nearby states, because they typically give large dipole moment derivatives.

The assignment of the lower frequencies out of plane modes (b_u, a_u) for the ground state was taken from our previous study.33 The calculated vibrational frequencies of the 1B_u states can be a guideline for the assignment of high-resolution absorption and emission spectra.

Table 3: Adiabatic Energy Differences (eV) with Respect to 1A_g State, and Oscillator Strength for the Three B_u States at Various Geometries

<table>
<thead>
<tr>
<th>geometry</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
<th>G4</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(C−C1)</td>
<td>4.50 (0.01)</td>
<td>4.50 (0.01)</td>
<td>4.50 (0.01)</td>
<td>4.50 (0.01)</td>
</tr>
<tr>
<td>r(C−C3)</td>
<td>5.70 (0.02)</td>
<td>5.70 (0.02)</td>
<td>5.70 (0.02)</td>
<td>5.70 (0.02)</td>
</tr>
<tr>
<td>CASCF</td>
<td>5.10 (0.01)</td>
<td>5.10 (0.01)</td>
<td>5.10 (0.01)</td>
<td>5.10 (0.01)</td>
</tr>
<tr>
<td>G1</td>
<td>5.30 (0.01)</td>
<td>5.30 (0.01)</td>
<td>5.30 (0.01)</td>
<td>5.30 (0.01)</td>
</tr>
<tr>
<td>G2</td>
<td>5.40 (0.02)</td>
<td>5.40 (0.02)</td>
<td>5.40 (0.02)</td>
<td>5.40 (0.02)</td>
</tr>
<tr>
<td>G3</td>
<td>5.50 (0.03)</td>
<td>5.50 (0.03)</td>
<td>5.50 (0.03)</td>
<td>5.50 (0.03)</td>
</tr>
<tr>
<td>G4</td>
<td>5.60 (0.04)</td>
<td>5.60 (0.04)</td>
<td>5.60 (0.04)</td>
<td>5.60 (0.04)</td>
</tr>
</tbody>
</table>

Table 4: MS-CASPT2 Mixing at the Various Geometries of the Three Lowest 1B_u States

<table>
<thead>
<tr>
<th>geometry</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>MSPT2</td>
<td>0.68</td>
<td>−0.73</td>
</tr>
<tr>
<td>S1 MSPT2</td>
<td>0.73</td>
<td>0.67</td>
<td>0.14</td>
</tr>
<tr>
<td>S2 MSPT2</td>
<td>−0.09</td>
<td>−0.11</td>
<td>0.99</td>
</tr>
<tr>
<td>G2</td>
<td>MSPT2</td>
<td>0.41</td>
<td>−0.91</td>
</tr>
<tr>
<td>S1 MSPT2</td>
<td>0.80</td>
<td>0.35</td>
<td>−0.49</td>
</tr>
<tr>
<td>S2 MSPT2</td>
<td>0.44</td>
<td>0.21</td>
<td>0.87</td>
</tr>
<tr>
<td>G3</td>
<td>MSPT2</td>
<td>0.37</td>
<td>−0.93</td>
</tr>
<tr>
<td>S1 MSPT2</td>
<td>0.78</td>
<td>0.31</td>
<td>0.54</td>
</tr>
<tr>
<td>S2 MSPT2</td>
<td>0.50</td>
<td>−0.20</td>
<td>0.84</td>
</tr>
<tr>
<td>G4</td>
<td>MSPT2</td>
<td>0.83</td>
<td>−0.49</td>
</tr>
<tr>
<td>S1 MSPT2</td>
<td>0.51</td>
<td>0.86</td>
<td>−0.00</td>
</tr>
<tr>
<td>S2 MSPT2</td>
<td>−0.24</td>
<td>0.15</td>
<td>0.96</td>
</tr>
<tr>
<td>S3 MSPT2</td>
<td>0.94</td>
<td>0.32</td>
<td>0.15</td>
</tr>
<tr>
<td>S1 MSPT2</td>
<td>−0.32</td>
<td>0.95</td>
<td>−0.00</td>
</tr>
<tr>
<td>S2 MSPT2</td>
<td>−0.15</td>
<td>−0.05</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Figure 2. Total energy as a function of the C1−C1 distance for S1 (solid line), S2 (dashed), and S3 states (dotted).
Franck–Condon factors that modulate the vibrational structure of electronic transitions depend heavily on the difference in equilibrium geometries of the initial and final states. Computed absorption spectrum of the $^{1}B_{u}(HL)$ $\rightarrow$ $^{1}A_{g}$ transition is shown in Figure 3. All computed spectra have been broadened with Lorentzian line shapes with fwhm = 2 meV (sharp lines) and 50 meV (broad peaks) to simplify comparison with experiment. The experimental spectrum (dashed curve) of Hohlneicher et al.\textsuperscript{11} has been inserted. The close resemblance agrees with the notion that the excited-state geometry of the strong HL state is close to G3. The $v_{1}$ and $v_{13}$ modes, showing the largest progressions, correspond to structures undergoing large displacements in the transition. We computed the absorption spectrum also for the weak $^{2}B_{u}$ state, which has its equilibrium geometry close to G2. The calculated spectrum is reported in Figure 4. It is very weak and shows no resemblance to the observed absorption spectrum. Because it is hidden under the stronger absorption of the $^{1}B_{u}$ state, it will be very difficult to observe.

Assignments of the most prominent features in the fluorescence spectra from the two $^{1}B_{u}$ states. The vibronic progressions, correspond to structures undergoing large displacements in the transition. We computed the absorption spectrum also for the weak $^{2}B_{u}$ state, which has its equilibrium geometry close to G2. The calculated spectrum is reported in Figure 4. It is very weak and shows no resemblance to the observed absorption spectrum. Because it is hidden under the stronger absorption of the $^{1}B_{u}$ state, it will be very difficult to observe.

In a similar way we calculated the vibrational envelope of the fluorescence spectra from the two $^{1}B_{u}$ states. The vibronic structure is governed in both spectra by the normal modes of deformation. The experimental spectrum agrees with the assignment that the geometry of the strong HL state is close to G3. The $v_{7}$ and $v_{11}$ modes, showing the largest progressions, correspond to structures undergoing large displacements in the transition.

The calculated emission spectra are shown in Figures 5 and 6. The calculated emission spectra are shown in Figures 5 and 6.

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G3. Comparing the absorption and emission spectra from this state (Figures 3 and 5) shows strong similarities, but also some differences. The ethylenic mode \( \nu_7 \) gives rise to strong bands in both spectra, while \( \nu_{13} \) and \( \nu_{15} \) (both CC stretch) are strong in absorption and emission, respectively (see Table 3 for the definitions of the different \( a_g \) modes). These features are also confirmed experimentally (cf. Table 9), which gives \( \nu(0,1) \) as a strong band at 1654 cm\(^{-1}\). Band \( \nu(0,1) \) appears as a strong feature at 1208 cm\(^{-1}\) experimentally, and at 1286 cm\(^{-1}\) in the theoretical spectrum. However, the activity of \( \nu_{25} \), (204 cm\(^{-1}\), the CCC bending localized in the ethylene moiety, is not well predicted. In the dispersed fluorescence spectrum the fundamental of \( \nu_{25} \) has a relative intensity of 71% of the 0-0 band and generates a progression comprising a number of overtones with significant intensity. The computed activity is much lower: the intensity of the fundamental is only 19% of the 0-0 band. According to the Franck–Condon analysis performed by Syage et al. the intensity distribution in this mode is accounted for by a difference of 1.3 \( \pm \) 0.3 degrees of the bending angle \( \mathrm{C}_1 \mathrm{C}_2 \mathrm{C}_3 \) (cf. Figure 1) between \( S_0 \) and \( S_1 \). The difference between the calculated and observed activity of \( \nu_{25} \) can be understood considering that the computed \( \mathrm{C}_1 \mathrm{C}_2 \mathrm{C}_3 \) angle, (118.5 \(^\circ\)), is the same in \( S_0 \) and \( S_1 \).

Table 9 lists only bands below 2500 cm\(^{-1}\) with a relative intensity larger than 1. The computed spectrum does not correspond strictly in all the details to the observed spectrum by Syage et al. because of the limited accuracy of the computed vibrational force fields of the \( S_0 \) and \( S_1 \) states.

If we disregard the fine details and model the spectrum at lower resolution, by broadening the line width of each band, we get better agreement between theory and experiment. This indicates that the calculation reproduces the main features of the geometry changes in the \( S_0 - S_1 \) transition and the overall shape of the spectra.

4. Conclusions

We have presented the results of a study of the \( 1^1A_g \) ground state and the two lowest excited states of \( 1^1B_u \) symmetry for
trans-stilbene. A weak state of the same symmetry was found in the vicinity of the well-known HOMO—LUMO 1B₁ state. The ordering of the two states has been shown to depend strongly on the level of approximation used in the calculations. Only at the MS—CASPT2 level of theory was the intense state found to be lower in energy. The vibronically resolved absorption and fluorescence spectra of the two states have been determined within the Franck—Condon approximation. The computed vibronic intensity distribution for the 1B₁ state is in close agreement with experiment, which confirms that the computed equilibrium geometry for this state is correct. The weak state gives rise to a completely different vibronic structure. The corresponding absorption band is hidden under the 1B₁ band and will be difficult to observe.

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References and Notes

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