

A Priori Scaled Quantum Mechanical Vibrational Spectra of *trans*- and *cis*-Stilbene

Juan Francisco Arenas, Isabel López Tocón, Juan Carlos Otero,* and Juan Ignacio Marcos

Department of Physical Chemistry, Faculty of Sciences, University of Málaga, E-29071 Málaga, Spain

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The vibrational frequencies of both isomers of stilbene have been computed at the *ab initio* 3-21G level by using the scaled quantum mechanical force field methodology. First, the force fields of benzene and ethylene have been computed and scaled, and then the so obtained scale factors have been transferred to *trans*- and *cis*-stilbene. The excellent agreement between the *a priori* computed frequencies and the experimental ones has allowed for the reassignment of the spectrum of *trans*-stilbene and proposal for the first time of a general assignment of *cis*-stilbene. The main differences between the spectra of both isomers are discussed on the basis of the respective molecular structures.

Introduction

The photophysics of the *trans*–*cis*-stilbene system has been widely studied. It is a classical example of a photoisomerization reaction between organic molecules,¹ even of biological interest, given that *cis*-stilbene isomerizes on a barrierless surface, as do rhodopsin and bacteriorhodopsin, for instance.² In many of the referred works, previous knowledge of the vibrational spectra of the involved molecules was unavoidable, and the spectra were therefore the subject of several studies. The vibrational spectrum of *trans*-stilbene has been much more widely studied than that of the *cis*-isomer in the ground electronic state,^{3–9} in excited electronic states,^{4, 9,10} and in radical ionic forms.^{9,11} The vibrational spectrum of *cis*-stilbene has been the subject of only a few studies because this molecule has no inversion center and therefore the analysis of the spectrum is not so easy. Moreover, the molecular structure of *cis*-stilbene is far from planarity¹² which also increases the difficulty of the assignment of the vibrations. Besides the theoretical estimation of the spectrum of *cis*-stilbene by Warshel,⁴ only one other work dealing with its spectrum in the ground state has been published,¹³ where several fundamental vibrations are empirically assigned by correlation with monosubstituted benzene derivatives. In that work, the presence of anomalous polarized Raman bands was detected in the low-frequency region that suggests a descent from C_{2v} to C_2 symmetry to assign them.

When one compares the assignments proposed for the vibrational spectrum of *trans*-stilbene, discrepancies involving the frequencies, the symmetries, and the assignments of the fundamentals can be seen. We have classified the published assignments into two groups: (a) those in which the assignment is done empirically but supported by isotopic shifts and (b) those in which some force field has been computed. In group a, the work of Meić and Güsten with deuterated derivatives⁵ as well as that with ¹³C derivatives⁸ must be mentioned. The usefulness of computing a force field in support of the empirical assignments becomes evident when the authors propose some changes in their own assignments for the in-plane vibrations.^{7,8} On the other hand, the transfer of the force constants from conjugated organic molecules to *trans*-stilbene has been successfully carried out by Palmö³ who uses the frequencies reported by Meić et al. What is not so obvious is that force constant transference could produce such good results for distorted molecules such as *cis*-stilbene.⁴

In this work, we propose a general assignment of the vibrational spectra of both isomers. First of all, we have tried to clarify the doubts concerning some fundamentals of *trans*-stilbene by means of the SQM methodology of Pulay et al.,¹⁴ which is suitable for large molecules with many fundamentals. This method obtains force constants from *ab initio* Hartree–Fock calculations, combined with an empirical “scaling”; the latter corrects for systematic errors characteristic of this level of theory and yields good results in predicting the vibrational spectrum when transferring scale factors between related molecules. In our case, given that stilbene possesses two benzene rings linked through an ethylenic double bond, we have started with the scaling of the force fields of benzene and ethylene. Thereafter, the scale factors have been directly transferred to *trans*-stilbene and very good results have been obtained that encouraged us to apply the method to *cis*-stilbene for which a complete assignment of the vibrational spectrum could be proposed.

Experiment and Calculations

trans-Stilbene from Aldrich was used without further purification, but *cis*-stilbene, also from Aldrich, was repeatedly distilled under low pressure in a distillator Büchi GKR-51 until fluorescence was removed from the background of the Raman records. The Raman spectra from microcrystalline *trans*-stilbene and pure liquid *cis*-stilbene were recorded in the range 4000–100 cm^{-1} on a Jobin Yvon U-1000 spectrometer fitted with a cooled Hamamatsu PMT 943–03, by using the 514.5 nm exciting line from a Spectra Physics Ar⁺ laser 2020. The respective infrared records were taken on a Perkin Elmer 1760X FTIR spectrometer in the range 4000–400 cm^{-1} .

All 3-21G calculations have been carried out using the GAUSSIAN-90 package of programs.¹⁵ Molecular geometries have been optimized with the default criteria therein implemented; the only restrictions imposed being the particular symmetry point groups. Thereafter, quadratic force fields have been computed by double analytical differentiation of the energy with respect to the Cartesian coordinates. Cartesian force constants were then transformed to internal coordinates and scaled as usual in the SQM methodology of Pulay et al.¹⁶ The program FLINT¹⁷ was written to perform that transformation, and the program QCPE#576¹⁸ was modified to carry out scaling. Initially, only the diagonal force constants were scaled and then some off-diagonal ones. Only one scale factor has been adjusted for each type of vibration in benzene and ethylene, and then directly transferred to *trans*- and *cis*-stilbene. Internal coordi-

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nates have been defined strictly according to the recommendations of Pulay et al.¹⁹

Results and Discussion

(i) Equilibrium Structures. The hypothetical planarity of the *trans*-stilbene molecule has been the subject of controversy for several years. For instance, it is related to the conducting properties of poly(*p*-phenylene).²⁰ While the molecule has been found to be essentially planar in the solid phase,²¹ results for the vapor phase are controversial. Fluorescence studies point toward a C_{2h} planar structure for the isolated molecule,²² but electron diffraction data suggest that both benzenic rings are rotated 32.5° with respect to each other which involves a descent in symmetry to a C_2 point group.²³ This distorted structure is also found in solution,²⁴ with arguments to conclude a C_2 symmetry rather than a C_i one.²⁵ Quite independently of the structural results, all the published works dealing with the vibrational spectrum of *trans*-stilbene in solution and in the solid phase have assumed a C_{2h} planar structure because no violation of the mutual exclusion principle is observed.

Previous 3-21G results show a distorted equilibrium structure with C_2 symmetry in which a small energy barrier hinders the internal rotation of the phenyl groups and therefore the conversion into C_i or C_{2h} structures.^{20a} Therefore, a rapid equilibrium between the mentioned structures may be assumed at room temperature yielding a planar average one. Our 3-21G results are similar to those reported by Lhost and Brédas^{20a} for geometries and barriers although some small numerical differences exist, which should be attributed to the convergence criteria in the minimization algorithms. However, the only significant differences involve the relative energy of the C_{2h} structure with respect to the C_2 equilibrium one, as well as the rotation dihedral angle of the phenyl group. Our results are 0.43 kcal/mol and 27.2°, respectively, while Lhost and Brédas report 0.20 kcal/mol and 15°. Although a good estimation of either dihedral angles or rotation barriers usually needs to use polarization functions,²⁶ the agreement of our value of 27.2° and the experimental one of 32.5°²³ is to be stressed.

On the other hand, the only published experimental data dealing with the molecular structure of *cis*-stilbene have been obtained using electron diffraction by Traetterberg and Franstsen.¹² Their results yield a C_2 symmetry with important steric hindrance occurring between the hydrogens that increases the $C_1-C_7-C_7'$ angle as well as the $C_6-C_1-C_7-C_7'$ dihedral angle (see Figure 1), with respect to their values in *trans*-stilbene.²³ This distortion decreases the electronic delocalization in the *cis*-isomer and should be responsible for the increase of the C_1-C_7 bond length with respect to the *trans*-isomer. This behavior of the experimental geometric parameters is reasonably well reproduced by the 3-21G results as can be seen in Table 1, where experimental and theoretical parameters are shown. Once again we must emphasize the good agreement of the experimental and theoretical values for the $C_6-C_1-C_7-C_7'$ dihedral angle. Table 2 shows the 3-21G results for the optimized geometry of *cis*-stilbene.

(ii) Vibrational Spectra. Benzene. The SQM methodology has been applied as described by Pulay et al. in their work on the vibrational spectrum of benzene.¹⁴ However, two differences must be mentioned. Firstly, the force fields have been computed for the equilibrium structure with no empirical correction of the optimized geometry. Secondly, we used the 3-21G basis instead of Pulay's 4-21G one. These differences are responsible for the need to compute new scale factors instead of using the published ones. Therefore, any comparison of his and our results must be made with care. The scaling process

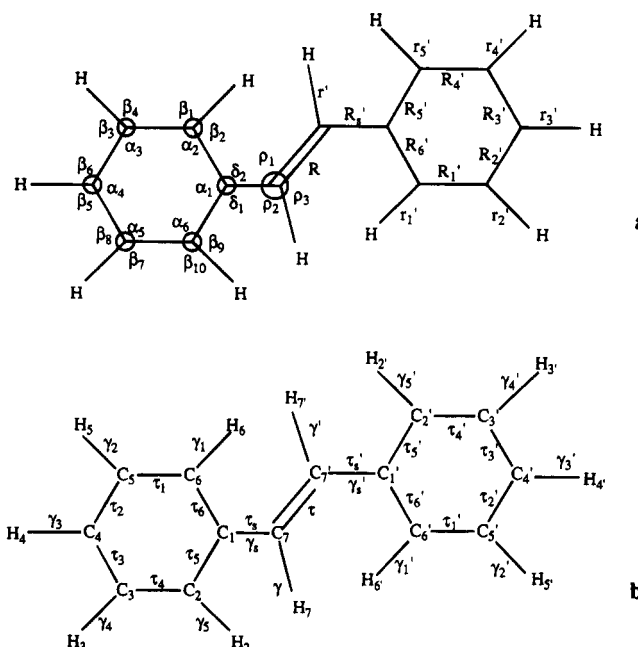


Figure 1. Atom numbering and internal coordinates defined in *trans*-stilbene.

TABLE 1: Experimental and Computed Structural Parameters in *trans*- and *cis*-Stilbene. Bond Lengths in angstroms, Angles in degrees

parameter	experimental ^a		calculated ^b	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
C_7-C_7' ^c	1.329	1.334	1.325	1.324
C_1-C_7'	1.481	1.489	1.477	1.484
$C-C$ ^d	1.398	1.398	1.386	1.385
$C-H$ ^d	1.095	1.095	1.072	1.072
$C_1-C_7-C_7'$	127.7	129.5	126.0	128.3
$C_6-C_1-C_7-C_7'$	32.5	43.2	27.2	44.7

^a From ref12. ^b 3-21G values, this work. ^c See Figure 1 for atom numbering. ^d Promedied C-H and C-C benzene bond lengths, respectively.

TABLE 2: Structural 3-21G Results for *cis*-Stilbene. Bond Lengths in angstroms, Angles in degrees^a

bond lengths		bond angles		dihedral angles	
C_1-C_2	1.390	$C_2-C_3-C_4$	120.045	$H_7-C_7-C_7'-H_7'$	2.89
C_2-C_3	1.383	$C_3-C_4-C_5$	119.628	$C_6-C_1-C_7-C_7'$	44.744
C_3-C_4	1.384	$C_4-C_5-C_6$	120.338	$C_1-C_7-C_7'-C_1'$	4.564
C_4-C_5	1.385	$C_5-C_6-C_1$	120.478	$C_5-C_6-C_1-C_7'$	178.048
C_5-C_6	1.382	$C_7-C_1-C_6$	121.816	$C_4-C_5-C_6-C_1$	-0.130
C_6-C_1	1.390	$C_7-C_7'-C_1$	128.297	$C_3-C_4-C_5-C_6$	-0.364
C_7-C_1	1.484	$H_2-C_2-C_3$	119.424	$C_2-C_3-C_4-C_5$	0.104
C_7-C_7'	1.324	$H_3-C_3-C_2$	119.828	$H_6-C_6-C_5-C_4$	-180.212
C_2-H_2	1.073	$H_4-C_4-C_5$	120.181	$H_5-C_5-C_4-C_3$	179.351
C_3-H_3	1.072	$H_5-C_5-C_6$	119.658	$H_4-C_4-C_3-C_2$	179.704
C_4-H_4	1.072	$H_6-C_6-C_5$	120.126	$H_3-C_3-C_2-C_1$	-179.571
C_5-H_5	1.072	$H_7-C_7-C_1$	117.409	$H_2-C_2-C_1-C_6$	179.136
C_6-H_6	1.070				
C_7-H_7	1.076				

^a See Figure 1 for atom numbering.

was started by adjusting the six force constants involved in stretching and in-plane and out-of-plane bendings of the CH and CC bonds. Table 3 shows the calculated frequencies as set I. Agreement between the experimental and set I frequencies is found to be satisfactory with the exception of vibration 14²⁷ and some γ (CH) modes, calculated at 1215, 802, and 632 cm^{-1} , respectively. To improve the agreement, two additional scale factors have been allowed to be adjusted involving off-diagonal force constants which describe the interaction between ν (CC)

TABLE 3: Experimental and Calculated Vibrational Frequencies (cm⁻¹) for Benzene

symm	mode ^c	character ^d	exp ^e	3-21G SET I ^a		3-21G SET II ^a		4-21G ^b
				calc	PED (%)	calc	PED (%)	calc
A _{1g}	2	$\nu(\text{C-H})$	3072	3086	100 $\nu(\text{C-H})$	3086	100 $\nu(\text{C-H})$	3096
E _{1u}	20a,b	$\nu(\text{C-H})$	3064	3072	99 $\nu(\text{C-H})$	3072	99 $\nu(\text{C-H})$	3080
E _{2g}	7a,b	$\nu(\text{C-H})$	3057	3056	99 $\nu(\text{C-H})$	3056	99 $\nu(\text{C-H})$	3061
B _{1u}	13	$\nu(\text{C-H})$	3056	3047	100 $\nu(\text{C-H})$	3047	100 $\nu(\text{C-H})$	3052
E _{2g}	8a,b	$\nu(\text{C-C})$	1599	1600	69 $\nu(\text{C-C})$, 24 $\delta(\text{C-H})$	1608	70 $\nu(\text{C-C})$, 24 $\delta(\text{C-H})$	1609
E _{1u}	19a,b	$\nu(\text{C-C})$	1482	1482	69 $\delta(\text{C-H})$, 31 $\nu(\text{C-C})$	1482	68 $\delta(\text{C-H})$, 32 $\nu(\text{C-C})$	1485
A _{2g}	3	$\delta(\text{C-H})$	1350	1363	100 $\delta(\text{C-H})$	1363	100 $\delta(\text{C-H})$	1358
B _{2u}	14	$\nu(\text{C-C})$	1309	1215	54 $\delta(\text{C-H})$, 48 $\nu(\text{C-C})$	1307	84 $\nu(\text{C-C})$, 18 $\delta(\text{C-H})$	1307
E _{2g}	9a,b	$\delta(\text{C-H})$	1178	1182	80 $\delta(\text{C-H})$, 20 $\nu(\text{C-C})$	1185	81 $\delta(\text{C-H})$, 21 $\nu(\text{C-C})$	1185
B _{2u}	15	$\delta(\text{C-H})$	1146	1129	84 $\nu(\text{C-C})$, 12 $\delta(\text{C-H})$	1167	84 $\delta(\text{C-H})$, 18 $\nu(\text{C-C})$	1145
E _{1u}	18a,b	$\delta(\text{C-H})$	1037	1035	69 $\nu(\text{C-C})$, 33 $\delta(\text{C-H})$	1036	69 $\nu(\text{C-C})$, 33 $\delta(\text{C-H})$	1036
B _{1u}	12	$\delta(\text{C-C})$	1010	1000	100 $\delta(\text{C-C})$	1000	100 $\delta(\text{C-C})$	1010
A _{1g}	1	$\nu(\text{C-C})$	993	994	100 $\nu(\text{C-C})$	990	100 $\nu(\text{C-C})$	993
B _{2g}	5	$\gamma(\text{C-H})$	990	1003	60 $\gamma(\text{C-H})$, 39 $\tau(\text{C-C})$	1001	66 $\gamma(\text{C-H})$, 32 $\tau(\text{C-C})$	996
E _{2u}	17a,b	$\gamma(\text{C-H})$	967	962	67 $\gamma(\text{C-H})$, 33 $\tau(\text{C-C})$	972	71 $\gamma(\text{C-H})$, 30 $\tau(\text{C-C})$	969
E _{1g}	10a,b	$\gamma(\text{C-H})$	846	802	99 $\gamma(\text{C-H})$	838	99 $\gamma(\text{C-H})$	843
B _{2g}	4	$\tau(\text{C-C})$	707	716	60 $\tau(\text{C-C})$, 42 $\gamma(\text{C-H})$	707	69 $\tau(\text{C-C})$, 30 $\gamma(\text{C-H})$	701
A _{2u}	11	$\gamma(\text{C-H})$	673	632	100 $\gamma(\text{C-H})$	668	100 $\gamma(\text{C-H})$	667
E _{2g}	6a,b	$\delta(\text{C-C})$	606	611	90 $\delta(\text{C-C})$	611	90 $\delta(\text{C-C})$	607
E _{2u}	16a,b	$\tau(\text{C-C})$	404	408	71 $\tau(\text{C-C})$, 28 $\gamma(\text{C-H})$	403	75 $\tau(\text{C-C})$, 24 $\gamma(\text{C-H})$	402

^a This work. ^b Scaled 4-21G values of set II from ref 14. ^c Wilson's nomenclature. ^d Qualitative description providing major contribution to the normal modes. Symbols used: ν , stretching; δ , in-plane bending; γ , out-of-plane bending; τ , torsion. ^e Experimental frequencies taken from ref 27.

in *ortho*-, *meta*-, and *para*-positions and interactions between $\gamma(\text{CH})$ in *ortho*-positions, respectively. In the SQM scheme, off-diagonal force constants are scaled by the geometric mean of the relevant two diagonal scale factors. It was already noted by Pulay, however, that the CC-CC interactions are seriously overestimated (in absolute value) in aromatic systems like benzene, necessitating the use of an extra factor for these couplings. Our set II results were obtained by using an extra factor for these CC-CC couplings, plus an additional $\gamma(\text{CH})$ factor and rescaling all the remaining ones. Table 3 shows the final results of this adjustment. As can be seen, the agreement between the experimental and set II frequencies is as good as found in Pulay's work.¹⁴ Table 3 also includes the elements of the PED matrix that are larger than 10%. It is evident that some descriptions contain a mixture of contributions of internal coordinates to the potential energy, but Wilson's traditional nomenclature²⁷ has been maintained for the benzene vibrations.

Ethylene. The vibrational spectrum of ethylene has been refined by introducing five scale factors involving $\nu(\text{C}=\text{C})$, $\nu(\text{CH})$, $\delta(\text{CH})$, $\tau(\text{CH})$, $\gamma(\text{CH})$, and $\tau(\text{C}=\text{C})$, respectively. Internal coordinates have been defined according to Pulay et al.²⁸ with the exception of the torsion which has been defined according to Hilderbrandt.²⁹ Computed frequencies agree reasonably well with the experimental ones (see Table 4), with the highest deviations being those of the wagging vibrations as also occurs with Pulay's results. These frequencies are quite sensitive to small variations in the scale factors; for instance, a change from 0.70 to 0.71 in the scale factor yields a change in frequencies from 932 and 967 cm⁻¹ to 939 and 974 cm⁻¹, respectively.

trans-Stilbene. When each aromatic ring links to the ethylene skeleton to yield stilbene, five new internal coordinates appear which have no equivalence in benzene or ethylene. These are $\nu(\text{CX})$, $\delta(\text{CX})$, $\gamma(\text{CX})$, $\tau(\text{CX})$, and $\delta(\text{C}_1-\text{C}_7-\text{C}_7')$, henceforth noted as $\delta(\text{CCC})$, where CX stands for the ring-substituent bond according to Varsányi's nomenclature.²⁷ There are no scale factors to be transferred from either benzene or ethylene, so we have adjusted the scale factor related to $\nu(\text{CX})$ up to 0.92 to reproduce the experimental frequencies at 1264 and 1193 cm⁻¹ and arbitrarily assigned a value of 0.80 to the remaining ones. The final assignment of $\nu(\text{CX})$ agrees with the results

TABLE 4: Experimental and Calculated Vibrational Frequencies (cm⁻¹) for Ethylene

symm	exp ^a	character ^b	3-21G ^c	PED (%) ^c	4-21G ^d
B _{2u}	3105	$\nu(\text{C-H})$	3110	100 $\nu(\text{C-H})$	3120
B _{1g}	3086	$\nu(\text{C-H})$	3081	100 $\nu(\text{C-H})$	3092
A _g	3026	$\nu(\text{C-H})$	3039	96 $\nu(\text{C-H})$	3042
B _{3u}	3021	$\nu(\text{C-H})$	3021	100 $\nu(\text{C-H})$	3022
A _g	1630	$\nu(\text{C}=\text{C})$	1628	61 $\nu(\text{C}=\text{C})$, 38 $\nu(\text{C-H})$	1626
B _{3u}	1444	$\delta(\text{C-H})$	1443	100 $\delta(\text{C-H})$	1455
A _g	1342	$\delta(\text{C-H})$	1343	64 $\delta(\text{C-H})$, 36 $\nu(\text{C}=\text{C})$	1345
B _{1g}	1220	$\tau(\text{C-H})$	1217	100 $\tau(\text{C-H})$	1222
B _{2u}	826	$\tau(\text{C-H})$	827	100 $\tau(\text{C-H})$	821
A _u	1023	$\tau(\text{C}=\text{C})$	1022	100 $\tau(\text{C}=\text{C})$	1025
B _{2g}	940	$\gamma(\text{C-H})$	967	100 $\gamma(\text{C-H})$	951
B _{1u}	949	$\gamma(\text{C-H})$	932	100 $\gamma(\text{C-H})$	933

^a Taken from ref 28. ^b Abbreviations used: τ , rocking. See also footnotes of Table 3. ^c This work. ^d 4-21G scaled values from ref 28.

reported by Palmö³ as well as with the correction given by Meiß et al.⁷ All the remaining scale factors have been directly transferred from ethylene and benzene.

The $3N - 6 = 72$ fundamentals of this molecule span the representation $\Gamma = 25\text{A}_g + 24\text{B}_u + 12\text{A}_g + 11\text{B}_g$ in C_{2h} or $\Gamma = 37\text{A} + 35\text{B}$ in C_2 . Given that the force field has been computed for a C_2 structure, the scaling process has been carried out for A and B species by using symmetry coordinates summarized in Table S3 (found in the Supporting Information). Although the equilibrium structure is not planar, in-plane and out-of-plane vibrations do not mix significantly as can be seen in the PED results shown in Table 5. This is of great help to ascending in symmetry from C_2 to C_{2h} and to interpreting the experimental results, which show no apparent violation of the mutual exclusion principle. Therefore, in-plane A vibrations should be A_g in C_{2h} and so on (see Table S3).

Table 5 shows the selected experimental and calculated frequencies as well as the PED and qualitative descriptions for each fundamental. Wilson's nomenclature has been maintained for fundamentals clearly involving ring stretching although some others with an important benzylic-CH contribution can be easily recognized too. The results from the scaled force field show that $\nu(\text{CH})$ do not mix with the benzylic ones and that their relative frequencies agree with the previously proposed ones

TABLE 5: Calculated and Observed Vibrational Frequencies (cm^{-1}) of Vibrational Spectra of *trans*-Stilbene^a

A symmetry				B symmetry			
PED (%)	calc	exp	character	PED (%)	calc	exp	
98 $\nu(\text{C-H})$	3084	3082 _{Ra}	$\nu(\text{C-H})$	99 $\nu(\text{C-H})$	3084	3095 _{IR}	
99 $\nu(\text{C-H})$	3074		$\nu(\text{C-H})$	98 $\nu(\text{C-H})$	3075	3076 _{IR}	
98 $\nu(\text{C-H})$	3065	3062 _{Ra}	$\nu(\text{C-H})$	98 $\nu(\text{C-H})$	3065		
99 $\nu(\text{C-H})$	3054		$\nu(\text{C-H})$	89 $\nu(\text{C-H})$	3055	3056 _{IR}	
95 $\nu(\text{C-H})$	3048	3040 _{Ra}	$\nu(\text{C-H})$	85 $\nu(\text{C-H})$, 15 $\nu(\text{C-H})_e$	3049	3031 _{IR}	
92 $\nu(\text{C-H})_e$	3037	3029 _{Ra}	$\nu(\text{C-H})_e$	73 $\nu(\text{C-H})_e$, 26 $\nu(\text{C-H})$	3044	3020 _{IR}	
54 $\nu(\text{C}=\text{C})$, 22 $\delta(\text{C-H})_e$, 14 $\nu(\text{C-X})$	1651	1639 _{Ra}	$\nu(\text{C}=\text{C})$				
66 $\nu(\text{C-C})$, 21 $\delta(\text{C-H})$	1616	1593 _{Ra}	8a $\nu(\text{C-C})$	66 $\nu(\text{C-C})$, 20 $\delta(\text{C-H})$	1619	1597 _{IR}	
64 $\nu(\text{C-C})$, 19 $\delta(\text{C-H})$	1588	1573 _{Ra}	8b $\nu(\text{C-C})$	68 $\nu(\text{C-C})$, 19 $\delta(\text{C-H})$	1592	1577 _{IR}	
63 $\delta(\text{C-H})$, 33 $\nu(\text{C-C})$	1494	1491 _{Ra}	19a $\delta(\text{C-H})$	59 $\delta(\text{C-H})$, 33 $\nu(\text{C-C})$	1500	1494 _{IR}	
58 $\delta(\text{C-H})$, 35 $\nu(\text{C-C})$	1450	1445 _{Ra}	19b $\delta(\text{C-H})$	55 $\delta(\text{C-H})$, 34 $\nu(\text{C-C})$	1455	1450 _{IR}	
81 $\delta(\text{C-H})$	1342	1338 _{Ra}	$\delta(\text{C-H})$	73 $\delta(\text{C-H})$, 18 $\delta(\text{C-H})_e$	1347	1332 _{IR}	
72 $\nu(\text{C-C})$	1299	1289 _{Ra}	14 $\nu(\text{C-C})$	69 $\nu(\text{C-C})$, 18 $\delta(\text{C-H})$	1320	1300 _{IR}	
47 $\delta(\text{C-H})_e$, 31 $\nu(\text{C-C})$	1319	1326 _{Ra}	$\delta(\text{C-H})_e$	36 $\delta(\text{C-H})_e$, 31 $\nu(\text{C-C})$	1224	1220 _{IR}	
32 $\nu(\text{C-X})$, 25 $\nu(\text{C-C})$, 17 $\delta(\text{C-H})$	1189	1193 _{Ra}	$\nu(\text{C-X})$	33 $\nu(\text{C-X})$, 35 $\nu(\text{C-C})$, 13 $\delta(\text{C-H})$, 12 $\delta(\text{C-H})_e$	1262	1264 _{IR}	
79 $\delta(\text{C-H})$, 21 $\nu(\text{C-C})$	1193	1184 _{Ra}	$\delta(\text{C-H})$	79 $\delta(\text{C-H})$, 17 $\nu(\text{C-C})$	1192	1182 _{IR}	
83 $\delta(\text{C-H})$, 18 $\nu(\text{C-C})$	1173	1156 _{Ra}	$\delta(\text{C-H})$	83 $\delta(\text{C-H})$, 18 $\nu(\text{C-C})$	1173	1155 _{IR}	
54 $\nu(\text{C-C})$, 39 $\delta(\text{C-H})$	1083	1093 _{Ra}	$\nu(\text{C-C})$	55 $\nu(\text{C-C})$, 37 $\delta(\text{C-H})$	1080	1071 _{IR}	
68 $\nu(\text{C-C})$, 19 $\delta(\text{C-H})$	1027	1026 _{Ra}	$\nu(\text{C-C})$	70 $\nu(\text{C-C})$, 20 $\delta(\text{C-H})$	1028	1028 _{IR}	
60 $\delta(\text{C-C})$, 32 $\nu(\text{C-C})$	994	998 _{Ra}	12 $\delta(\text{C-C})$	62 $\delta(\text{C-C})$, 30 $\nu(\text{C-C})$	994	1001 _{IR}	
66 $\gamma(\text{C-H})$, 28 $\tau(\text{C-C})$	992	984 _{IR}	$\gamma(\text{C-H})$	67 $\gamma(\text{C-H})$, 23 $\tau(\text{C-C})$	991	985 _{Ra}	
71 $\gamma(\text{C-H})$, 29 $\tau(\text{C-C})$	970	971 _{IR}	$\gamma(\text{C-H})$	70 $\gamma(\text{C-H})$, 29 $\tau(\text{C-C})$	970	969 _{Ra}	
48 $\gamma(\text{C-H})_e$, 40 $\tau(\text{C}=\text{C})$	956	966 _{IR}	$\gamma(\text{C-H})_e$	63 $\gamma(\text{C-H})_e$, 26 $\gamma(\text{C-H})$	855	854 _{Ra}	
64 $\gamma(\text{C-H})$, 13 $\tau(\text{C-C})$	922	909 _{IR}	$\gamma(\text{C-H})$	59 $\gamma(\text{C-H})$, 16 $\gamma(\text{C-H})_e$, 14 $\tau(\text{C-C})$, 11 $\gamma(\text{C-X})$	927	912 _{Ra}	
23 $\nu(\text{C-C})$, 30 $\delta(\text{CCC})$, 12 $\delta(\text{C-C})$	865	866 _{Ra}	1 $\nu(\text{C-C})$	35 $\nu(\text{C-C})$, 31 $\delta(\text{C-C})$, 27 $\gamma(\text{C-X})$	812	824 _{IR}	
99 $\gamma(\text{C-H})$	831	847 _{IR}	$\gamma(\text{C-H})$	94 $\gamma(\text{C-H})$	830	838 _{Ra}	
49 $\gamma(\text{C-H})$, 25 $\gamma(\text{C-X})$, 14 $\tau(\text{C-C})$	766	764 _{IR}	$\gamma(\text{C-H})$	56 $\gamma(\text{C-H})$, 15 $\gamma(\text{C-X})$, 15 $\gamma(\text{C-X})$, 14 $\tau(\text{C-C})$	739	734 _{Ra}	
59 $\gamma(\text{C-H})$, 35 $\tau(\text{C-C})$	693	692 _{IR}	4 $\tau(\text{C-C})$	56 $\gamma(\text{C-H})$, 39 $\tau(\text{C-C})$	693	686 _{Ra}	
64 $\delta(\text{C-C})$, 18 $\delta(\text{CCC})$	645	640 _{Ra}	6a $\delta(\text{C-C})$	79 $\delta(\text{C-C})$	537	541 _{IR}	
88 $\delta(\text{C-C})$	623	616 _{Ra}	6b $\delta(\text{C-C})$	87 $\delta(\text{C-C})$	625	620 _{IR}	
36 $\gamma(\text{C-X})$, 25 $\tau(\text{C-C})$, 20 $\gamma(\text{C-H})$	525	528 _{IR}	$\gamma(\text{C-X})$	29 $\gamma(\text{C-X})$, 18 $\tau(\text{C-C})$, 18 $\delta(\text{CCC})$, 14 $\delta(\text{C-X})$, 12 $\gamma(\text{C-H})$	502	466 _{Ra}	
73 $\tau(\text{C-C})$, 25 $\gamma(\text{C-H})$	405	410 _{IR}	16a $\tau(\text{C-C})$	73 $\tau(\text{C-C})$, 25 $\gamma(\text{C-H})$	405	412 _{Ra}	
39 $\delta(\text{C-X})$, 20 $\tau(\text{C-C})$	341	336 _{Ra}	$\delta(\text{C-X})$	40 $\delta(\text{C-X})$, 15 $\gamma(\text{C-X})$, 14 $\delta(\text{CCC})$, 13 $\tau(\text{C-C})$	425	419 _{IR} ^b	
24 $\tau(\text{C-C})$, 17 $\delta(\text{C-C})$	257	268 _{IR} ^c	16b $\tau(\text{C-C})$	43 $\tau(\text{C-C})$, 18 $\tau(\text{C-X})$, 14 $\gamma(\text{C-X})$	212	227 _{Ra}	
32 $\delta(\text{C-X})$, 21 $\delta(\text{CCC})$, 20 $\tau(\text{C-C})$	173	198 _{Ra}	$\delta(\text{CCC})$	43 $\delta(\text{CCC})$, 33 $\tau(\text{C-X})$, 13 $\delta(\text{C-X})$	57		
28 $\gamma(\text{C-H})_e$, 27 $\tau(\text{C}=\text{C})$, 15 $\tau(\text{C-C})$, 22 $\gamma(\text{C-X})$	55		$\tau(\text{C}=\text{C})$				
73 $\tau(\text{C-X})$	25		$\tau(\text{C-X})$	74 $\tau(\text{C-X})$	114		

^a See footnotes of Tables 3 and 4 for symbols and abbreviations. ^b Taken from ref 6. ^c Taken from ref 7.

found in the literature. The overestimation of frequencies for $\nu(\text{C}=\text{C})$ and 8ab; $\nu(\text{CC})$ fundamentals points out that 3-21G does not account sufficiently for electronic delocalization and explains that the scale factor found for $\nu(\text{CX})$, amounting to 0.92, is above the mean values for C-C stretchings in either benzene or ethylene. On the contrary, frequencies for 19ab; $\nu(\text{CC})$ fundamentals are not affected by the low delocalization because of the high $\delta(\text{CH})$ participation in its PED. The frequencies for the IR and Raman fundamentals in the region between 3100 and 1000 cm^{-1} coincide with those reported by Baranović et al.⁸ in the solution phase as well as do their assignments, although our PED results agree more closely with Palmö's ones.³ For instance, it is well-known that vibration 12; $\delta(\text{CC})$ always appears close to 1000 cm^{-1} and does not shift significantly by the effect of substitution in benzene derivatives.²⁷ In our results, the fundamentals at 1001 and 998 cm^{-1} show a participation of 60% $\delta(\text{CC})$, while in Baranović's paper this coordinate contributes only some 15% to the PED of those fundamentals but 36% to the PED of that at 1031 cm^{-1} . Table 5 shows that no significant contribution of $\delta(\text{CC})$ occurs in the fundamental at 1026–1028 cm^{-1} . Likewise, the Raman fundamental at 1326 cm^{-1} is described with 47% of $\delta(\text{CH})_e$ contribution while in Baranović's work this coordinate participates with 26% to the PED of the Raman fundamental at 1338 cm^{-1} which in turn

includes some 50% of $\nu(\text{CC})$.⁸ On the other hand, Baranović's paper describes the fundamental at 1214 cm^{-1} as $\delta(\text{CH})_e$, with 81% participation, while we have recorded it at 1220 cm^{-1} with only 36% of this coordinate. However, Palmö³ assigns it to the IR band at 1181 cm^{-1} . Note the difference in frequencies between the A and B fundamentals assigned in Table 5 to $\nu(\text{CX})$ and $\delta(\text{CH})_e$, which cannot be predicted with the help of the characteristic frequencies tables, while the remaining vibrations appear at quite close frequencies in the A and B blocks and with almost the same PED description.

Infrared bands at 984, 971, 909, and 847 cm^{-1} correspond with those recorded at 985, 969, 912, and 838 cm^{-1} in the Raman spectrum, respectively. Our results described them as $\gamma(\text{CH})$ fundamentals in agreement with Palmö's assignments.³ The empirical assignment by Meić and Güsten⁵ is also the same in the infrared, but they assign the Raman band recorded at 969 cm^{-1} to a $\gamma(\text{CH})_e$ fundamental with the shoulder at 999 cm^{-1} also being attributed as a $\gamma(\text{CH})_e$ fundamental. Thereafter^{7,8} they have used this latter Raman frequency to assign vibration 12, so we believe that our results are more reliable.

Vibrations $\gamma(\text{CH})_e$;A and B have been assigned to the bands at 966 and 854 cm^{-1} in IR and Raman, respectively, bearing in mind that the band at 854 cm^{-1} has never been assigned before to any fundamental in spite of its intensity. Our computed

frequencies of 956 and 855 cm^{-1} support this assignment, giving a splitting between A and B modes similar to that of $\nu(\text{CX})$. As concerns the IR bands at 971 and 966 cm^{-1} , it is difficult to decide which one is the $\gamma(\text{CH})\text{e}$ and which one is the benzenic $\gamma(\text{CH})$. As we have said before, the $\gamma(\text{CH})$ ethylenic frequencies are quite sensitive to the scale factor and the spectrum has also been computed with $f = 0.71$. However, in *trans*-stilbene the greater mixing of internal coordinates is responsible for a greater stability of such frequencies. The new computed frequencies amount to 967 and 858 cm^{-1} , respectively, still in good agreement with the proposed assignments. The frequencies computed by Palmö³ amount in turn to 946 and 962 cm^{-1} , respectively, and he assigns two fundamentals to the Raman band at 969 cm^{-1} . We think it is improbable that a so small difference between the frequencies of two modes can exist, and we suggest that perhaps the value of the off-diagonal force constant is not well chosen.

The in-plane benzenic modes $1;\nu(\text{CC})$ and $6\text{a,b};\delta(\text{CC})$ have been assigned to the IR bands at 824, 541, and 620 cm^{-1} and to the Raman bands at 866, 640, and 616 cm^{-1} , respectively. Their symmetry species being B and A, respectively. These assignments agree with those of Meić et al.⁷ given that the IR band at 528 cm^{-1} must be assigned to $\gamma(\text{CX})$ according to the PED, with either A symmetry in C_2 or Au in C_{2h} . However, Palmö assigned this band at 528 cm^{-1} to both the 6a and $\gamma(\text{CX})$ fundamentals.

The vibrations $4;\tau(\text{CC})$ A and B exhibit frequencies close to 690 cm^{-1} . The frequency computed by Palmö agrees with our results although he did not assign it to any band; however, his source of experimental data is ref 5 where no fundamental is assigned to these particular bands. Vibration $16\text{a};\tau(\text{CC})$ has been assigned to the bands recorded at 410 and 412 cm^{-1} in the IR and Raman, respectively, while 16b, which is much more sensitive to substitution,²⁷ is shifted down to the 200 cm^{-1} region. The infrared band recorded by Pecile and Lunelli⁶ at 419 cm^{-1} has been assigned as $\delta(\text{CX});\text{Bu}$. However, the scaled force field yields a frequency of 341 cm^{-1} for the A mode, which leads us to assign the Raman band at 336 cm^{-1} to an Ag fundamental instead of a Bg one.⁵ This final assignment of $\delta(\text{CX})$ modes differs from the previously reported ones, but the assignment of $\gamma(\text{CX})$ modes agrees with that by Palmö.³

Finally, we have to point out that the low-frequency region is much more difficult to assign because of the low intensity of the IR bands, the presence of lattice modes in the Raman records, the uncertainty in the scale factors, and so on. However, the agreement between the experimental and the computed frequencies is rather satisfactory. The highest difference being found for the Raman band recorded at 466 cm^{-1} , $\gamma(\text{CX});\text{B}$, of uncertain assignment, which is computed at 502 cm^{-1} with a rather complex description. As Table 5 shows, there is no significant mixing between in-plane and out-of-plane coordinates, with the exception of the $\delta(\text{CX})$ fundamental.

cis-Stilbene. The force field for this molecule has been scaled by using the same scale factors and symmetry coordinates as in *trans*-stilbene. Given that the symmetry is C_2 , every fundamental must be IR and Raman active. It is possible to identify A and B components of each vibration only where they are resolved through the depolarization ratio; otherwise both of them are assigned to the same band if the calculated frequencies lie close together. Table 6 shows the computed frequencies as well as the proposed assignments for the vibrational spectrum of *cis*-stilbene. The qualitative descriptions are not shown because they are generally much more complex than those in *trans*-stilbene.

In the 3000 cm^{-1} region, we have recorded five frequencies belonging to $\nu(\text{CH})$ fundamentals. Unlike *trans*-stilbene, $\nu(\text{CH})\text{e};\text{A}$ and B frequencies are computed to be quite far apart, 3040 and 3016 cm^{-1} , respectively, and in the PED of mode A this coordinate is mixed with the $\nu(\text{CH})$ ones of benzene. We think that the scaled force field overestimates the coupling and even inverts the order of appearance of both vibrations. The study of deuterated derivatives will help with these assignments.³⁰

In-plane fundamentals appear in the region 1700–1000 cm^{-1} . The ethylenic double bond stretching, $\nu(\text{C}=\text{C})$, is recorded clearly polarized in the Raman spectrum at 1629 cm^{-1} . Vibrations 8ab are recorded at very close frequencies both in the Raman and infrared; each one being assigned to only one band which contains the A and B modes. The respective Raman bands appear polarized provided that the A component is totally symmetric and is usually stronger than the non-totally symmetric B one. All these vibrations are computed at overestimated frequencies as in *trans*-stilbene. The splitting of the bands at 1490 and 1449 cm^{-1} has been previously reported by Bree and Zwarich.¹³ The resulting four frequencies belong to the pairs 19ab, each one with symmetry A and B, respectively. Raman records show only the A components being clearly polarized while the B components, which are much weaker, are not observed in the Raman. The medium intensity band recorded at 1406 cm^{-1} in the IR, Raman depolarized, has been easily assigned to $\delta(\text{CH})\text{e};\text{B}$ which is computed at 1402 cm^{-1} , although the correlation with the spectrum of *trans*-stilbene is not evident because in this case the nearest fundamental recorded at 1338 cm^{-1} is assigned to $\delta(\text{CH})$. The coordinate $\delta(\text{CH})\text{e};\text{A}$, in turn, participates in the PED of several fundamentals; that computed at 1244 cm^{-1} has the highest contribution, amounting to some 31%, and is recorded as a polarized Raman band at 1234 cm^{-1} . It is seen that in the *cis*-isomer $\delta(\text{CH})\text{e}$ vibrations behave differently than in the *trans*-isomer because their coupling is stronger when both C–H bonds lie at the same side of the double bond. A similar case is found for $\nu(\text{CX})$ vibrations: they appear as two relatively close bands in *trans*-stilbene with majority participation of the respective internal coordinate; however, in *cis*-stilbene the contribution of the $\nu(\text{CX})$ coordinate to the PED is much more scattered. The bands at 1203 and 1143 cm^{-1} are the ones with the highest participation of this coordinate with symmetry B and A, respectively.

The remaining fundamentals in this region have been assigned easily. In all cases, the modes with symmetry A and B show frequencies that are quite close and therefore they are assigned to a nonresolved band. Their description is always a ring vibration, weakly coupled with its counterpart of the other ring. So the bands recorded at some 1330, 1305, 1193, 1180, 1074, 1029, and 1001 cm^{-1} in the *cis*-stilbene spectrum correspond with those in *trans*-stilbene at 1330, 1300, 1180, 1155, 1080, 1026, and 1000 cm^{-1} , respectively, and can be assigned in turn as $\delta(\text{CH})$, 14, $\delta(\text{CH})$, $\delta(\text{CH})$, $\nu(\text{CC})$, $\nu(\text{CC})$, and 12.

Vibration $\gamma(\text{CH})\text{e};\text{A}$ is calculated at 984 cm^{-1} . Thus, the Raman polarized band at 983 cm^{-1} is assigned to this fundamental, but a $\gamma(\text{CH});\text{B}$ mode is computed at 992 cm^{-1} . The vibration $\gamma(\text{CH})\text{e};\text{B}$ is calculated in turn at 724 cm^{-1} with a participation of 46% of this coordinate, so the IR band at 732 cm^{-1} and the Raman band at 731 cm^{-1} have been consequently assigned to it. This particular assignment supports that of $\gamma(\text{CH})\text{e};\text{B}$ in *trans*-stilbene at 850 cm^{-1} and not to some other band above 950 cm^{-1} as proposed by others. The difference between the frequencies of $\gamma(\text{CH})\text{e};\text{A}$ and B amounts more or less to 260 cm^{-1} unlike that of *trans*-stilbene where it only amounts to 100 cm^{-1} . When the respective scale factor is set

TABLE 6: Calculated and Observed Vibrational Frequencies (cm⁻¹) of Vibrational Spectra of *cis*-Stilbene^a

IR	Raman ^b	A symmetry		B symmetry	
		calc	PED (%)	calc	PED (%)
3079		3073	100 $\nu(\text{C-H})$	3073	100 $\nu(\text{C-H})$
	3061 p	3060	98 $\nu(\text{C-H})$	3060	99 $\nu(\text{C-H})$
3054	3049 dp	3047	98 $\nu(\text{C-H})$	3047	99 $\nu(\text{C-H})$
		3040	84 $\nu(\text{C-H})\text{e}$, 15 $\nu(\text{C-H})$		
		3036	87 $\nu(\text{C-H})$, 11 $\nu(\text{C-H})\text{e}$	3036	98 $\nu(\text{C-H})$
3024	3030 dp	3028	97 $\nu(\text{C-H})$	3028	98 $\nu(\text{C-H})$
3012	3014 p			3016	97 $\nu(\text{C-H})\text{e}$
	1629 p	1656	56 $\nu(\text{C=C})$, 17 $\nu(\text{C-X})$		
1600	1599 p	1615	64 $\nu(\text{C-C})$, 19 $\delta(\text{C-H})$	1617	66 $\nu(\text{C-C})$, 20 $\delta(\text{C-H})$
1576	1573 p	1588	66 $\nu(\text{C-C})$, 19 $\delta(\text{C-H})$	1591	69 $\nu(\text{C-C})$, 20 $\delta(\text{C-H})$
1495				1498	58 $\delta(\text{C-H})$, 34 $\nu(\text{C-C})$
1490	1490 p	1494	63 $\delta(\text{C-H})$, 33 $\nu(\text{C-C})$		
1449				1452	55 $\delta(\text{C-H})$, 33 $\nu(\text{C-C})$
1444	1443 p	1448	60 $\delta(\text{C-H})$, 34 $\nu(\text{C-C})$		
1406	1405 dp			1402	69 $\delta(\text{C-H})\text{e}$, 14 $\nu(\text{C-X})$
1336	1333 dp	1339	84 $\delta(\text{C-H})$	1336	82 $\delta(\text{C-H})$, 14 $\nu(\text{C-C})$
	1305 p	1312	70 $\nu(\text{C-C})$, 14 $\delta(\text{C-H})\text{e}$, 13 $\delta(\text{C-H})$	1295	85 $\nu(\text{C-C})$
	1234 p	1244	46 $\nu(\text{C-C})$, 31 $\delta(\text{C-H})\text{e}$		
1203	1203 dp			1203	33 $\nu(\text{C-X})$, 24 $\nu(\text{C-C})$, 15 $\delta(\text{C-H})$
	1193 p	1191	82 $\delta(\text{C-H})$, 17 $\nu(\text{C-C})$	1190	81 $\delta(\text{C-H})$, 18 $\nu(\text{C-C})$
1180	1182 p	1173	78 $\delta(\text{C-H})$, 21 $\nu(\text{C-C})$	1172	80 $\delta(\text{C-H})$, 19 $\nu(\text{C-H})$
1156	1149 p	1143	23 $\nu(\text{C-C})$, 22 $\nu(\text{C-X})$, 18 $\delta(\text{C-H})\text{e}$, 15 $\delta(\text{C-C})$		
1074		1078	57 $\nu(\text{C-C})$, 38 $\delta(\text{C-H})$	1082	54 $\nu(\text{C-C})$, 41 $\delta(\text{C-H})$
1029	1029 p	1026	70 $\nu(\text{C-C})$, 18 $\delta(\text{C-H})$	1027	66 $\nu(\text{C-C})$, 21 $\delta(\text{C-H})$
1001	1001 p	998	43 $\delta(\text{C-C})$, 24 $\nu(\text{C-C})$	995	62 $\delta(\text{C-C})$, 38 $\nu(\text{C-C})$
	992 ?	992	63 $\gamma(\text{C-H})$, 28 $\tau(\text{C-C})$	992	69 $\gamma(\text{C-H})$, 30 $\tau(\text{C-C})$
983		984	47 $\gamma(\text{C-H})\text{e}$, 32 $\tau(\text{C=C})$		
966	965 p	972	70 $\gamma(\text{C-H})$, 29 $\tau(\text{C-C})$	972	71 $\gamma(\text{C-H})$, 29 $\tau(\text{C-C})$
925				936	59 $\gamma(\text{C-H})$, 13 $\tau(\text{C-C})$, 11 $\gamma(\text{C-X})$
	912 p	919	76 $\gamma(\text{C-H})$, 16 $\tau(\text{C-C})$		
863	863 dp			861	28 δCCC , 24 $\gamma(\text{C-H})$, 16 $\nu(\text{C-C})$
844	846 p	835	100 $\gamma(\text{C-H})$	834	100 $\gamma(\text{C-H})$
781	782 dp			774	27 $\gamma(\text{C-H})$, 21 $\gamma(\text{C-H})\text{e}$, 13 $\delta(\text{C-C})$, 13 $\gamma(\text{C-X})$
771	769 p	776	33 $\gamma(\text{C-H})$, 23 $\gamma(\text{C-X})$		
752	752 p	751	34 $\delta(\text{C-C})$, 20 $\nu(\text{C-X})$		
732	731 dp			724	46 $\gamma(\text{C-H})\text{e}$, 13 $\delta(\text{C-C})$, 12 $\delta(\text{CCC})$, 11 $\nu(\text{C-C})$
698	699 dp	695	59 $\gamma(\text{C-H})$, 35 $\tau(\text{C-C})$	695	55 $\gamma(\text{C-H})$, 37 $\tau(\text{C-C})$
	682 dp			676	35 $\gamma(\text{C-H})$, 18 $\gamma(\text{C-H})\text{e}$, 15 $\delta(\text{CCC})$, 14 $\delta(\text{C-C})$
619	619 dp	625	87 $\delta(\text{C-C})$	623	89 $\delta(\text{C-C})$
561	561 p	557	28 $\tau(\text{C=C})$, 16 $\gamma(\text{C-X})$, 15 $\tau(\text{C-C})$		
519	519 p	521	45 $\delta(\text{C-C})$, 14 $\delta(\text{CCC})$		
502				500	54 $\delta(\text{C-C})$, 13 $\gamma(\text{C-X})$, 11 $\nu(\text{C-X})$
443	449 dp			440	32 $\gamma(\text{C-X})$, 27 $\tau(\text{C-C})$
		420	20 $\tau(\text{C-C})$, 15 $\tau(\text{C=C})$, 14 $\delta(\text{C-C})$, 13 $\gamma(\text{C-X})$		
	403 p	407	71 $\tau(\text{C-C})$, 24 $\gamma(\text{C-H})$	403	73 $\tau(\text{C-C})$, 26 $\gamma(\text{C-H})$
	261 p	248	28 $\tau(\text{C-C})$, 20 $\delta(\text{CCC})$, 20 $\delta(\text{C-X})$	259	55 $\delta(\text{C-X})$, 14 $\tau(\text{C-C})$
	166 p	149	26 $\tau(\text{C-X})$, 22 $\delta(\text{C-X})$, 19 $\tau(\text{C=C})$, 11 $\gamma(\text{C-H})\text{e}$	149	41 $\tau(\text{C-C})$, 21 $\gamma(\text{C-X})$, 15 $\delta(\text{CCC})$
		65	23 $\gamma(\text{C-X})$, 29 $\tau(\text{C-C})$, 20 $\tau(\text{C-X})$		
		36	50 $\tau(\text{C-X})$, 38 $\delta(\text{CCC})$		
				23	77 $\tau(\text{C-X})$, 11 $\delta(\text{C-X})$

^a See footnotes of Tables 3 and 4 for symbols and abbreviations. ^b Symbols used: p, polarized; dp, depolarized.

to 0.71 the $\gamma(\text{CH})\text{e}$ frequencies increase by 4 and 2 cm⁻¹, respectively, so we think that no doubts exist in these assignments, although the spectrum of the deuterated derivatives will be of great help.³⁰

On the other hand, there are several pairs of vibrations in which the description of modes A and B are more or less the same and the respective frequencies are quite close, so they have been assigned to the same IR or Raman band. In all cases they are vibrations of the aromatic rings: for instance, the frequencies computed at 992, 972, 835, and 695 cm⁻¹ are essentially out-of-plane $\gamma(\text{CH})$ modes which are computed in *trans*-stilbene at 992, 970, 831, and 693 cm⁻¹, respectively, the latter one being vibration 4; $\gamma(\text{CC})$. However in *cis*-stilbene the $\gamma(\text{CH})$ vibration appearing just over 900 cm⁻¹ is computed at significantly different frequencies when belonging to either B or A symmetry: 936 and 919 cm⁻¹, respectively. Therefore it is assigned to the experimental frequencies at 925 and 912 cm⁻¹. The latter one is polarized in the Raman.

The frequency of vibration 6b has been found to be quite insensitive to substitution, as is usual in monosubstituted benzenic derivatives.²⁷ It is assigned to the band recorded at 619 cm⁻¹ both in Raman and IR spectra. The modes A and B of vibration 6a are computed at 521 and 500 cm⁻¹, respectively and observed in turn at 519 and 502 cm⁻¹, the one at higher frequency being a Raman polarized band.

Concerning the modes of symmetry B, three fundamentals are computed at 861, 774 and 676 cm⁻¹ which correspond quite well with the experimental frequencies at 863, 782, and 682 cm⁻¹, respectively, being depolarized Raman bands in the three cases. Mixing of the coordinates is found in their PED descriptions. These vibrations have no counterpart in the A-type block, in the same way as those computed at 776 and 751 cm⁻¹ have no B-type counterpart. This nonsystematic behavior is not foreseeable without the help of a force field calculation and can also be observed for vibrations under 600 cm⁻¹. With the exception of vibration 16a, which is systematically recorded at

TABLE 7: Refined Scale Factors and Scaled Force Constants for *trans*- and *cis*-Stilbene

coordinate ^a	factor	scaled force constants ^b trans	
		trans	cis
$\nu(\text{C}-\text{C})$	0.87	6.436–6.762	6.468–6.737
$\nu(\text{C}-\text{X})$	0.92	4.894–4.972	4.739–4.793
$\nu(\text{C}-\text{H})$	0.83	5.126–5.180	5.058–5.232
$\nu(\text{C}-\text{H})_e$	0.83	5.094–5.092	5.022–5.055
$\nu(\text{C}=\text{C})$	0.78	8.483	8.641
$\delta(\text{C}-\text{H})$	0.78	0.505–0.518	0.505–0.515
$\delta(\text{C}-\text{X})$	0.80	0.889–0.908	0.770–0.798
$\delta(\text{C}-\text{C})$	0.76	1.219–1.282	1.221–1.271
$\delta(\text{C}-\text{H})_e$	0.77	0.499–0.565	0.535–0.539
$\delta(\text{CCC})$	0.80	0.786–0.846	0.684–1.050
$\gamma(\text{C}-\text{H})$	0.70	0.304–0.314	0.307–0.314
$\gamma(\text{C}-\text{X})$	0.80	0.435–0.440	0.416–0.446
$\gamma(\text{C}-\text{H})_e$	0.70	0.220–0.268	0.264–0.204
$\tau(\text{C}=\text{C})$	0.77	0.462	0.586
$\tau(\text{C}-\text{C})$	0.77	0.301–0.367	0.309–0.372
$\tau(\text{C}-\text{X})$	0.80	0.055–0.051	0.032–0.186
$\nu(\text{C}-\text{C})_o$	0.69	0.614–0.656	0.622–0.655
$\nu(\text{C}-\text{C})_m$	0.69	–0.433––0.406	–0.414––0.436
$\nu(\text{C}-\text{C})_p$	0.69	0.419–0.441	0.429–0.445
$\gamma(\text{C}-\text{H})_o$	0.99	0.015–0.017	0.015–0.018

^a See footnotes of Tables 3–5 for symbols and abbreviations.

^b Extreme values for each type of coordinate. Stretching force constants in mdyN/Å; bending force constants in mdyN Å/rad².

400 cm^{–1} in all monosubstituted benzenes, fundamentals of A symmetry have no B-type counterpart neither in frequency nor in description, those computed at 149 cm^{–1} being just a coincidence. Generally speaking, fundamentals in this region have complex descriptions and there is no way of identifying vibrations 16b, δ and $\gamma(\text{CX})$, and $\tau(\text{C}=\text{C})$. In spite of this, the agreement between the computed and the experimental frequencies is very good as is the case with *trans*-stilbene.

Finally, it is to be stressed that the fact that the Raman bands at 965, 912, 846, 769, 561, and 403 cm^{–1} are clearly polarized points out that the operative symmetry is C₂ provided that in C_{2v} they should be either A₂ or B₁ and therefore depolarized in Raman.

Table 7 shows the scale factors as well as the scaled force constants in symmetry coordinates both for *trans*- and *cis*-stilbene. The differences between the scaled force constants for both molecules are small, the only significant ones being those related to the central skeleton of the molecules, i.e., those involving C=C, CX, or CCC where differences between the geometrical parameters of both isomers are significant. Given the planar structure of *trans*-stilbene, the π -conjugation is wider than in the *cis*-isomer and therefore the ethylenic C=C bond possesses a smaller double bond character. This is the reason why the force constants for the coordinates $\nu(\text{C}=\text{C})$ and $\tau(\text{C}=\text{C})$ are higher in the *cis*-isomer and why the CX bond exhibits more single bond character in the *cis*-isomer and therefore the force constants for the $\tau(\text{CX})$ are quite small. Only the A-type torsion of *cis*-stilbene has a non-negligible force constant amounting to 0.186 mdyN Å/rad² because this movement involves an important interaction between the *ortho*-hydrogens of both benzene rings.

Conclusions

Given the agreement between the computed frequencies and the experimental ones for *trans*- and *cis*-stilbene, we think that the here obtained results provide a fairly good example of the usefulness of the SQM methodology to study the vibrational

spectra of complex molecules. Transference of the scale factors from benzene and ethylene has been a powerful tool to simultaneously explain the vibrational spectra of both isomers. On this basis, alternative assignments have been proposed for some fundamentals of *trans*-stilbene as well as a general assignment of the more complex spectrum of *cis*-stilbene.

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Supporting Information Available: Three tables dealing with refined scale factors and scaled force constants for benzene and ethylene and symmetry coordinates defined in *trans*-stilbene (3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Saltiel, J.; Sun, Y. P. *J. Phys. Chem.* **1989**, *93*, 6246. Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4706. Sension, R. J.; Repinec, S. T.; Skarza, A. Z. *J. Chem. Phys.* **1993**, *98*, 6291. For a review, see: Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.
- (2) Myers, A. B.; Mathies, R. A. *J. Chem. Phys.* **1984**, *81*, 1552 and references therein.
- (3) Palmö, K. *Spectrochim. Acta* **1988**, *44A*, 341.
- (4) Warshel, A. *J. Chem. Phys.* **1975**, *62*, 214.
- (5) Meić, Z.; Güsten, H. *Spectrochim. Acta* **1978**, *34A*, 101.
- (6) Pecile, C.; Lunelli, B. *Can. J. Chem.* **1969**, *47*, 243.
- (7) Meić, Z.; Baranović, B.; Škare, D. *J. Mol. Struct.* **1986**, *141*, 375.
- (8) Baranović, G.; Meić, Z.; Güsten, H.; Mink, J.; Keresztury, G. *J. Phys. Chem.* **1990**, *94*, 2833.
- (9) Butler, R. M.; Lynn, M. A.; Gustafson, T. L. *J. Phys. Chem.* **1993**, *97*, 2609.
- (10) Ikegaya, T.; Azumi, T. *J. Chem. Phys.* **1988**, *92*, 1383.
- (11) Schneider, S.; Scharnagl, Ch.; Bug, R.; Baranović, G.; Meić, Z. *J. Phys. Chem.* **1992**, *96*, 9748.
- (12) Traetterberg, M.; Frantsen, E. B. *J. Mol. Struct.* **1975**, *26*, 69.
- (13) Bree, A.; Zwarich, R. *J. Mol. Struct.* **1981**, *75*, 213.
- (14) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999.
- (15) Frisch, H. M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, X.; Pople, J. A. *GAUSSIAN 90*, revision; Gaussian, Inc.: Pittsburgh, PA, 1990.
- (16) Zhon, X.; Fogarasi, G.; Liu, R.; Pulay, P. *Spectrochim. Acta* **1993**, *49A*, 1499.
- (17) Arenas, J. F.; López-Navarrete, J. T.; Marcos, J. I.; Otero, J. C. *Spectrochim. Acta* **1986**, *42A*, 1343.
- (18) McIntosh, D. F.; Peterson, M. R. General Vibrational Analysis System, QCPE # 576, 1989.
- (19) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550.
- (20) (a) Lhost, O.; Brédas, J. L. *J. Chem. Phys.* **1991**, *96*, 5279. (b) Galvão, D. S.; Soos, Z. G.; Ramasesha, S.; Etemad, S. *J. Chem. Phys.* **1993**, *98*, 3016 and references therein.
- (21) Bernstein, J. *Acta Crystallogr.* **1975**, *B31*, 1268.
- (22) Spangler, L. H.; Van Zee, R.; Zwier, T. S. *J. Phys. Chem.* **1987**, *91*, 6077. Spangler, L. H.; Van Zee, R.; Zwier, T. S. *J. Phys. Chem.* **1987**, *91*, 2782. Chanpagne, B. B.; Pfanstiel, J. F.; Plusquellic, D. F.; Pratt, D. W.; Van Herpen, W. M.; Meerts, W. L. *J. Phys. Chem.* **1990**, *94*, 6.
- (23) Traetterberg, M.; Frantsen, E. B.; Mijlthoff, F. C.; Hoekstra, A. *J. Mol. Struct.* **1975**, *26*, 57.
- (24) Bree, A.; Edelson, M. *Chem. Phys.* **1980**, *51*, 77.
- (25) Syage, J. A.; Felker, P. M.; Zewail, A. H. *J. Chem. Phys.* **1984**, *81*, 4685.
- (26) Otero, J. C.; Marcos, J. I.; López-Cantarero, E.; Chacón, A. *Chem. Phys.* **1991**, *157*, 201.
- (27) Varsányi, G. *Vibrational spectra of benzene derivatives*; Academic Press: New York, 1969.
- (28) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7037.
- (29) Hilderbrandt, R. L. *J. Mol. Spectrosc.* **1972**, *44*, 599.
- (30) Recently a study dealing with deuterated derivatives of *cis*-stilbene has been presented in EUCMOS XXII by Meić, Z.; Suste, T.; Baranović, G.; Smrečky, V.; Holly, S.; Keresztury, G.; Essen, Germany, 1994.