# *Ab initio* study of styrene and $\beta$-methyl styrene in the ground and in the two lowest excited singlet states

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The structure and vibrational frequencies of styrene and *trans*-$\beta$-methyl styrene in the lowest three singlet states ($S_0$, $S_1$, and $S_2$) have been calculated using *ab initio* quantum chemical methods. The frequencies are compared with experimental data obtained in the bulk and in a supersonic jet. The calculation shows that in the ground state the molecules have a broad shallow potential as a function of the torsional angle, are essentially planar, but may be slightly bent. In the $S_1$ and $S_2$ states, the molecules are planar; In $S_1$, the main structural change is in the aromatic ring, that is somewhat expanded. In $S_2$, the C═C vinyl double bond elongates, while the C1—C$\alpha$ single bond becomes shorter, bringing these two bonds to almost equal length. Correlation diagrams connecting ground state vibrational modes with ones belonging to electronically excited states are given; they show that for many out-of-plane modes the vibrational frequencies decrease upon electronic excitation. This is accounted for in terms of the changes in the $\pi$ electron distribution taking place upon optical excitation that result in decreasing the force constants characterizing these vibrations. The frequencies of most in-plane modes change very little, but mixing between $S_0$ modes is indicated in some cases, and a few vibrations, among them a Kekulé-type mode, undergo considerable change. The relation to the spectroscopy of the corresponding transitions in benzene is briefly discussed. © *1995 American Institute of Physics.*

## I. INTRODUCTION

*Ab initio* quantum chemical (QC) methods are increasingly being used to calculate the properties of molecules in their electronically excited states. Self-consistent field (SCF) methods are widely used to study the electronic ground state potential surface, but their application to excited states is hampered by the fact that the wave function tends to converge to ground state geometry in the energy optimization process (see, e.g., Ref. 1). Several schemes have been recently developed to allow approximate solutions to the problem. Robb and co-workers have used the complete active space SCF (CASSCF) method to calculate the properties of electronically excited benzene[2] and other molecules. Pople and co-workers[3] propose the configuration interaction singles (CIS) as a viable means for electronically excited states calculations. In this approximation the excited state wave functions are written as a linear combination of all possible singly excited configurations. In contrast to CASSCF, which is computationally expensive, the CIS method is relatively simple and may be applied more easily using large basis sets. It has been used to calculate the properties of molecules such as ethylene,[4] butadiene and bicyclobutane,[5] hexatriene,[6] benzene,[7] and others. Double and triple excitation [implemented in various configuration interaction schemes such as QICSD and QICSD(T)] have been used to improve the accuracy of the computations,[8,9] but they become very computationally expensive when applied to large molecules, and at the moment do not seem to be feasible for conveniently treating molecules as large as styrene.

High resolution fluorescence excitation and resonant enhanced multiphoton ionization (REMPI) have been used over the last 20 years to obtain detailed information on the vibrational structure of electronically excited states of many molecules in a supersonic jet environment. The extreme cooling made possible by this method essentially eliminates hot bands from the fluorescence (or MPI) excitation spectrum, simplifying the analysis considerably. Another low temperature method that is widely used—matrix isolation spectroscopy—also provides a wealth of information on the vibronic structure of electronic transitions of large molecules.

The calculation of vibrational frequencies traditionally relies on consistent force field methods,[10] using empirically optimized parameters. Application of these methods to electronically excited states requires the development of a suitable set of parameters, a task that has yet to be accomplished. Many vibronic structure analyses rely on comparisons with the ground state's frequencies and the usual spectroscopic methods such as isotopic substitution.

*Ab initio* QC methods are being increasingly used to calculate the vibrational modes of polyatomic molecules in the ground electronic, the required programs being commercially available (e.g., Gaussian, Ref. 11). For electronically excited states, only a few examples of *ab initio* vibrational analysis are available (see Ref. 12 and references therein) and a more commonly used approach utilizes semiempirical methods. The latter are open to criticism, since they require the use of parameters that are often derived from, and optimized for, ground state properties. Recently, we presented an analysis of the vibronic structure of the $S_0 \leftrightarrow S_1$ transition of anthracene.[12] In that case it turned out that a single configuration was sufficient to account for many properties of the features of the $S_1$ state; in particular, the calculated vibrational frequencies were found to be in very good agreement with the experimental ones. In contrast, it has been shown[13] that for the $S_1$ state of other molecules such as benzene or naphthalene, several configurations are required.

In this paper we present an *ab initio* study of styrene (STY) and of *trans*-$\beta$-methyl styrene (BMS), whose fluorescence excitation and emission spectra have been recently recorded in our laboratory.[14,15] The low lying electronic states of styrene, which is the simplest molecule containing both an aromatic ring and a double bond, have been extensively studied experimentally[16–20] and theoretically.[21–25] Experimental data based primarily on UV spectroscopy indicate that the molecule is planar in both the ground and the first electronically excited singlet states. The small dipole moment of styrene made the measurement of the microwave spectrum extremely difficult. It was first reported in 1988,[20] using a pulsed Fourier transform spectrometer. The planarity of the molecular structure of styrene was conclusively established, and a structure, based on *ab initio* calculations,[21] was found to be compatible with the measured rotational constants.

Considerable effort has been invested in elucidating the correct form of the torsional potential around the C1—C$\alpha$ bond (see Fig. 1 for notation). It is now accepted that this potential is very shallow in $S_0$, and much steeper in $S_1$; Hollas and co-workers have given a complete analysis of the emission spectrum, and fitted the data to an empirical potential of the form $V(\phi)=\Sigma_i(V_i/2)(1-\cos n\phi)$ ($n$ runs over even integers only). The contribution of the $n=4$ term was found to be significant, and the potential is essentially flat in the $-20°<\phi<20°$ range.[16] A recent similar analysis for BMS shows that in fact a small barrier exists in this molecule at $\phi=0°$, so that this molecule is slightly twisted in the ground electronic state.[26]

The dipole moment of the $S_0\rightarrow S_1$ transition in styrene lies in the molecular plane and is long axis polarized[27] in contrast with the short axis polarization of many other substituted benzenes. All observed vibronic bands are of $a'$ symmetry in $C_s$ (in plane), and the vibronic intensity distribution is essentially determined by the Franck–Condon overlap factors. Therefore, the out-of-plane modes ($a''$ in $C_s$ symmetry) are observed only in even combination bands. Hollas and co-workers[18,19,28] reported considerable Duschinsky mixing between the two lowest frequency out-of-plane modes $\nu''_{41}$ and $\nu''_{42}$.[29] They found that in $S_1$ there is a large increase in mode $\nu_{42}$ frequency as compared to the ground state, and a large decrease in $\nu_{41}$ and assigned a frequency interval of 186 cm$^{-1}$ to the former (as compared to 38 cm$^{-1}$ in the ground state) and of 97 cm$^{-1}$ to the latter (199 cm$^{-1}$ in $S_0$). Hemley *et al.*,[22,23] based on a PPP calculation, reversed the assignment.

Many theoretical calculations of the structure of styrene in both $S_0$ and $S_1$ states have been published. The ground state was invariably found to be bent, with an equilibrium torsional angle of 15°–20°.[24,25,30] Head-Gordon and Pople[24] found that the torsion barrier is very small (0.04 kcal/mol) at the HF/6-31G* level of theory, and *increased* to 0.21 kcal/mol at a higher level (MP2/6-311G**//HF/6-31G*). All calculations agree that the torsional potential is very flat,[25] and that the molecule is essentially planar in the ground state. In the excited state, the molecule was found to be strictly planar by both semiempirical[22,23] and *ab initio* calculations[31,32] with a fairly deep well in the torsional degree of freedom.

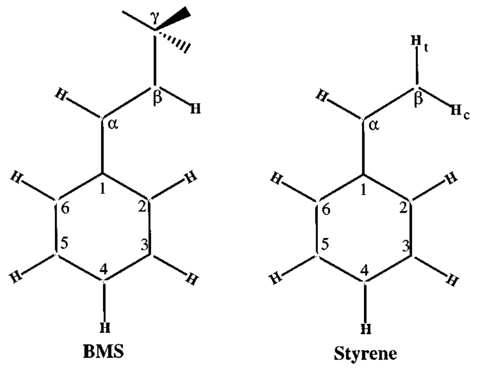

FIG. 1. The atom numbering convention for styrene and BMS.

In this paper we present an *ab initio* calculation of the vibrational levels of styrene, some of its isotopomers, and BMS in the ground state, obtaining very good agreement with experimental results. The calculation was extended to the first and second excited singlet states, $S_1$ and $S_2$, in the case of styrene and of BMS. The latter molecule was studied in order to assign the jet cooled fluorescence excitation and emission spectra reported in the companion paper.[15] The structures of these molecules and the atom numbering convention are shown in Fig. 1.

The excited states were studied using the configuration interaction singles (CIS) method,[3] with full optimization of the geometry. Hemley *et al.*[22,23] showed that there is only a small contribution from doubly excited configurations to the wave functions of $S_0$ and $S_2$ in their PPP and complete neglect of differential overlap (CNDO) studies of the molecule. For $S_1$, *two* singly excited configurations were found to contribute significantly, and in addition, a small but non-negligible contribution of two *doubly* excited configurations was required to reproduce the correct level ordering and the small oscillator strength of the $S_1\leftrightarrow S_0$ transition. Starting with the computationally convenient CIS method, we show in this paper that the vibrational levels of the $S_1$ and $S_2$ states can be reasonably well calculated, and that the changes in vibrational mode frequencies can be related to the electronic structure of the excited states.

## II. COMPUTATIONAL DETAILS

Calculations were performed using the GAUSSIAN 92 program package,[11] run on a Silicon Graphics Indigo R4000/48MB/2GBHD work station. The ground state ($S_0$) calculations were performed at the HF/4-31G level of theory, while for $S_1$ and $S_2$ we used the configuration interaction singles (CIS) procedure,[3] also using the 4-31G basis set.[33] In this procedure, all singly excited configurations are considered, and it turned out that for both molecules the dominant contribution in the case of $S_2$ comes from the configuration due to the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) excitation. For the $S_1$ state, the main contribution comes from two configurations, arising from a single electron excitation from the HOMO$-$1 orbital to the LUMO one, and from the HOMO to the

LUMO+1. As shown in previous *ab initio*[31] and semiempirical calculations,[22,23] singly excited configurations alone do not reproduce the correct excited states level order, while the addition of doubly excited configurations sufficed to reconstruct it. Upon applying a MP2 correction to the CIS/4-31G calculation, we found that the correct level ordering was obtained, as judged by the magnitude of the oscillator strengths for the $S_0$ to $S_i$ transitions. The vibrational calculations (normal modes shapes, force constants and frequencies) were performed at the HF and CIS levels, respectively, for the ground and excited states.

In all computations, no constraints were imposed on the geometry of the molecule. Full geometrical optimization was performed for each state, and the attainment of the energy minimum was verified by calculating the vibrational frequencies (no imaginary values). The vibrational frequencies, at the harmonic approximation, were obtained by computing the Hessian matrix. The required second derivatives of the potential were calculated analytically for $S_0$, and numerically for $S_1$ and $S_2$. All frequencies quoted below were obtained from the computed ones by multiplying with appropriate scaling factors.[34] The same factors (0.89 for the in-plane, and 0.85 for the out-of-plane modes) were used for all electronic states.

## III. RESULTS

### A. Styrene

The torsional potential well in $S_0$ was found to be very shallow for styrene, and the exact location of the minimum depended sensitively on many different coordinates. We assume, along with previous workers,[24,25] that the small deviation from planarity is due to a computational deficiency. For the calculation of all vibrational frequencies, a well-defined energy minimum is required. A minimum was located for a torsional angle $\tau$ of 10.5° (namely, a small deviation from planarity) and the remaining hump in the planar conformation ($\tau=0°$) is small ($\sim 20\ \mathrm{cm}^{-1}$). Therefore, the calculated frequencies are likely to be close to the ones that would have been obtained for the true planar minimum, with possible deviations for the lowest out-of-plane vibrations. The frequency of the torsional mode $\nu''_{42}$, obtained in this manner, was found to be about $2\ \mathrm{cm}^{-1}$. Experimentally, the potential for this mode is known to be extremely anharmonic,[16] and we did not make an extended effort to optimize the motion along the corresponding normal mode. The main emphasis in this work is directed at understanding properties of the electronically excited states, which were not studied before by an *ab initio* method, such as the vibrational frequencies.

In contrast with the case of $S_0$, the $S_1$ and $S_2$ states were found to be strictly planar, with a well-defined minimum along the torsional coordinate. The calculated C—C bond lengths and torsional angles of the ground, the $S_1$ and the $S_2$ states are shown in Fig. 2 (the C—H bond lengths and the valence angles are practically unchanged upon excitation; they are available from the authors on request). The most significant change in $S_1$ is the expansion of the aromatic ring; in addition, the C$\alpha$—C$\beta$ bond is slightly lengthened and the C1—C$\alpha$ bond shortens a little. In $S_2$ the geometrical changes are more extensive: the C$\alpha$—C$\beta$, C1—C2, C1—C6, and C4—C5 bonds are lengthened, while the C1—C$\alpha$ bond concomitantly shortens resulting in considerable stiffening of the C1—C$\alpha$—C$\beta$ structure. The aromatic character of the ring is considerably reduced in this state, since the C—C bond lengths are not equal to each other as in the ground state.

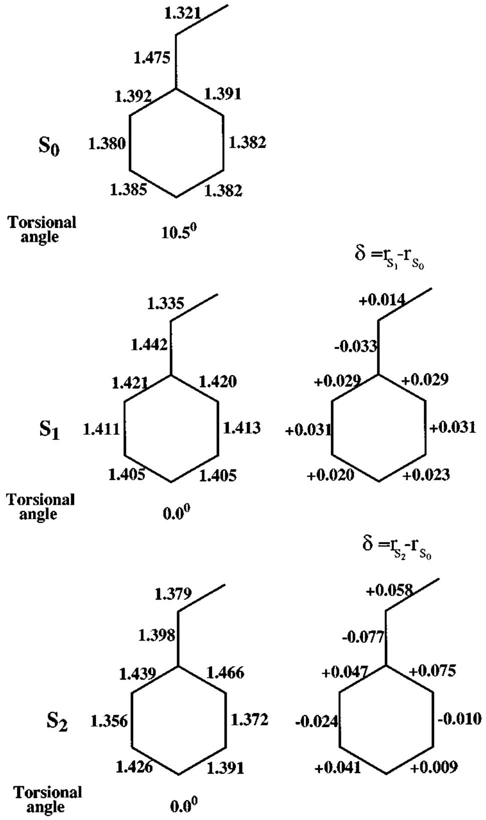

FIG. 2. The calculated structure of styrene in $S_0$, $S_1$, and $S_2$.

Within the CIS/4-31G approximation, the main contribution to the $S_1$ electronic state is from two configurations: the one arising from a single electron transfer from the HOMO−1 to the LUMO orbital (27→29), and the one arising from the 28→30 excitation (HOMO to LUMO+1). These two configurations contribute about equally to the excited state, and together represent ~50% of the total probability. The oscillator strength calculated for the $S_0 \rightarrow S_1$ transition was 0.0038 compared to the estimated experimental value of 0.002.[23] However, the energy of this state was found to be *higher* than that of the $S_2$ state (mainly HOMO→LUMO excitation, see the next paragraph) by about 0.25 eV. As discussed in Ref. 3, the second-order perturbation correction (MP2) to the energy involves summation over matrix elements between the zeroth-order state (obtained by the CIS method) and doubly substituted determinants from this state. This implies that it should involve double and triple excitation from the *ground* state. Therefore, the MP2 treatment provides an approximate way of assessing the contribution of double and triple excitation configurations to the electronically excited state. Upon running this calculation, the correct order was obtained, and the $S_1$ state lies about 0.8 eV lower than the next one (the experimental separation is about 0.57 eV).

Summarizing, the transition involves primarily the partial excitation of an electron from the HOMO$-$1 orbital to orbital the LUMO one, and of an electron from the HOMO orbital to the LUMO+1 orbital, leading to a long axis polarized transition moment. In the CIS calculation, the coefficients of these two components are almost equal, but of opposite signs (0.49 and $-$0.46, respectively). Since these terms make opposite contributions to the $S_0 \leftrightarrow S_1$ transition moment, the net result is a small oscillator strength, in accord with previous workers.[22,31] These transitions lead to population of antibonding orbitals, mainly in the aromatic ring part of the molecule, and therefore result in expansion of the benzene ring and contraction of the C1—C$\alpha$ bond. The C$\alpha$—C$\beta$ bond is only very slightly elongated (cf. Fig. 2). We conclude that the CIS-MP2/4-31G calculation of the $S_1$ state provides a reasonable approximation for the properties of the state.

The main contribution to the $S_2$ electronic state is due to the configuration arising from a single electron transfer from the HOMO to the LUMO orbital (28→29). A small (~5%) contribution was calculated for the configuration arising from 27→30 excitation. The minimum to minimum energy gap between $S_0$ and $S_2$ was calculated to be 5.1647 eV, as compared to the experimental value of ~4.80 eV.[35] Taking the zero-point energies into account (see below for the calculated vibrational frequencies), we obtain an expected 0,0 transition at 5.05 eV. The discrepancy is reasonable for this level of calculation (CIS/4-31G). The calculated oscillator strength is 0.55, compared to an estimated experimental value of 0.24,[23] which may involve some contribution from the $S_0 \rightarrow S_3$ transition.

### 1. The vibrational frequencies of styrene in the $S_0$ state

The normal mode frequencies were calculated for several isotopomers of styrene, as summarized in Table I, along with the experimental values.[29] We have used the work of Refs. 28 and 37 as the source for experimental data and find very good agreement between our calculated values and the experimental ones, upon using a uniform 0.89 scaling factor for in-plane vibrations, and 0.85 for out-of-plane ones. The order of the calculated frequencies agrees with the experimental ones in all cases, except for an interchange between the vinyl $\nu''_{30}$ and the ring $\nu''_{31}$ modes, which are of very similar values both experimentally and computationally. It is seen that the calculation reproduces nicely the observed isotope effects and in fact resolves some remaining difficulties mentioned in the literature. For instance, the $\nu_{14}$ assignment for STY-D$_2$ to the observed band at 1024 cm$^{-1}$ was considered dubious in Ref. 28. Our calculated value of 1034 cm$^{-1}$ is in fact in very good agreement with that assignment. Table I also includes the classification due to Whiffen,[36] that provides an approximate description of the main motions of the atoms. According to this classification, the $o$-type vibration is an in-plane CC atom Kekulé vibration (i.e., a motion that distorts the ring to a Kekulé structure) and the $e$-type one mainly a CH in-plane bending one (modes 17 and 15, respectively, for styrene). However, inspection of the displacement atomic vectors calculated for these modes shows that in fact, both involve carbon *and* hydrogen atom movements. A separate calculation showed that this mixed character holds also for benzene itself, in accord with Wilson's result (cf. Fig. 3 in Ref. 37).

The good agreement of most assignments with experiment warrants discussion of some apparent disagreements with the published data. For instance, the $\nu''_{15}$ mode of STY-D$_5$ and STY-D$_8$ were assigned to the observed bands at 1285 cm$^{-1}$. We propose that they be assigned to the 1184 and 1179 cm$^{-1}$ bands, respectively, and that the 1285 cm$^{-1}$ band in STY-D$_5$ is due to the $\nu''_{34} + \nu''_{39}$ combination band, while the 1285 cm$^{-1}$ band in STY-D$_8$ is due to the $\nu''_{33} + \nu''_{37}$ combination band. In both cases there is a small redshift of the combination band with respect to the sum frequency of the fundamentals (13 and 16 cm$^{-1}$, respectively for STY-D$_5$ and STY-D$_8$). The $\nu''_{18}$ fundamental for STY-D$_5$ and STY-D$_8$ were assigned as 1154 and 1179 cm$^{-1}$, in gross disagreement with the calculated values of 871 cm$^{-1}$ for both isotopomers. We propose that the observed 871 and 870 cm$^{-1}$, assigned to the $\nu''_{19}$ mode, should be assigned to the $\nu''_{18}$ one, and the observed bands at 1154 cm$^{-1}$ (STY-D$_5$) and 1168 cm$^{-1}$ (originally considered as a combination band in STY-D$_8$ in Ref. 38), are due to the $\nu''_{19}$ fundamental. The 837 cm$^{-1}$ band of STY-D$_2$ was assigned to both $\nu''_{22}$ and $\nu''_{35}$. We propose that the medium strong IR band at 907 cm$^{-1}$ is due to the $\nu''_{22}$ mode, in accidental degeneracy with the $\nu''_{34}$ mode. The $\nu''_{33}$ mode is then the strong 727 cm$^{-1}$ band. Support for this suggestion comes from the very large calculated IR intensity for this band (103 km/mol), as compared to that of the $\nu''_{34}$ mode (904 cm$^{-1}$, 0.15 km/mol). Another dubious assignment discussed by Ref. 38 is that of the $\nu''_{38}$ fundamental. The strong feature at 517 cm$^{-1}$ was apparently dismissed in favor of the weaker 571 cm$^{-1}$ one, since the deuterium shift and IR intensities were considered to be too large when compared to the protonated analogs. However, the calculation actually predicts an even larger frequency shift (to 497 cm$^{-1}$), and a fairly large IR intensity enhancement (18.2 vs 0.25 km/mol for STY-H$_8$). It is thus proposed to adopt the 517 cm$^{-1}$ assignment for the $\nu''_{38}$ fundamental, and assign the weak 571 cm$^{-1}$ band to a combination band, possibly $\nu''_{39} + \nu''_{29}$.

### 2. The vibrational frequencies of styrene in the $S_1$ and $S_2$ states

The calculated frequencies of styrene in the $S_1$ and $S_2$ electronic states are listed in Table II, along with available experimental values and the results of the only previous theoretical calculation (Ref. 22, PPP level). The computed results are listed in a descending order of the frequencies; It is more instructive to use the ground state designation for vibrational modes having the same character, even if a different frequency order is found in the excited state. Unfortunately, the available experimental data for $S_1$ frequencies are not as extensive as for $S_0$ and the experimental assignments are not as certain. Strong Duschinsky mixing was proposed for some modes, indicating that a given excited state mode may correlate with more than a single $S_0$ one. This point was

TABLE I. Experimental and calculated vibrational frequencies of some styrene isotopomers in $S_0$.[a]

| Mode | Approximate description[b] | | $C_6H_5CHCH_2$ | | $C_6H_5CHCD_2$ | | $C_6H_5CDCD_2$ | | $C_6D_5CHCH_2$ | | $C_6D_5CDCD_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| In plane modes[c] | | | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. | Expt. | Calc. |
| $\nu_1$ | $\nu CH_2$ | | 3106 | 3031 | 2308 | 2256 | 2329 | 2257 | 3092 | 3031 | 2292 | 2257 |
| $\nu_2$ | ring $\nu$CH | | 3091 | 3009 | 3100 | 3010 | 3104 | 3010 | 2292 | 2234 | 2320 | 2234 |
| $\nu_3$ | ring $\nu$CH | | 3084 | 2999 | 3083 | 3000 | 3084 | 3000 | 2277 | 2222 | 2277 | 2222 |
| $\nu_4$ | ring $\nu$CH | | 3061 | 2990 | 3066 | 2989 | 3061 | 2989 | 2283 | 2212 | 2292 | 2113 |
| $\nu_5$ | ring $\nu$CH | | 3055 | 2978 | 3054 | 2978 | 3051 | 2978 | 2271 | 2200 | 2267 | 2202 |
| $\nu_6$ | ring $\nu$CH | | 3029 | 2972 | 3020 | 2971 | 3026 | 2971 | 2262 | 2193 | 2261 | 2193 |
| $\nu_7$ | vinyl $\nu$CH | | 3009 | 2946 | 3003 | 2950 | 2244 | 2154 | 3009 | 2946 | 2250 | 2154 |
| $\nu_8$ | $\nu CH_2$ | | 2981 | 2965 | 2214 | 2175 | 2207 | 2201 | 2983 | 2966 | 2215 | 2200 |
| $\nu_9$ | $\nu C{=}C$ | | 1630 | 1663 | 1570 | 1619 | 1562 | 1593 | 1629 | 1661 | 1574 | 1591 |
| $\nu_{10}$ | ring $\nu$CC | [*k*] | 1600 | 1609 | 1600 | 1606 | 1602 | 1611 | 1575 | 1569 | 1563 | 1566 |
| $\nu_{11}$ | ring $\nu$CC | [*l*] | 1575 | 1582 | 1595 | 1575 | 1585 | 1573 | 1539 | 1540 | 1536 | 1534 |
| $\nu_{12}$ | ring $\nu$CC | [*m*] | 1494 | 1500 | 1494 | 1499 | 1491 | 1497 | 1377 | 1368 | 1377 | 1364 |
| $\nu_{13'}$ | ring $\nu$CC | [*n*] | 1450 | 1460 | 1445 | 1450 | 1445 | 1448 | 1328 | 1309 | 1327 | 1313 |
| $\nu_{14}$ | $\beta{=}CH_2$ | | 1411 | 1434 | 1024 | 1034 | 1048 | 1060 | 1425 | 1443 | 1050 | 1037 |
| $\nu_{15}$ | aryl $\beta$CH | [*e*] | 1334 | 1353 | 1331 | 1354 | 1332 | 1344 | **1184** | 1191 | **1179** | 1184 |
| $\nu_{16}$ | aryl $\beta$CH | | 1303 | 1319 | 1300 | 1314 | 1003 | 1012 | 1305 | 1328 | 1001 | 1014 |
| $\nu_{17}$ | ring $\nu$CC | [*o*] | 1289 | 1227 | 1280 | 1222 | 1290 | 1220 | 1054 | 1065 | 1028 | 1065 |
| $\nu_{18}$ | aryl $\beta$CH | [*q*] | 1203 | 1186 | 1210 | 1189 | 1225 | 1189 | **871** | 871 | **870** | 871 |
| $\nu_{19}$ | $\nu C1C\alpha$ | [*a*] | 1181 | 1189 | 1180 | 1193 | 1181 | 1205 | **1154** | 1138 | **1168** | 1162 |
| $\nu_{20}$ | aryl $\beta$CH | [*c*] | 1156 | 1142 | 1153 | 1141 | 1156 | 1142 | 841 | 845 | 841 | 846 |
| $\nu_{21}$ | $\beta$CH | [*d*] | 1083 | 1084 | 1080 | 1084 | 1081 | 1085 | 825 | 880 | 825 | 829 |
| $\nu_{22}$ | $\beta{=}CH_2$ | | 1032 | 1037 | **907** | 909 | 831 | 835 | 1006 | 1017 | 810 | 816 |
| $\nu_{23}$ | $\beta$CH | [*b*] | 1019 | 1021 | 1030 | 1022 | 1027 | 1022 | 841 | 839 | 841 | 841 |
| $\nu_{24}$ | ring deform | [*p*] | 999 | 999 | 997 | 1003 | 995 | 958 | 953 | 958 | 955 | 955 |
| $\nu_{25}$ | *X*-sens ($\alpha$C—C—C) | [*r*] | 776 | 762 | 735 | 732 | 735 | 731 | 729 | 719 | 699 | 696 |
| $\nu_{26}$ | $\alpha$C—C—C | [*s*] | 621 | 631 | 618 | 631 | 622 | 631 | 595 | 605 | 594 | 605 |
| $\nu_{27}$ | $\beta C{=}C$ | | $553^{\dagger}$ | 556 | 513 | 513 | 510 | 508 | 541 | 542 | 498 | 498 |
| $\nu_{28}$ | *X*-sens ($\alpha$C—C—C) | [*t*] | $437^{\dagger}$ | 431 | 426 | 431 | 420 | 428 | 433 | 430 | 408 | 408 |
| $\nu_{29}$ | *X*-sens ($\beta C—CHCH_2$) | [*u*] | $228^{\dagger}$ | 232 | 218 | 215 | 220 | 214 | 231 | 224 | 211 | 206 |
| Out of plane[c] | | | | | | | | | | | | |
| $\nu_{30}$ | vinyl $\gamma$CH | | 992 | 997 | 941 | 957 | 788 | 814 | 989 | 998 | 789 | 818 |
| $\nu_{31}$ | aryl $\gamma$CH | [*j*] | 985 | 1009 | 987 | 1003 | 986 | 1002 | 825 | 866 | 825 | 869 |
| $\nu_{32}$ | aryl $\gamma$CH | [*h*] | 970 | 980 | 980 | 980 | 970 | 980 | 786 | 801 | 789 | 801 |
| $\nu_{33}$ | vinyl $\gamma$CH | | 909 | 943 | **727** | 749 | 710 | 710 | 909 | 943 | 708 | 710 |
| $\nu_{34}$ | aryl $\gamma$CH | [*i*] | 909 | 924 | **907** | 915 | 913 | 928 | 780 | 789 | 747 | 763 |
| $\nu_{35}$ | aryl $\gamma$CH | [*g*] | 841 | 851 | 837 | 851 | 840 | 851 | 657 | 654 | 656 | 637 |
| $\nu_{36}$ | aryl $\gamma$CH | [*f*] | 776 | 777 | 764 | 768 | 742 | 752 | 679 | 672 | 647 | 637 |
| $\nu_{37}$ | ring deform. | [*v*] | 699 | 685 | 693 | 682 | 692 | 680 | 541 | 528 | 554 | 534 |
| $\nu_{38}$ | vinyl $\gamma$CH | | 640 | 626 | 568 | 558 | 571 | 558 | (595) | 568 | **517** | 503 |
| $\nu_{39}$ | ring puckering | [*x*] | 433 | 435 | 408 | 387 | 407 | 385 | 391 | 383 | 369 | 361 |
| $\nu_{40}$ | ring deform. | [*w*] | $399^{\dagger}$ | 398 | 394 | 400 | 398 | 399 | 354 | 343 | 354 | 342 |
| $\nu_{41}$ | C1—C$\alpha$ bend | [*y*] | $199^{\dagger}$ | 191 | 199 | 180 | 192 | 173 | 205 | 182 | 182 | 165 |
| $\nu_{42}$ | C1—C$\alpha$ torsion | | $38^{\dagger}$ | 2 | 37 | 2 | ⋯ | 2 | ⋯ | 2 | ⋯ | 2 |

[a] Experimental data from Refs. 37 and 28. All frequencies are for liquid solutions, except those marked by † which are gas phase values. Boldface entries are reassignments offered by us based on the experimental data, see the text. Entries in parentheses are experimental values whose proposed assignment is uncertain and does not fit in with the calculation.

[b] $\nu$—stretch, $\alpha$—in plane ring angle bend, $\beta$—in-plane bend, $\gamma$—out-of-plane bend, $\phi$—torsion or twist, *X*-sens—a vibration sensitive to the substituent. Symbols in square brackets are according to Whiffen's classification (Ref. 36) of benzene substituted compounds.

[c] The scaling factor for in-plane modes is 0.89, for out-of-plane modes, 0.85.

discussed extensively by Hemley and co-workers[22] vis-a-vis the experimental analysis of Hollas and co-workers.[16,18]

The calculations indicated considerable changes in the force constants and reduced mass of some vibrational modes, possibly leading to a qualitative change in the character of certain normal modes. Therefore, it was deemed necessary to establish the correlation between $S_0$ and the excited states' modes. This was done by considering parameters provided by the calculation: the symmetry, force constants, and reduced masses of each mode, but mostly the detailed description of each normal mode in terms of the individual motion of atoms. Figure 3 shows the correlation diagram obtained. It is seen that on the transition from $S_0$ to $S_1$, most of the $a'$ (in-plane) modes appear not to change their frequency appreciably; among the out-of-plane ones, many ring modes show a considerable frequency *decrease*, while the $\nu_{30}$, $\nu_{33}$, and $\nu_{38}$, which are predominantly vinyl-type ones are changed to a much smaller extent.

Although a cursory inspection of Fig. 3 indicates a 1:1 correlation between the vibrational modes of styrene in $S_0$

TABLE II. The vibrational frequencies of styrene in $S_1$ and in $S_2$.

| | $S_1$ | | | | $S_2$ | |
|---|---|---|---|---|---|---|
| Mode | Expt. Ref. 16 | Expt. Ref. 42 | Calc. Ref. 22 | This work[a] | This work[a] | Expt. Ref. 35 |
| In plane modes | | | | | | |
| $\nu_1$ | | | 3092 | 3040 | 3042 | |
| $\nu_2$ | | | 3063 | 3030 | 3021 | |
| $\nu_3$ | | | 3089 | 3021 | 3008 | |
| $\nu_4$ | | | 3088 | 3011 | 2995 | |
| $\nu_5$ | | | 3087 | 3001 | 2980 | |
| $\nu_6$ | | | 3086 | 2996 | 2976 | |
| $\nu_7$ | | | 3084 | 2969 | 2956 | |
| $\nu_8$ | | | 2985 | 2945 | 2966 | |
| $\nu_9$ | | | 1624 | 1628 | 1590 | 1573 |
| $\nu_{10}$ | 1608 | | 1556 | 1607 | 1508 | |
| $\nu_{11}$ | | | 1578 | 1568 | 1463 | |
| $\nu_{12}$ | 1474 | | 1481 | 1507 | 1453 | |
| $\nu_{13}$ | 1428 | | 1509 | 1455 | 1428 | |
| $\nu_{14}$ | | | 1434 | 1442 | 1373 | |
| $\nu_{15}$ | | | 1382 | 1400 | 1323 | |
| $\nu_{16}$ | 1299 | 1299 | 1284 | 1330 | 1300 | |
| $\nu_{17}$ | | | 1340 | 1301 | 1222 | |
| $\nu_{18}$ | 1208 | 1209 | 1261 | 1201 | 1197 | |
| $\nu_{19}$ | | | 1160 | 1169 | 1169 | |
| $\nu_{20}$ | 1114 | 1146 | 1141 | 1164 | 1115 | |
| $\nu_{21}$ | | | 1079 | 1059 | 1072 | |
| $\nu_{22}$ | 959[b] | | 1007 | 992 | 998 | |
| $\nu_{23}$ | 940[b] | | 1032 | 980 | 951 | |
| $\nu_{24}$ | | | 1041 | 956 | 929 | |
| $\nu_{25}$ | 746 | 746 | 814 | 730 | 723 | |
| $\nu_{26}$ | 544 | 523[b] | 657 | 587 | 587 | |
| $\nu_{27}$ | 437[c] | 437[c] | 605 | 536 | 535 | |
| $\nu_{28}$ | 394 | 394 | 470 | 416 | 424 | |
| $\nu_{29}$ | 237 | | 279 | 232 | 233 | 248 |
| Out of plane | | | | | | |
| $\nu_{30}$ | | | 944 | 970 | 966 | |
| $\nu_{31}$ | | | 964 | 900 | 951 | |
| $\nu_{32}$ | | | 930 | 845 | 899 | |
| $\nu_{33}$ | | | 858 | 799 | 817 | |
| $\nu_{34}$ | | | 916 | 755 | 792 | |
| $\nu_{35}$ | | | 794 | 642 | 719 | |
| $\nu_{36}$ | | | 709 | 626 | 701 | |
| $\nu_{37}$ | | | 609 | 615 | 560 | |
| $\nu_{38}$ | | | 527 | 381 | 451 | |
| $\nu_{39}$ | | | 407 | 325 | 380 | |
| $\nu_{40}$ | 253 | | 343 | 258 | 283 | |
| $\nu_{41}$ | 97 | | 220 | 155 | 156 | |
| $\nu_{42}$ | 186 | | 128 | 33 | 67 | |

[a] In-plane frequencies scaled by 0.89, out-of-plane frequencies by 0.85.

[b] Part of a multiplet.

[c] This assignment deviates significantly from our calculated value. We tentatively propose the combination band $40_0^1 41_0^1$ as the assignment of the observed 437 cm$^{-1}$ band, using 253 and 186 cm$^{-1}$ for $\nu'_{40}$ and $\nu'_{41}$, respectively. See Table VII for a different option.

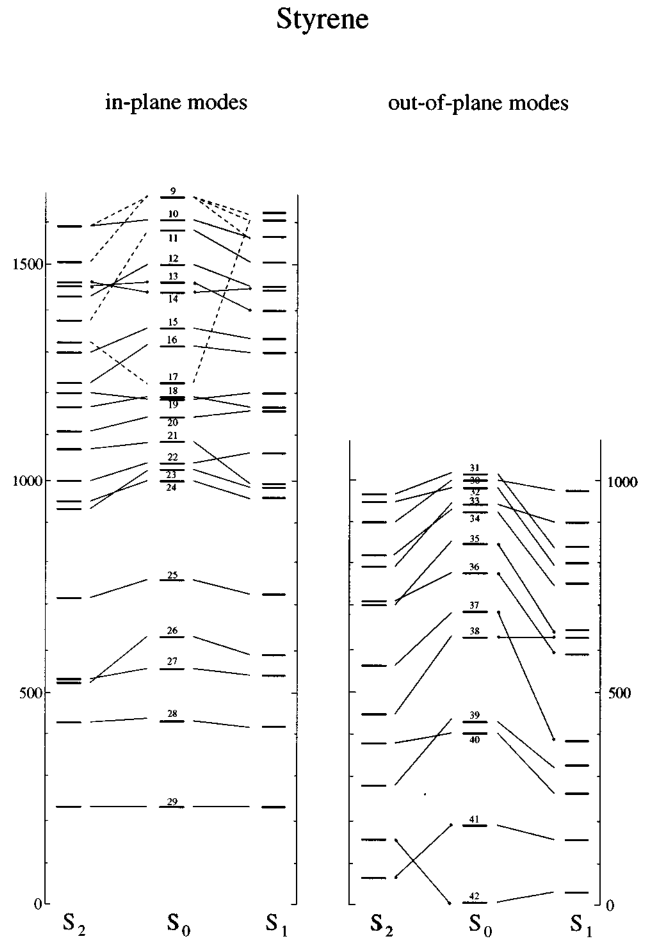

FIG. 3. The correlation between $S_0$, $S_1$, and $S_2$ vibrational modes of styrene, excluding CH stretch modes, as found in the calculations. The numbers shown are the mode designation, based on the $S_0$ energy order. Vibrational levels of $S_1$ and $S_2$ correlated with $S_0$ ones are connected by thin solid lines, if the mode character is largely maintained. Dashed lines indicate some correlation, accompanied by extensive changes in mode character. Mode mixing is indicated by the small filled circles at the end of the connecting lines. Note that the ring mode $\nu_{31}$ is calculated to have a slightly higher frequency than the vinyl $\nu_{30}$ one (1009 vs 997 cm$^{-1}$, respectively). Experimentally, the order is reversed (985 as compared to 992 cm$^{-1}$). We used the numbering order as determined by the experimental determination, for consistency with previous papers.

and $S_1$ (or $S_2$) in many cases, a closer inspection shows that in fact, for many $S_1$ and $S_2$ vibrational modes, atom displacements may be considered as containing contributions from more than one $S_0$ mode. It is found that except for strongly localized modes, such as the CH stretch ones, many modes change their form somewhat upon excitation. The fact that a mode is shown to correlate with a single excited state mode means that the excited state mode should be understood as indicating that this mode has predominantly, but not exclusively, the same vector displacements as that of the ground state mode. An illustration of a mode mixing example is given in Fig. 4; the displacement vectors of the $\nu_{11}$ mode of $S_1$ and $\nu_9$ mode of $S_2$ are seen to be a combination of the C=C vinyl stretch $\nu_9$ mode and the ring CC stretch $\nu_{10}$ of $S_0$. In a similar way, the out-of-plane $S_0$ ring modes $\nu''_{35}$, $\nu''_{36}$, and $\nu''_{37}$ are mixed on excitation to $S_1$ with the largely vinyl mode $\nu''_{38}$ to produce the corresponding excited state modes, in which the ring or vinyl characters are decidedly less pronounced. Strong mixing is calculated also for the $\nu''_{41}$ and $\nu''_{42}$ upon transition to $S_2$. Table III lists the calculated frequencies, reduced masses, and force constants of vibrational modes that appear to change significantly their character on electronic excitation to $S_1$. The listing takes into account the correlations, so that the numbering system (increasing frequency with decreasing mode number) holds only for the $S_0$ modes.

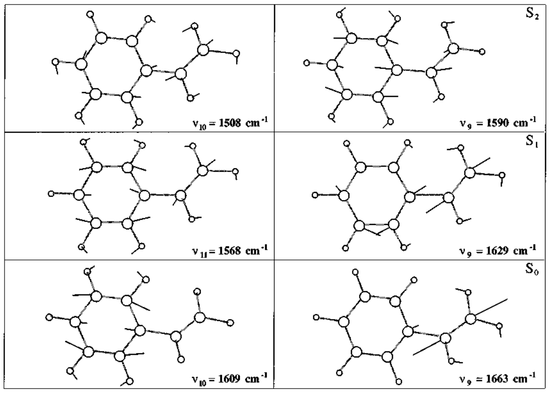

FIG. 4. The calculated changes in the C=C stretch mode of styrene upon electronic excitation. The C$\alpha$—C$\beta$ double bond stretch motion dominates mode $\nu_9$ in $S_0$, and is spread over several modes in $S_1$ and in $S_2$. This is an example of mode mixing in the excited states.

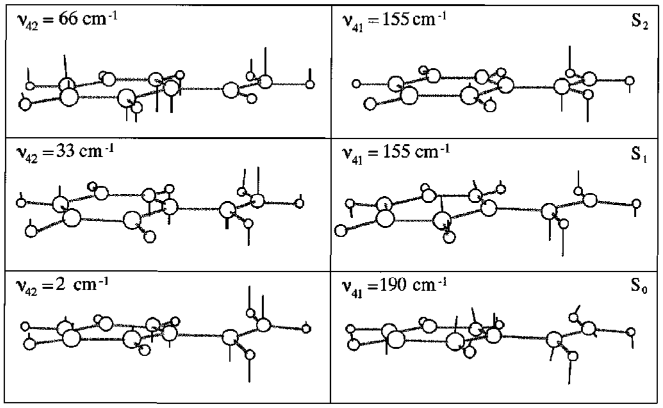

FIG. 5. The vector displacements calculated for the low frequency $\nu_{42}$ and $\nu_{41}$ modes in $S_0$, $S_1$, and in $S_2$. Mode mixing is evident in $S_2$, but only slightly so in $S_1$.

Not much experimental information is available for $S_2$ modes; only two frequencies were reported—at 248 and 1573 cm$^{-1}$.[35] Nonetheless, it is instructive to consider the trends expected according to the calculation. As Fig. 3 shows, for some high frequency skeletal modes, a considerable frequency decrease is calculated. A notable example is the $\nu_9$ mode, which in the ground state is almost exclusively a C=C stretch mode; in the excited state there is no equivalent normal mode, as shown in Fig. 4. A similar, but less pronounced change is found for $S_1$.

Mode crossing often takes place upon electronic excitation for both in-plane and out-of-plane modes. One example is the ring modes $\nu_{32}$ (at 980 cm$^{-1}$ in $S_0$) correlates with the 799 cm$^{-1}$ mode in $S_1$, a significant frequency decrease, while the primarily vinyl mode $\nu_{33}$ (at 943 cm$^{-1}$ in $S_0$) correlates with the 900 cm$^{-1}$ mode in $S_1$. The $\nu_{32'}$ mode is thus found at a lower energy in $S_1$ than the $\nu_{33'}$ one. Likewise, the CH in-plane bending mode ($\nu_{23}$) in $S_0$ has a higher frequency than the ring deformation mode ($\nu_{24}$), and the order is reversed in $S_2$.

As seen from Fig. 5, the out-of-plane low frequency vibration ($\nu''_{42}$), is essentially a C1–C$\alpha$ torsional mode in $S_0$. In $S_2$, the lowest frequency mode is seen to have a different character—it involves almost exclusively out-of-plane bending motion of the whole molecular skeleton (ring+vinyl). The $\nu''_{41}$ mode in $S_0$, is a combined torsion–bending motion, while in $S_2$ it is practically identical in form to the $\nu''_{42}$ mode in $S_0$. In $S_1$, the calculation does not indicate extensive mode mixing. According to the currently prevailing interpretation it is large enough to be measurable, and is expressed by the experimentally observed Duschinsky mixing.[16,18]

TABLE III. Calculated characteristics of the vibrational modes of styrene whose calculated properties change appreciably upon electronic excitation to $S_1$.

| | Frequency (cm$^{-1}$)[b] | | Red. mass (amu)[c] | | Force const. (mdyn/Å)[c] | |
|---|---|---|---|---|---|---|
| Mode[a] | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| In plane | | | | | | |
| $\nu_{20}$ | 1142 | 1164 | 1.99 | 1.17 | 1.93 | 1.18 |
| $\nu_{17}$ | 1227 | 1607 | 2.16 | 6.28 | 2.42 | 12.05 |
| $\nu_{11}$ | 1582 | 1507 | 4.62 | 3.31 | 8.59 | 5.59 |
| $\nu_{10}$ | 1609 | 1568 | 5.07 | 3.83 | 9.76 | 7.01 |
| $\nu_9$ | 1663 | 1628 | 4.13 | 5.09 | 8.50 | 10.04 |
| Out of plane | | | | | | |
| $\nu_{40}$ | 398 | 258 | 2.73 | 2.44 | 0.35 | 0.13 |
| $\nu_{39}$ | 435 | 325 | 2.72 | 2.44 | 0.42 | 0.13 |
| $\nu_{37}$ | 685 | 381 | 1.40 | 1.89 | 0.53 | 0.22 |
| $\nu_{36}$ | 777 | 587 | 1.82 | 1.19 | 0.89 | 0.34 |
| $\nu_{35}$ | 851 | 642 | 1.25 | 1.31 | 0.72 | 0.44 |
| $\nu_{34}$ | 924 | 755 | 1.46 | 1.81 | 1.02 | 0.84 |
| $\nu_{32}$ | 980 | 799 | 1.41 | 1.50 | 1.10 | 0.78 |
| $\nu_{31}$ | 1009 | 845 | 1.41 | 1.70 | 1.17 | 0.99 |

[a] Mode numbering as in $S_0$, the corresponding modes in the excited states are selected according to the correlation diagram of Fig. 3.

[b] In-plane frequencies scaled by 0.89, out-of-plane frequencies by 0.85.

[c] Reduced masses and force constants are reported as calculated (no scaling applied).

## B. *Trans-β*-methylstyrene (BMS)

The general pattern found for styrene was repeated with this molecule as well. The $S_1$ and $S_2$ states were found to be strictly planar, while for the ground state a very broad and shallow potential well for the torsional potential around the C1—C$\alpha$ bond was found, with a small hump at the planar configuration. This hump may be due to a lingering computational artifact, although a recent study[26] indicates a small local maximum for the planar form. The main configurations forming the $S_1$ and $S_2$ states are analogous to those found for styrene itself: the $S_2$ state arises primarily from a HOMO–LUMO transition and is calculated at 5.027 eV (4.90 eV including zero-point energy) above the ground state. The experimental 0,0 band is at about 4.7 eV.[35] The $S_1$ state arises primarily from two singly excited configurations, HOMO$-$1 to LUMO and HOMO to LUMO+1 and is found to be at a higher energy than $S_2$, unless the MP2 correction is applied, restoring the correct order. Figure 6 shows that the main structural changes are very similar to those found for styrene itself (cf. Fig. 2).

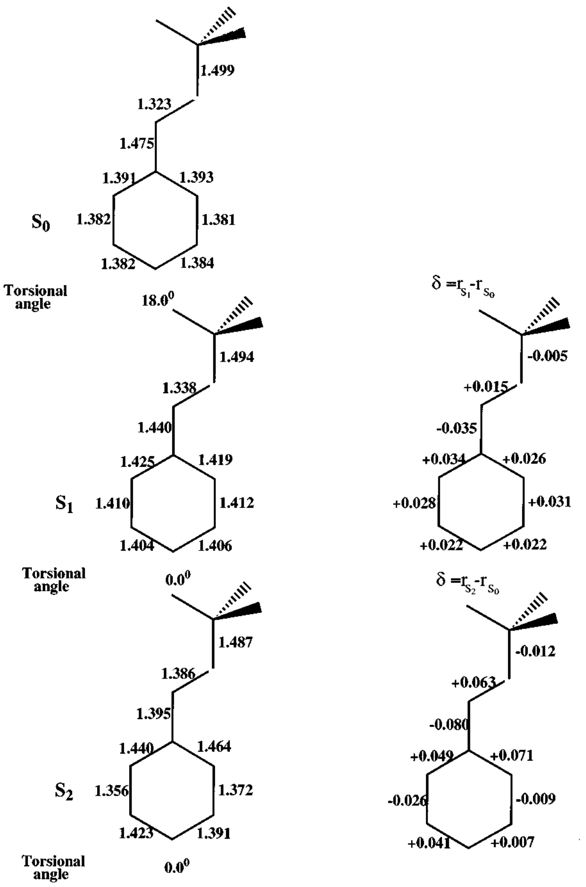

FIG. 6. The calculated structure of BMS in $S_0$, $S_1$, and $S_2$.

#### *1. The frequencies of BMS in the $S_0$, $S_1$, and $S_2$ states*

The calculated frequencies of BMS in the three electronic states are listed in Table IV, along with some experimental values. The correlation between the ground and excited states modes was determined, as in the case of styrene, by considering the symmetry, force constants, reduced masses, and atomic displacements of each vibration and is shown in Fig. 7. The main patterns observed for styrene were repeated: a large number of modes were not appreciably changed upon electronic excitation and could be correlated in a 1:1 manner with $S_0$ modes. Methyl group modes, such as $\nu_{14}$, $\nu_{16}$, $\nu_{35}$, $\nu_{36}$, and $\nu_{37}$, remain largely unchanged upon excitation. As in the case of styrene, for many $a''$ ring modes a decrease in frequency due primarily to the reduced force constants was revealed for $S_1$. Table V lists the frequencies, reduced masses, and force constants for the $S_0$ and $S_1$ vibrational modes that undergo considerable change upon electronic excitation.. The detailed structure of the mode must be considered in the analysis, and the atomic displacement vectors are of prime help. As an example, it is noticed that a 735 cm$^{-1}$ frequency was calculated for out-of-plane modes in both states, and that the two modes were found to have essentially the same reduced masses and force constants. Yet, the $S_0$ one is an $f$-type[36] mode, while the $S_1$ mode is an $i$-type one, and correlates with the $S_0$ mode calculated at 923 cm$^{-1}$.

## IV. DISCUSSION

### A. Comparison with previous work

The calculated properties of the ground state of styrene compare well with those of previous workers;[21,24,25,30] It appears that the 4-31G basis set used by us leads to essentially the same results as those obtained with larger ones, such as 6-31G[21] or even 6-311G**.[24] Table VI shows that the calculated moments of inertia and dipole moments of styrene agree reasonably well with available experimental information. This encourages us to believe that the results obtained for BMS are useful for analysis of experimental data as well, and the calculated values of these parameters for BMS, for which experimental data are yet to be obtained, are also shown in Table VI. Table I, that lists the calculated frequencies for several isotopomers of styrene, shows that they agree quite well with experimental values. The only exception is the low frequency $\nu''_{42}$ torsional mode, which previous *ab initio* calculations have also found to elude proper calculation.

The main novelty in this paper is the use of the CIS method to calculate and analyze the properties of the electronically excited states. The $S_1$ and $S_2$ states' geometries obtained in this work are similar to those calculated by the extended PPP–CI and CNDO/S–CI semiempirical method.[22,23] The oscillator strength found for the $S_0 \rightarrow S_1$ transition is in better agreement with experiment than the semiempirical result. However, the principal efforts were directed at the calculation of the vibrational frequencies of the excited singlet states and correlating them with ground state ones.

Inspection of Table II shows that our calculated frequencies for styrene in $S_1$ are in reasonable agreement with previous experimental assignments for in-plane modes (though a few reassignments needed to be done), but that the two lowest out-of-plane vibrational frequencies differ considerably from published assignments. The $\nu'_{42}$ mode calculated frequency (33 cm$^{-1}$) is very close to that found experimentally for $S_0$ (38 cm$^{-1}$), and the $\nu'_{41}$ mode's frequency is calculated to be 155 cm$^{-1}$, rather than to 97 cm$^{-1}$.[18] This value is fairly close to 186 cm$^{-1}$, a frequency interval often observed in $S_1$ and assigned to the $\nu'_{42}$ frequency in Ref. 18. For modes with higher frequency, the calculation is in good agreement with available experimental values; for instance, that of the $\nu'_{40}$ mode, 258 cm$^{-1}$, agrees closely with the experimental value of 253 cm$^{-1}$.

These results led us to reinspect some excitation and emission spectra of styrene, and to run a few on our jet apparatus.[39] The calculation suggests a possible reassignment of some of the bands in the excitation spectrum of Ref. 42, as shown in Table VII. Some lines in previously reported emission spectra of styrene need to be reassigned if the calculation is correct. For instance, the hot band appearing at $\nu_0^0+59$ cm$^{-1}$, which was assigned[17] as $41_0^1\ 42_1^0$, is now proposed to be due to $42_1^3$, and the emission bands redshifted by 102, 161, and 217 cm$^{-1}$ from the excitation frequency, are assigned to $42_3^3$, $41_1^0\ 42_0^3$, and $42_5^3$, respectively. Furthermore, the $\nu_0^0+282$ cm$^{-1}$ excitation band may be assigned to the $40_0^1 42_0^1$ combination rather than to the $41_0^1 42_0^1$ one. These new

TABLE IV. Calculated and experimental vibrational frequencies of *trans*-$\beta$-methyl styrene in $S_0$, $S_1$, and $S_2$ (cm$^{-1}$).

| Mode | Approx. descr.[a] | $S_0$ | | $S_1$ | | $S_2$ |
|---|---|---|---|---|---|---|
| | | Calc.[b] | Expt.[c] | Calc.[b] | Expt.[c] | Calc.[b] |
| In-plane modes | | | | | | |
| $\nu_1$ | ring $\nu$CH | 3008 | 3082 | 3027 | 3063 | 3021 |
| $\nu_2$ | ring $\nu$CH | 2998 | 3062 | 3011 | | 3006 |
| $\nu_3$ | ring $\nu$CH | 2988 | 3025 | 2996 | | 2992 |
| $\nu_4$ | ring $\nu$CH | 2977 | | 2983 | | 2972 |
| $\nu_5$ | ring $\nu$CH | 2970 | 2963 | 2980 | | 2992 |
| $\nu_6$ | vinyl $\nu$CH | 2957 | 2934 | 2975 | | 2973 |
| $\nu_7$ | vinyl $\nu$CH | 2938 | 2915 | 2949 | | 2950 |
| $\nu_8$ | methyl $\nu$CH | 2890 | 2873 | 2873 | | 2869 |
| $\nu_9$ | methyl $\nu$CH | 2820 | 2852 | 2785 | | 2770 |
| $\nu_{10}$ | vinyl | 1686 | 1664 | 1638 | | 1599 |
| $\nu_{11}$ | $[k]$ | 1608 | 1598 | 1608 | | 1513 |
| $\nu_{12}$ | $[l]$ | 1580 | 1578 | 1566 | | 1468 |
| $\nu_{13}$ | $[m]$ | 1499 | 1497 | 1498 | 1513 | 1458 |
| $\nu_{14}$ | methyl | 1471 | 1479 | 1473 | 1487 | 1436 |
| $\nu_{15}$ | $[n]$ | 1451 | 1440 | 1454 | 1457 | 1381 |
| $\nu_{16}$ | methyl | 1413 | 1390 | 1421 | 1433 | 1400 |
| $\nu_{17}$ | $[e]$ | 1357 | 1377 | 1407 | | 1342 |
| $\nu_{18}$ | vinyl | 1326 | 1332 | 1349 | 1335 | 1323 |
| $\nu_{19}$ | vinyl | 1309 | 1306 | 1315 | 1324 | 1306 |
| $\nu_{20}$ | $[o]$ | 1223 | 1244 | 1299 | 1291 | 1226 |
| $\nu_{21}$ | $[q]$ | 1190 | 1210 | 1207 | 1211 | 1208 |
| $\nu_{22}$ | $[a]$ | 1189 | 1179 | 1171 | 1151(?) | 1172 |
| $\nu_{23}$ | $[c]$ | 1141 | 1155 | 1164 | 1146 | 1129 |
| $\nu_{24}$ | methyl | 1092 | 1105 | 1099 | | 1078 |
| $\nu_{25}$ | $[d]$ | 1066 | 1070 | 1007 | 977 | 1041 |
| $\nu_{26}$ | $[b]$ | 1020 | 1002 (or $\nu_{38}$) | 982 | 965 | 979 |
| $\nu_{27}$ | $[p]$ | 997 | 965 | 965 | 933 | 941 |
| $\nu_{28}$ | vinyl | 926 | 946 | 923 | 915 | 899 |
| $\nu_{29}$ | $[r]$ | 809 | 809 | 790 | 803 | 764 |
| $\nu_{30}$ | $[s]$ | 632 | | 577 | 585 | 600 |
| $\nu_{31}$ | methyl | 619 | 613 | 575 | 572 | 576 |
| $\nu_{32}$ | $[t]$ | 401 | 409 | 401 | 388 | 395 |
| $\nu_{33}$ | vinyl | 340 | 337 | 335 | 337 | 335 |
| $\nu_{34}$ | $[u]$ | 144 | 155 | 157 | 156 | 153 |
| Out-of-plane modes | | | | | | |
| $\nu_{35}$ | methyl | 2736 | 2732 | 2690 | | 2669 |
| $\nu_{36}$ | methyl | 1400 | 1377 | 1399 | | 1389 |
| $\nu_{37}$ | vinyl | 1032 | 1031 | 1026 | | 989 |
| $\nu_{38}$ | $[j]$ | 1007 | 1002 (or $\nu_{26}$) | 847 | | 965 |
| $\nu_{39}$ | $[h]$ | 978 | 981 | 782 | | 951 |
| $\nu_{40}$ | vinyl | 963 | 962 | 935 | | 904 |
| $\nu_{41}$ | $[i]$ | 923 | 910 | 735 | | 808 |
| $\nu_{42}$ | $[g]$ | 839 | | 624 | | 718 |
| $\nu_{43}$ | vinyl | 821 | 809 | 800 | | 703 |
| $\nu_{44}$ | $[f]$ | 735 | 736 | 609 | | 646 |
| $\nu_{45}$ | $[v]$ | 680 | 692 | 458 | | 562 |
| $\nu_{46}$ | $[x]$ | 488 | 498 | 364 | 358(?) | 394 |
| $\nu_{47}$ | $[w]$ | 398 | 394 | 249 | 226 | 380 |
| $\nu_{48}$ | | 273 | 285 | 223 | 213 | 198 |
| $\nu_{49}$ | | 168 | 176 | 189 | 184 | 93 |
| $\nu_{50}$ | | 121 | 127 | 107 | 100 | 69 |
| $\nu_{51}$ | | 26 | 31 | 27 | 22 | 51 |

[a] Approximate mode description using Whiffen's classification (Ref. 36). Vinyl and methyl vibrations are designated separately. This description refers for $S_0$ modes only, see Fig. 7 for correlation with modes of $S_1$ and $S_2$.

[b] This work.

[c] Experimental data of Refs. 15 and 26.

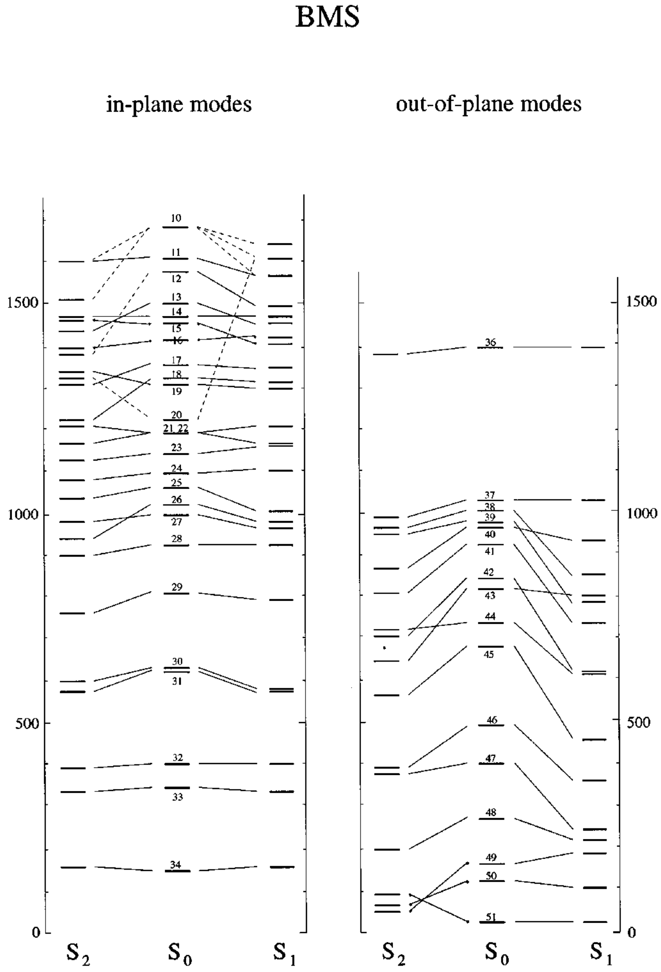

FIG. 7. The correlation between normal modes of BMS in $S_0$, $S_1$, and $S_2$ (excluding CH stretch modes), as found in the calculations. The meaning of the symbols is as in Fig. 3.

assignments rely on two results of the computations: First, the value of the $\nu'_{42}$ mode frequency, 33 $\text{cm}^{-1}$, which is compatible with a value of 97 $\text{cm}^{-1}$ for the second overtone of this vibration $[E(v=3)-E(v=0)]$. The 97 $\text{cm}^{-1}$ interval, often appearing in the $S_0 \rightarrow S_1$ spectrum, was interpreted by Hollas *et al.* as the fundamental frequency of $\nu'_{41}$. The second *ab initio* result is the apparent absence of mode mixing between $\nu_{41}$ and $\nu_{42}$ in $S_1$, in contrast with the analysis of Ref. 18.

These reinterpretations, intriguing as they are, must be regarded as tentative at best at this point. The accuracy of the calculation of low frequency torsional modes such as $\nu_{42}$ in electronically excited states cannot be properly estimated at this stage, as we and others found even in the case of the ground state ($S_0$). We have used a limited basis set, and the effect of diffusion functions, which may be important for a proper description of the excited states vibrational modes, has not been checked. The computational effort involved in using a larger basis set is much larger than needed for the present work, and its execution was not attempted. It is therefore premature to conclude that mode mixing is really absent for the two low lying out-of-plane modes of styrene. Nonetheless, it is interesting to note that an assignment of the vibronic structure of the $S_0 \leftrightarrow S_1$ spectrum is possible, assuming that the $S_1$ calculation is correct. In that case, each mode maintains its character, and the $\nu_{42}$ mode is nearly harmonic in $S_1$, with the following energy intervals with respect to $v=0$: 30, 62, 97, 129, 160, and 193 $\text{cm}^{-1}$ for $\Delta v=1$ through 6. The 186 $\text{cm}^{-1}$ frequency interval is adopted, in this interpretation, as the $\nu'_{41}$ mode's frequency, as shown in Table VII.

## B. Correlation between the changes in electronic charge distribution and vibrational motions

The $S_0 \rightarrow S_1$ electronic excitation affects mostly the aromatic ring, while the main effect of the $S_0 \rightarrow S_2$ transition, is the transfer of an electron from the HOMO $\pi$ orbital, to the LUMO $\pi^*$ one, affecting the whole $\pi$ electron structure. This results in considerable weakening of several double bonds, primarily the vinyl one and the C1—C6, C1—C2, and C4—C5 ring ones, and to strengthening of the C1—C$\alpha$ one. These changes are expected to affect the nature of several group frequencies in the vicinity of the relevant bonds, mainly the in-plane ones. In addition, the excitation involves the transfer of an electron from a $\pi$ orbital to a $\pi^*$ one, leading to reduction of the $\pi$ electron density due to the more "inflated" character of the $\pi^*$ orbitals compared to the $\pi$ ones. This is expected to reduce the force constant (and thus the frequency) of some out-of-plane vibrations. It turns out that these expectations are largely borne out by experiment, as detailed in the next two subsections.

The vibrational modes of monosubstituted benzenes are often discussed in terms of Wilson's classification[37] using Whiffen's notations.[36] This classification was found to be useful also in the construction of the diagrams correlating

TABLE V. Calculated characteristics of the vibrational modes of BMS whose properties are calculated to change appreciably upon electronic excitation.

| | Frequency ($\text{cm}^{-1}$) | | Red. mass (amu) | | Force const. (mdyn/Å) | |
|---|---|---|---|---|---|---|
| Mode | $S_0$ | $S_1$ | $S_0$ | $S_1$ | $S_0$ | $S_1$ |
| In plane | | | | | | |
| $\nu_{27}$ | 997 | 965 | 4.78 | 3.13 | 3.54 | 2.17 |
| $\nu_{26}$ | 1020 | 982 | 2.21 | 3.66 | 1.72 | 2.62 |
| $\nu_{23}$ | 1141 | 1164 | 1.99 | 1.14 | 1.93 | 1.15 |
| $\nu_{20}$ | 1223 | 1608 | 2.35 | 9.87 | 2.62 | 19.0 |
| $\nu_{12}$ | 1580 | 1498 | 4.81 | 3.37 | 8.94 | 5.62 |
| $\nu_{11}$ | 1608 | 1566 | 5.11 | 4.20 | 9.83 | 7.67 |
| $\nu_{10}$ | 1686 | 1638 | 5.45 | 4.94 | 11.54 | 9.86 |
| out of plane | | | | | | |
| $\nu_{48}$ | 273 | 223 | 3.20 | 2.34 | 0.195 | 0.096 |
| $\nu_{47}$ | 398 | 249 | 2.76 | 2.44 | 0.359 | 0.124 |
| $\nu_{46}$ | 488 | 364 | 2.70 | 2.33 | 0.528 | 0.251 |
| $\nu_{45}$ | 680 | 458 | 1.77 | 2.07 | 0.669 | 0.354 |
| $\nu_{44}$ | 735 | 609 | 1.48 | 1.22 | 0.650 | 0.368 |
| $\nu_{42}$ | 839 | 624 | 1.26 | 1.27 | 0.726 | 0.404 |
| $\nu_{41}$ | 923 | 735 | 1.47 | 1.53 | 1.02 | 0.674 |
| $\nu_{38}$ | 978 | 782 | 1.47 | 1.50 | 1.15 | 0.750 |
| $\nu_{37}$ | 1007 | 847 | 1.42 | 1.65 | 1.18 | 0.966 |

TABLE VI. Calculated and experimental properties of styrene and BMS in $S_0$ and in $S_1$.

| | Expt. | | | Calc. | | |
|---|---|---|---|---|---|---|
| Rotational constants (MHz) | $S_0$ | $S_1$ | $S_2$ | $S_0$ | $S_1$ | $S_2$ |
| | | | Styrene | | | |
| *A* | 5163.4[a] | 4979.1[b] | | 5278.3 | 5131.4 | 4989.5 |
| *B* | 1545.9 | 1526.5 | | 1557.6 | 1537.2 | 1590.1 |
| *C* | 1189.6 | 1169.6 | | 1204.7 | 1182.9 | 1205.8 |
| Dipole moment (*D*) | 0.1222 | 0.25[c] | | 0.138 | 0.438 | 0.385 |
| Oscillator strength ($S_0 \rightarrow S_i$) | | 0.002 | 0.24 | | 0.0038 | 0.55 |
| | | | BMS | | | |
| Rotational constants (MHz) | | | | | | |
| *A* | | | | 5107.1 | 4960.8 | 4858.3 |
| *B* | | | | 870.9 | 866.9 | 885.7 |
| *C* | | | | 749.7 | 741.3 | 752.6 |
| Dipole moment (*D*) | | | | 0.3905 | 0.568 | 0.593 |
| Oscillator strength ($S_0 \rightarrow S_i$) | | | | | 0.0050 | 0.67 |

[a] Reference 20.

[b] Reference 20 combined with data of Ref. 27, in which the changes of the rotational constants upon electronic excitation.

[c] Reference 20 combined with data of Ref. 41, in which the changes of the dipole moment upon electronic excitation were reported.

excited states' vibrational modes with ground state ones (Figs. 3 and 7). In many cases, an approximate one to one correlation could satisfactorily account for the properties of the $S_1$ and $S_2$ states vibrational modes with those of $S_0$. This conclusion was reached by considering the calculated force constants, reduced mass, and mostly the individual atom displacements of each mode. Since vibrational frequencies reflect the properties of the potential surface near the minimum position, this result must be interpreted as indicating that the potential surface remains relatively unchanged along many coordinates upon electronic excitation. It is also in line with the rather small overall calculated geometry changes incurred upon excitation.

However, the approximate nature of this simple correlation must be emphasized, and a certain degree of mode mixing, namely a non-negligible contribution of more than one $S_0$ mode to an excited state mode, is a common occurrence. As shown in Figs. 3 and 8, several "crossings" take place, in which the calculated frequency for a given mode is lower than that of other mode(s) in $S_1$ or $S_2$ although it is higher in $S_0$. In most of these cases, the modes involved are coupled to a certain extent. In particular, it was found that while in the ground state, vibrational modes could often be assigned as primarily "ring" or "vinyl" modes, in the excited states many modes included contribution from both groups. This was discussed vis-a-vis the $\nu_9$ mode of styrene (Fig. 4), and is apparent, for instance, also for the $S_0$ vinyl mode $\nu_{14}$ that mixes strongly with the ring $\nu_{13}$ mode upon excitation to $S_2$ (Fig. 3).

Examination of $S_2$ modes provides another example of ground state modes that cannot be readily related to excited state's ones after all others have been paired is that of the $\nu_9''$ (vinyl) and $\nu_{11}''$ modes (*l*-type) of $S_0$. The former may be related with some difficulty to both 1590 and 1508 cm$^{-1}$ modes ($\nu_9$ and $\nu_{10}$ in $S_2$) and the latter with the much lower frequency $\nu_9$ mode of $S_2$ at 1373 cm$^{-1}$. However, the 1590 cm$^{-1}$ mode is much better correlated with the $\nu_{10}''$ mode, and

TABLE VII. A possible new assignment of the excitation spectrum of styrene in a supersonic jet.

| Expt. (cm$^{-1}$) (Ref. 42) | Assignment (Ref. 42) | New assignment |
|---|---|---|
| 59.5 | $41_0^1 42_1^0$ | $42_1^3$ |
| 193.2 | $41_0^2$ | $42_0^6$ |
| 237.2 | $29_0^1$ | $29_0^1$ |
| 282.4 | $41_0^1 42_0^1$ | $40_0^1 42_0^1$ |
| 349.1 | $40_0^1 41_0^1$ | $39_0^1 42_0^1$ or $40_0^1 42_0^3$ |
| 371.0 | $42_0^2$ | $41_0^2$ |
| 394.5 | $28_0^1$ | $28_0^1$ |
| 437.1 | $27_0^1$ | $41_0^2 42_0^2$ or $40_0^1 41_0^1$ |
| 505.5 | $40_0^2$ | $40_0^2$ |
| 517.5 | $29_0^1 28_0^1$ | $29_0^1 40_0^1 41_0^1$ |
| 523.2 | | $28_0^1 42_0^4$ |
| 528.2 | $26_0^1$ | $27_0^1$ |
| 537.3 | | $38_0^1 42_0^5$ |
| 548.7 | | $28_0^1 42_0^5$ |
| 563.6 | $41_0^2 42_0^2$ | $40_0^2 42_0^2$ |
| 630.0 | $29_0^1 28_0^1$ | $29_0^1 28_0^1$ |
| 678.7 | $28_0^1 40_0^1 41_0^1$ | $27_0^1 41_0^1 42_1^0$ |
| 745.8 | $25_0^1$ | $25_0^1$ |
| 862.2 | | $28_0^1 29_0^2$ |
| 940.4 | $22_0^1$ | $37_0^1 39_0^1$ |
| 947.8 | $24_0^1$ | $24_0^1$ |
| 959.1 | $23_0^1$ | $23_0^1$ |
| 965.4 | $20_0^1$ | $35_0^1 39_0^1$ |
| 972.4 | ? | $37_0^1 38_0^1$ |
| 980.7 | $19_0^1$ | $25_0^1 29_0^1$ |
| 983.0 | $21_0^1$ | $22_0^1$ |
| 987.3 | $25_0^1 29_0^1$ | $31_0^1 42_0^3$ |
| 1029.2 | $25_0^1 41_0^1 42_0^1$ | $21_0^1$ |
| 1095.8 | $25_0^1 40_0^1 41_0^1$ | $25_0^1 39_0^1 42_0^1$ |
| 1117.9 | | $25_0^1 41_0^2$ |
| 1138.6 | $25_0^1 28_0^1$ | $25_0^1 28_0^1$ |
| 1145.8 | $17_0^1$ | $20_0^1$ |
| 1153.0 | ? | $21_0^1 42_0^4$ |
| 1184.6 | ? | $19_0^1$ |
| 1195.7 | | $23_0^1 29_0^1$ |
| 1209.0 | $18_0^1$ | $18_0^1$ |

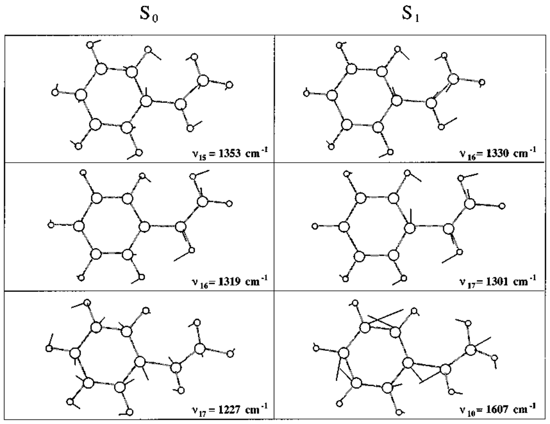

FIG. 8. The vector displacements calculated for the nominally $e$-type, vinyl stretch and $o$-type vibrational modes in $S_0$ ($\nu_{15}$, $\nu_{16}$, and $\nu_{17}$, respectively), and the corresponding modes in $S_1$ ($\nu_{16}$, $\nu_{17}$, and $\nu_{10}$, respectively). See the text for discussion.

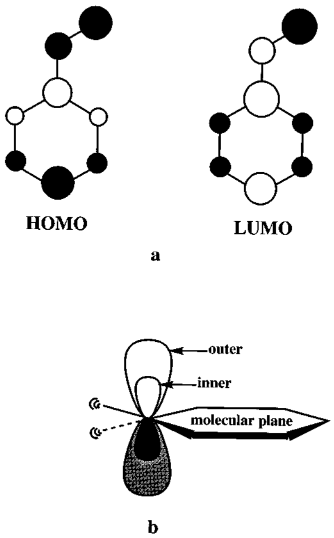

FIG. 9. (a) A schematic representation of the calculated $\pi$ electron distribution in the HOMO and LUMO molecular orbitals of styrene. (b) A schematic view of the inner and outer $p_z$ orbitals used in the 4-31G split valence basis set. Upon electronic excitation, the outer orbital contribution to the $\pi$ electron density increases significantly. The reduced electron density may lead to a smaller force constant for out-of-plane vibrations, shown schematically in the figure.

it may be concluded that these two high frequency modes of $S_0$ have no proper match in $S_2$.

### 1. In-plane vibrations

The correlation diagrams are a powerful qualitative tool to point out one to one correlations between ground and excited state modes, and mode mixing. In addition, they provide an opportunity to consider the few cases that do not fit with either description. As an example, consider the styrene 1607 cm$^{-1}$ mode in $S_1$ (in this section all numerical values refer to the *calculated* quantities). It could not be properly correlated with any $S_0$ mode; in other words, after all modes were correlated, it remained unmatched with any ground state normal mode. Inspection of its vector displacements shows that it is an essentially Kekulé ring carbon atom distortion mode (Fig. 8), combined with a vinyl C═C stretch. Its force constant and reduced mass are calculated to be very large by comparison to all other modes (see Table III). The $S_0$ mode that remains unpaired is the nominally $o$-type one at 1227 cm$^{-1}$, $\nu''_{17}$, also shown in the Fig. 8. It is clear from the drawing that, as discussed in Sec. III A 1, this mode involves a Kekulé-type distortion in which both C and H atoms participate. Figure 8 shows also the nominally $e$-type modes in the two electronic states: the $\nu''_{15}$ at 1353, involving primarily ring hydrogen atom breathing (together with some vinyl hydrogen motion) and the $\nu'_{16}$ one at 1330 cm$^{-1}$, which is calculated to have very nearly the same shape, reduced mass, and force constant. By comparison, Fig. 8 displays the nominally vinyl mode ($\nu''_{16}$ and $\nu'_{17}$ in $S_0$ and $S_1$, respectively), which is seen also to maintain its character on electronic excitation. Similar effects may be seen in the corresponding calculated BMS modes.

The exceptionally large force constant calculated for the $\nu'_{10}$ mode (12 mdyn/Å) arises in part from the change from a mixed H and C atom mode in $S_0$ ($\nu''_{17}$) to a mode involving almost exclusively carbon atoms motion. However, this appears to be only a partial explanation. As shown by a computation run on benzene,[46] this effect is even more pronounced for the $\nu_{14}(b_{2u})$ mode, which is known to undergo a significant frequency increase upon excitation to $S_1$;[43,44] this mode is a Kekulé-type one, which distorts the molecule to a Kekulé form. Inspection of the $S_0$ ($\nu''_{17}$) and $S_1$ ($\nu'_{10}$) modes (Fig. 8) shows that the ring carbons undergo this motion in styrene. It is proposed that the large increase in force constant is due to the fact that the $\pi$ electrons in aromatic molecules tend to distort the molecule to a Kekulé form;[45] further discussion of this point is deferred to a separate communication.[46]

The $S_0 \rightarrow S_2$ transition is different in nature and leads primarily to changes in the vinyl part of the molecule. The nature of two styrene modes, the vinyl C═C stretch ($\nu_9$) and the ring *1*-type CC stretch ($\nu_{11}$) undergoes a considerable change upon this transition (cf. Fig. 3). No single $S_2$ modes can be correlated with either of these $S_0$ ones, and the most suitable ones have much lower frequencies, force constants, and reduced masses. A similar change is calculated for the analogous modes of BMS, $\nu_{10}$ and $\nu_{12}$ (cf. Fig. 7). The almost equal frequency $k$-type mode ($\nu_{10}$ in styrene, $\nu_{11}$ in BMS) is essentially unchanged upon this excitation.

These trends are readily explained in terms of the calculated changes in electronic density: In fact, one can account for them by considering the HOMO–LUMO changes only. The reduction of the double-bond character of the C═C vinyl bond and of the C1—C2, C1—C6, and C4—C5 bonds, is directly reflected in the reduction of the force constants of the associated vibrational mode frequencies. The reduced masses of the normal modes decrease in the excited states, since now the modes are less localized, and involve smaller amplitude motions of more atoms. It is found that these changes are expressed primarily in only two high frequency modes, although, as mentioned above, a small degree of mode mixing is found for many more modes.

TABLE VIII. The calculated properties of the HOMO and LUMO orbitals of BMS.

| | HOMO | LUMO |
|---|---|---|
| Energy (hartree) | −0.2948 | 0.1219 |
| | Carbon atom $p_z$ orbital coefficients[a,b] | |
| Atom | | |
| 1 | −0.227 092 | 0.231 545 |
| | −0.234 159 | 0.387 554 |
| 2 | −0.158 198 | −0.171 334 |
| | −0.153 267 | −0.314 332 |
| 3 | 0.092 926 | −0.064 735 |
| | 0.089 963 | −0.125 086 |
| 4 | 0.233 615 | 0.234 359 |
| | 0.241 456 | 0.433 596 |
| 5 | 0.095 842 | −0.126 358 |
| | 0.095 875 | −0.248 058 |
| 6 | −0.156 680 | −0.127 028 |
| | −0.160 573 | −0.204 362 |
| 7 | 0.192 799 | 0.156 626 |
| | 0.201 411 | 0.283 715 |
| 8 | 0.238 703 | −0.233 516 |
| | 0.243 545 | −0.405 327 |
| 9 | −0.061 268 | 0.007 167 |
| | −0.042 213 | −0.027 817 |

[a] Carbon atom numbering as in Fig. 1.

[b] The first entry for each atom is the coefficient of the inner, and the second entry of the outer, basis set functions.

### 2. Out-of-plane modes

Another effect of the electronic excitation is the ''swelling'' of the $\pi$ electron charge distribution, which is schematically shown in Fig. 9. In split valence basis sets, such as 4-31G, two sizes of atomic orbitals are used to construct the molecular orbitals. In particular, the HOMO$-1$, HOMO, LUMO, and LUMO$+1$ molecular orbitals contain two $p_z$-type atomic orbitals. Table VIII lists the coefficients of the ''inner'' and ''outer'' $p_z$ orbitals in these molecular orbitals. It is seen that the contribution of the outer orbital increases significantly upon electronic excitation in all the carbon atoms: in the HOMO orbital the coefficients are essentially equal, while in the LUMO one the outer orbital is almost twice as big as that of the inner one. This is a manifestation of a ''dilution'' of charge density normal to the molecular plane that occurs on electronic excitation. Using the split valence basis set helps in clearly visualizing the ''outwards'' displacement of the $\pi$ electrons. This change affects mostly the out-of-plane vibrations, resulting in reduction of the force constants. The physical reason for this appears to be that the highly localized $\pi$ electron density near the molecular plane results in a larger restoring force for out-of-plane motion than the more dispersed electron cloud in the $\pi^*$ orbital.

The dilution effect results from the changes in the *relative* contribution of the inner and outer basis set functions in the HOMO and LUMO orbitals. In order to account for the observed changes in the vibrational frequencies (summarized in Tables III and VI and Figs. 3 and 9), one must also consider the absolute change in $\pi$ electron density in the different parts of the molecule.

The transition $S_0 \rightarrow S_1$ affects mostly the aromatic ring, and indeed large frequency reductions are found for ring-centered modes. It is found that this is often due to a reduction of the force constant, while the reduced mass is relatively unaffected. Examples are the $\nu_{40}$, $\nu_{39}$, and $\nu_{37}$ modes of styrene, for which the reduced masses that are 2.44, 2.30, and 1.40 amu in $S_0$ change to 2.73, 2.72, and 1.87 amu in $S_1$, while the force constants change from 0.35, 0.42, and 0.53 to 0.13, 0.20 and 0.22 mdyn/Å, respectively (Table III). In contrast, the largely vinyl modes $\nu_{38}$, $\nu_{33}$, and $\nu_{30}$ whose frequencies are calculated to be 626, 943, and 997 cm$^{-1}$ in $S_0$, change very little in $S_1$ (to 626,900 and 971), reflecting a small change in both reduced mass (1.88–1.42, 1.31–1.29, and 1.28–1.22 amu, respectively) and force constants (0.60–0.45, 0.95–0.85 and 1.03–0.94 mdyn/A). As Fig. 3 shows, many $a''$ modes in the 600–1000 cm$^{-1}$ range in $S_0$ undergo a 15%–25% frequency reduction in $S_1$; The change can be generally connected with the reduction in force constant, but one notices a rather extensive mode mixing as well.

A further prediction may be made concerning some vibrations of the second excited state; inspection of Fig. 9 shows that the largest $\pi$ electron density in both HOMO and LUMO orbitals is near the carbon atoms 1, 4, and 8 and the smallest, near ring atoms 2, 3, 5, and 6. Consequently, for $S_2$ vibrations, the dilution effect is expected to be effective mostly in cases where the out-of-plane deformations involve large amplitude motion of atoms C1 and C4 or the hydrogen atoms bonded to them, while modes involving motions near the side carbon atoms (C2, C3, C5, and C6) are expected to be affected to a lesser extent. One example for this effect involves the $\nu_{39}$ and $\nu_{40}$ pair of styrene. In $S_0$, the $w$-type mode ($\nu_{40}$) vibrational frequency (397 cm$^{-1}$) is lower than that of the $x$-type one ($\nu_{39}$, 435 cm$^{-1}$), while in the $S_2$ state, the frequency of the $x$-type mode is strongly reduced (to 283 cm$^{-1}$) due to the dilution effect, while that of the $w$-type one (calculated 380 cm$^{-1}$) is hardly affected, leading to order inversion. It is noted that while the $x$-type mode force constant is reduced by almost a factor of 4, from 0.42 mdyn/Å in $S_0$ to 0.12 mdyn/Å in $S_2$, that of the $w$-type one is hardly changed—0.35 in $S_0$ as compared to 0.32 in $S_2$. Inspection of the approximate mode diagrams[36] shows that in the $w$-type mode the C1 and C4 atoms are practically immobile, while in the $x$-type mode their amplitude is large. Excitation to $S_1$ changes the electron density in a different way—here all ring atoms are similarly affected. As a result, the frequencies of both $\nu_{39}$ and $\nu_{40}$ are reduced by roughly the same proportion.

A similar situation is found for the $\nu_{30}$, $\nu_{32}$ pair: in $S_0$, the $\nu_{32}$ mode is primarily an $h$-type one, involving mostly side carbon–hydrogen deformation. This motion dominates the $h$-type $\nu_{31}$ mode in $S_2$ leading to very similar force constants (1.10 vs. 1.02 mdyn/Å) and frequencies (980 and 951 cm$^{-1}$). The $\nu_{30}$ in $S_0$ is primarily a vinyl group CH deformation, as is the $\nu_{32}$ in $S_2$. Its frequency is reduced since the $\pi$ electron density is large near the C$\beta$ atom. The classification to pure ring versus vinyl modes is, of course, only approximate and in fact the $S_2$ modes can be correlated to a certain extent to both $S_0$ modes, but the essential physical effects seem to be accounted for by the qualitative description. This is due to the fact that even in cases of mode coupling, one often finds that the contribution of one of the $S_0$ modes to the properties of the $S_2$ one is dominant.

In BMS, the dilution effect is much smaller for out-of-plane vibrations that involve primarily a methyl group, and indeed, the $\nu_{35}$, $\nu_{36}$, and $\nu_{37}$ mode frequencies of BMS do not change much on electronic excitation.

### C. Correlation between styrene and BMS vibrational modes

The effect of replacing a $\beta$ vinyl hydrogen atom by a methyl group on the normal modes can be determined by inspection of the calculated normal modes' coordinates. Considering the ground state modes, one can clearly distinguish between three types of modes in BMS: those that are essentially unchanged, those that are almost totally located in the methyl group, and mixed modes, in which the methyl group motion is strongly coupled to the rest of the molecule.

The first group is readily recognized by the fact that the methyl atoms are almost stationary. It follows that the reduced mass ($\mu$) and the force constants ($k$) hardly change on the substitution. Attention is drawn in particular the $a'$ modes (corresponding styrene modes in parentheses) $\nu_{30}$ ($\nu_{26}$), $\nu_{23}$ ($\nu_{20}$), $\nu_{21}$ ($\nu_{19}$), $\nu_{22}$ ($\nu_{18}$) and the $a''$ modes $\nu_{47}$ ($\nu_{40}$), $\nu_{42}$ ($\nu_{35}$), $\nu_{41}$ ($\nu_{34}$), $\nu_{39}$ ($\nu_{32}$) and $\nu_{38}$ ($\nu_{31}$). The calculated reduced masses and force constants are changed in these cases by less than 1% on the substitution of a hydrogen atom by the methyl group. The pair of accidentally nearly degenerate modes $\nu_{18}$ and $\nu_{19}$ in styrene is interesting. The calculated frequencies are 1189 and 1185 cm$^{-1}$, respectively. The corresponding frequencies in BMS are 1189 and 1190 cm$^{-1}$ (modes $\nu_{22}$ and $\nu_{21}$). The reduced mass and force constant for the styrene $\nu_{18}$ mode are 1.15 amu and 1.21 mdyn/Å, respectively, and are unchanged in BMS. The mode is identified as a ring breathing mode with a large hydrogen atoms' in-plane motion. For the styrene $\nu_{19}$ mode, $\mu$=2.27 amu and $k$=2.34 mdyn/Å and the carbon atoms' amplitude is much larger. The changes upon methyl substitution are slightly larger than in the former case, $\mu$=2.12 amu and $k$=2.23 mdyn/Å in BMS. The analysis thus shows that the calculated degeneracy is due to a simultaneous similar increase of both $\mu$ and $k$, leading to an almost identical frequency for the two modes.

The almost pure methyl modes are the in-plane modes (in parentheses—frequencies in cm$^{-1}$) $\nu''_{14}$ (1471), $\nu''_{16}$ (1413), and $\nu''_{24}$ (1092) and the out-of-plane mode $\nu''_{36}$ (1400), in addition to the three CH stretch modes (see Table IV). The classification of the three 1400 cm$^{-1}$ methyl bending modes to $a'$ and $a''$ representations might appear at first sight as somewhat arbitrary, since the methyl group breaks the $C_s$ symmetry. However, inspection of the vector displacements of these modes shows that making these assignments is straightforward; For instance, the $\nu''_{14}$ and $\nu''_{16}$ modes, (calculated 1471 and 1413 cm$^{-1}$, respectively), show an almost exclusive methyl motion, in which the $\gamma$ carbon atom is strongly displaced in the *molecular plane* with respect to the methyl hydrogen atoms, while all other atoms are practically fixed at their equilibrium positions. In the case of the 1400 cm$^{-1}$ out-of-plane mode ($\nu''_{36}$), inspection shows that the $\gamma$ carbon moves perpendicular to the molecular plane, and that except for the methyl hydrogen atoms, all other atoms are immobile.

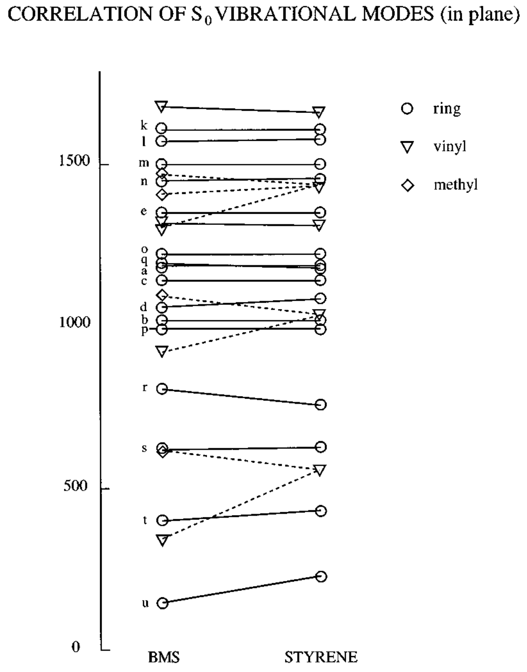

FIG. 10. The correlation between in-plane normal modes of styrene and BMS (excluding CH stretch modes). Primarily vinyl group modes are marked by a triangle, and primarily methyl group modes by diamonds. The dashed lines show styrene modes that correlate with two or more BMS modes, which often may be considered as a mixed vinyl–methyl modes (see the text). The letter designation shown uses Whiffen's notation (Ref. 36) for substituted benzenes.

The relation between BMS and styrene ground state in-plane modes is shown in the correlation diagram, Fig. 10. It is seen that several styrene modes related to the vinyl group can be considered as being split by the substitution into two levels, whose frequency shift with respect to the original vibration is of opposite sign. The lower level largely maintains the vinyl mode character, and the higher frequency one can be considered as a methyl group vibration. Thus, the 553 cm$^{-1}$ ($\nu''_{27}$) mode is split into the 340 and 619 cm$^{-1}$ ones; The 1037 cm$^{-1}$ mode into the 926 and 1092 cm$^{-1}$ ones, while the 1434 cm$^{-1}$ vinyl mode, is found to correlate with three BMS modes: the largely methyl ones at 1413 and 1471 cm$^{-1}$ and the vinyl one at 1309 cm$^{-1}$. Likewise, the out-of-plane modes (not shown in the diagram) 860 and 1081 cm$^{-1}$ of BMS are correlated with the 988 cm$^{-1}$ mode of styrene. We note that the $\nu_{16}$ mode of styrene (calculated 1303 cm$^{-1}$) is largely a $H_\alpha$–$H_c$ in-plane bend, maintains its character upon the substitution of the *trans*-H atom by a methyl group, and the nature of the mode hardly changes in BMS (mode $\nu_{18}$, calculated 1326 cm$^{-1}$).

We conclude this section by noting that in general, the calculation shows a strong correlation between styrene and BMS modes in all three electronic states. Trends found for the changes induced in the nature of vibrational modes of styrene upon electronic excitation are generally found also in BMS. This allows the use of known styrene band assignments to help in making BMS ones, and vice versa. As an example we refer again to the $o$-type vibration, which was found to be mixed with $e$-type one in $S_0$, but became a pure C ring breathing in $S_1$. This was accompanied by a large increase in the reduced mass, and more so in the force constant of the mode (Table III). This trend is repeated for BMS, and the change in the force constant is even more pronounced: in $S_1$ the frequency of this mode ($\nu'_{11}$, 1608 cm$^{-1}$) is calculated to be similar to that of high frequency modes in $S_0$, but the force constant is to 19.0 mdyn/Å! [By comparison, the force constant for the $\nu'_{10}$ mode (1638 cm$^{-1}$) is 9.8, and that of the $S_0$ $\nu''_{11}$ one (1686 cm$^{-1}$) is 9.8 mdyn/Å]. The very large force constant indicates a strong tightening of the CC breathing mode notion, and is a unique property of the first excited state. In $S_2$ the force constant for this motion is quite similar to that of $S_0$.

### D. In-plane–out-of-plane mode mixing

In some cases, $a'$ and $a''$ modes appear to be mixed. Thus, one finds considerable out-of-plane activity in the nominally $\nu''_{26}$ mode of BMS at 1020 cm$^{-1}$, the $\nu''_{28}$ mode at 926 cm$^{-1}$, the $\nu''_{32}$ mode (401 cm$^{-1}$), the $\nu''_{33}$ mode (340 cm$^{-1}$), and the $\nu''_{34}$ mode at 144 cm$^{-1}$. In styrene, the $\nu''_{28}$ mode (431 cm$^{-1}$) shows considerable out-of-plane activity, and the almost iso energetic $\nu''_{39}$ mode (433 cm$^{-1}$), is strong in plane motion. The $\nu''_{24}$ mode (992 cm$^{-1}$) has a large $a''$ contribution, primarily from out of plane vinyl bending. These mixings arise from the fact that the calculation did not reproduce the planar structure of the styrenes in the ground state, so that the symmetry is not strictly $C_s$. In view of the experimental evidence that the torsional potential is very flat in styrene, and that BMS may in fact be a nonplanar molecule, we believe that the in- and out-of-plane vibrations may be coupled in the real molecule, since the low frequency vibrations strongly distort the planarity of the molecule.

### E. A note on the intensity of some vibronic transitions in the $S_0 \leftrightarrow S_1$ spectrum

In this paper we have often used the notation introduced by Wilson[37] and Whiffen[36] to describe the approximate nature of styrene vibrational modes. Substitution of the benzene ring reduces the symmetry of the molecule, making the $S_0 \leftrightarrow S_1$ transition less forbidden. Since the double bond of the vinyl group can in principle interact with the ring $p$ electrons by conjugation, the perturbing effect might be expected to be larger in styrene than in substituted benzenes having no $p$ electrons in the substituting group. Indeed, the 0,0 transition of styrene is redshifted from that of benzene to a much larger extent than those of toluene or ethyl benzene, for instance. However, the $S_0 \leftrightarrow S_1$ transition in styrene is still a rather forbidden one, as its small oscillator strength indicates. In benzene, this transition involves an electron transfer from the degenerate $e_{1g}$ to the degenerate $e_{2u}$ molecular orbital; the degeneracy is lifted in styrene, but the fact that the $S_0 \rightarrow S_1$ is calculated to involve partial electron transfer from the two highest occupied MOs to the two lowest unoccupied ones is a reflection of the similarity to the benzene case. The vibronic intensity analysis of the styrene spectrum has been performed on a Franck–Condon basis in a previous work.[22,23] It is well known that in benzene the transition is made possible by a Herzberg–Teller coupling mechanism;[47,48] therefore, one may expect to find evidence for this coupling in some vibronic bands. We have not carried out an intensity analysis in this work and suffice in making a few qualitative comments. The $S_0 \rightarrow S_1$ transition in benzene is dominated by the $e_{2g}\nu_{6b}$ mode, whose frequency in $S_0$ is 608 cm$^{-1}$ and in $S_1$–522 cm$^{-1}$.[47] In styrene there is a group of bands between $\Delta E = 500$ and 560 cm$^{-1}$, some of which were assigned[42] to a multiplet arising from the $\nu_{26}$ mode (calculated 587 cm$^{-1}$, Table II; see Table VII for another possible assignment, also involving this mode). We found[39] that the intensity of some of these bands is very sensitive to complexation with rare gas atoms and small molecules in a supersonic jet expansion. The $\nu_{26}$ mode is a CC ring breathing mode, similar to the $\nu_{6b}$ mode of benzene, and this extreme sensitivity to van der Waals forces may reflect Herzberg–Teller activity.

It was stated that the $o$-type mode appears to undergo a significant frequency change upon electronic excitation. Such changes are usually reflected by a strong Franck–Condon activity in the absorption and emission spectra. The weak band observed in the styrene fluorescence spectrum at 1608 cm$^{-1}$ (Ref. 42) may indeed be due to this mode, but its weak intensity appears to be at variance with the expected strong activity. Comparison with benzene may help to resolve this apparent discrepancy: the corresponding mode in benzene is the $\nu_{14}$ one, which is symmetry forbidden for any one-photon transition, and indeed is not observed in the usual absorption spectrum of benzene. This mode is, however, clearly observed in the two-photon fluorescence excitation spectrum[43,44] and in fact is by far the strongest band. An unusually large frequency change is found for this mode, from 1309 cm$^{-1}$ in $S_0$ to 1566 cm$^{-1}$ in $S_1$; this large increase is similar to (though somewhat smaller than) the one calculated by us for the $o$-type mode of styrene. Our result is in line with a recent *ab initio* study on benzene,[13] in which a similar increase in the $\nu_{14}$ mode was calculated for $S_1$. Based on the similarity between styrene and benzene, it is predicted that the 1608 cm$^{-1}$ band will be prominent in the two-photon absorption spectrum of styrene.

## V. SUMMARY

The energies, geometries, and vibrational frequencies of the three lowest singlet states of styrene and $\beta$-methylstyrene were calculated using an *ab initio* method at the CIS-MP2/4-31G level of theory. The ground state appears to be slightly nonplanar, while the two excited states are strictly planar. Good agreement with experiment is obtained for the excitation energies as well as for the oscillator strengths of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions. The electric dipole moments of these transition are found to lie along the long axis in the molecular plane, also concurring with experiment.

The first excited singlet arises mostly from an in-ring excitation, the vinyl group being only mildly affected: the double bond maintains its length, while the C1—C$\alpha$ one is shortened a bit. In $S_2$, the C1—C$\alpha$ and C$\alpha$—C$\beta$ bonds are almost of the same length, and internal rotation around the bond becomes more hindered, as reflected by a large increase in the torsional frequency.

Most of the calculated vibrational frequencies are found to be in very good agreement with available information. It is therefore concluded that a calculation based on the CIS/4-31G approximation may serve as a good starting point for calculating the vibrational frequencies of styrene derivatives in $S_1$. The frequency of the torsional mode ($\nu_{42}$ in styrene, $\nu_{51}$ in BMS), is severely underestimated in the ground state for styrene. This may be related to the fact that the torsional potential in this state is extremely anharmonic, and is very flat for a large range of torsional angles. Interestingly, a fair agreement with experiment is obtained for BMS, for which a nonplanar structure is also calculated. The torsional mode is known to be anharmonic, and the harmonic approximation yields a value close to the experimental $v=0\rightarrow v=1$ transition frequency. The calculation does not reproduce the strong mode mixing effect between the two lowest lying modes ($\nu_{41}$ and $\nu_{42}$) claimed to take place in $S_1$.[16] A small effect is observed, which appears to become more pronounced in $S_2$. This discrepancy may be due to the limited basis set chosen, and a more extensive calculation (for instance including diffusion functions) may be necessary to reproduce the effect, that proved to lead to a satisfactory assignment of the styrene spectrum.

On the whole, the CIS method appears to be very useful for the vibrational analysis of the $S_0\rightarrow S_1$ fluorescence excitation and emission spectra of styrene, in agreement with a similar work on anthracene.[40] It thus appears that the Franck–Condon region of aromatic molecules may be mapped with reasonable accuracy using this relatively simple configuration interaction variant.

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[29] Following the prevailing convention (Refs. 16 and 28), the normal modes of styrene and BMS are described under the assumption that both molecules belong to the $C_s$ point group. This approximation is strictly correct for styrene in the $S_1$ state, and nearly true for styrene in $S_0$ and for BMS in both states, neglecting the fact that some methyl hydrogen atoms are out of the plane defined by the carbon skeleton. Consequently, the normal vibrational modes transform either as $a'$ (in-plane modes) or as $a''$ (out-of-plane ones). Ground state vibrational modes are designated by a double dash ($''$) and $S_1$ levels by a single dash ($'$). The notation used for the vibrational modes is therefore as follows: For styrene, the 29 in-plane vibrations are numbered 1–29, in decreasing order of the frequency, and the 13 out-of-plane modes are numbered 30–42. This convention holds for the ground ($S_0$) state order. The C1–C$\alpha$ torsional mode, having the lowest frequency in $S_0$, is thus the $\nu''_{42}$ mode. In BMS, the 34 in-plane vibrations are likewise numbered 1–34, and the 17 out-of-plane ones, are numbered 35–51, in decreasing order of the vibrational frequencies. The numbering sequence in each electronic state is according to the order found in the calculation (the only exception being the $\nu_{30}$ and $\nu_{31}$ order change, see the caption to Fig. 3); Since mode crossing and mixing takes place, the correlation diagrams (Figs. 3 and 7) should be consulted for the approximate nature of the excited state modes in terms of $S_0$ modes.

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