

# Ab Initio Study of the Low-Lying Electronic States of Indene<sup>†</sup>

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An ab initio calculation of the properties of the ground state and some low-lying electronic states of indene is reported. The results are compared with experimental data obtained by infrared and Raman spectroscopy, and with a recent fluorescence and resonance enhanced multiphoton ionization spectra obtained in a supersonic jet. The results show that the configuration interaction singles method can be used as a good approximation to calculate the molecular frequencies of the electronically excited states. It is found that as in other small aromatic molecules, the frequencies of out-of-plane modes tend to decrease, while those of in-plane ones are not changed significantly, except for a Kekulé type vibration, that shows a dramatic increase in the  $S_1$  state. In contrast with the  $S_1$  state, which is found to be bound, the  $S_2$  state is reactive. This is compatible with the diffuse absorption spectrum and the photochemical activity of this state. These results are compared with a similar recent study of styrene.

## I. Introduction

The properties of the electronic excited states of aromatic molecules can be deduced from absorption spectra and from studies of processes taking place after the molecule has been promoted to the excited state, such as fluorescence and resonance-enhanced multiphoton ionization (REMPI). In particular, the rotational and vibrational structures of the absorption bands are used to calculate the structure of the molecules in the excited states, the force constants controlling vibrational motions, and hence the nature of the bonding and pathways for chemical transformations. Details of the electronic transitions are often masked at elevated temperatures (including room temperature) due to spectral congestion arising from the thermal population of excited rovibrational levels in  $S_0$ . Cooling in a supersonic jet or in a low-temperature matrix largely removes this congestion and in recent years has allowed the accumulation of a large body of detailed and accurate information on the vibrational and rotational levels of many aromatic (and other polyatomic) molecules.

This situation calls for a parallel effort for developing theoretical methods on electronically excited states that will be compatible with the experimental accuracy. Highly refined force fields for ground state molecules are available, allowing the exact prediction of infrared and Raman spectra. Quantum chemical ab initio methods are now routinely used to analyze, assign, and even predict such spectra. Ground state generated force fields were used in the past to assign also the vibronic structure of electronic spectra, necessarily leading sometimes to erroneous results. Semiempirical quantum chemical methods (such as CNDO, CNDO/S, INDO/S, and PPP) are extensively used for this purpose. They are, however, inherently limited by the fact that the parametrization is usually optimized to reproduce a given property (excitation energy, geometry, charge distribution, etc.) and a single method cannot usually yield the correct result for other properties. Furthermore, semiempirical calculations require a complete new set of parameters for substituted molecules, and the systematic comparison between chemically similar molecules is not always easy.

Standard program packages for ab initio calculations are now easily commercially available, and relatively cheap workstations

have made them accessible to the general chemical community. Recently, several methods allowing the ab initio calculation of the properties of electronically excited states have been developed. Most of them are based on the molecular orbital (MO) method, and all of them involve configuration interaction (CI). One of the simplest, and easily applicable, adopts the concept of considering all singly excited configurations, while neglecting any higher (doubly, triply, etc.) excited ones. This so called configuration interaction singles (CIS) method, introduced by Pople and co-workers in 1992,<sup>1</sup> was incorporated into the Gaussian 92 Program Package.<sup>2</sup> Since *all* singly excited configurations are considered, one need not worry about which configurations should be included as is the case with other CI methods such as CASSCF. However, the neglect of doubly (and higher) excited configurations may be such a severe approximation as to render the method useless in some cases.

We have recently applied the CIS method to study the properties of the electronically excited states of some aromatic molecules, in particular the vibronic assignment of the  $S_0 \rightarrow S_1$  transition.<sup>3–5</sup> It was found that the method is useful for this purpose, as judged by comparison with experimental results. Practical considerations limited the size of the basis set that could be used in these calculations. The more diffuse electronic density distribution of the excited state as compared to the ground state calls for the introduction of diffuse functions, and the different charge distribution for the use of polarization functions. We found that an essential requirement is the use of split valence state basis functions, since the single valence ones do not allow the flexibility to properly reproduce the required changes in the electronic distribution. Rather modest sized basis sets were found to lead to satisfactory results 4-31G for benzene and its derivatives (such as styrene) and 3-21G for anthracene. These computations were run on a modest size workstation (Silicon Graphics Indigo 4000, 48 MB/2 GB HD).

The CIS method, as applied here, systematically overestimated the excitation energies by about 1 eV; in order to reproduce the correct order of the excited states in benzene, naphthalene, and their derivatives, second-order perturbation theory (MP2) had to be applied. These shortcomings of the method do not appear to affect the calculation of the vibrational frequencies. They are also overestimated, as usual in HF/SCF calculations,<sup>6</sup> but a single scaling factor for in-plane vibration

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(0.89), and another single one for out-of-plane ones (0.85), are sufficient to reproduce experimental data to about 3%.

In this paper, we further extend the method to compute the properties of electronically excited indene which was recently studied in our laboratory.<sup>8</sup> Like styrene, indene has a double conjugated to the aromatic ring, but in contrast with the latter, no torsional motion is possible in indene around the single CC bonds adjacent to the aromatic ring.

The similar electronic structure of indene to that of styrene appears to be the cause for the practically identity in the onset of the  $S_0 \rightarrow S_1$  transition of these two molecules (they differ only by about  $50\text{ cm}^{-1}$  at the origin<sup>9</sup>), as suggested long ago.<sup>10</sup> On the other hand, indene is much more rigid molecule than styrene, as the frequency of its lowest lying vibration is  $187.7\text{ cm}^{-1}$ ,<sup>11,12</sup> compared to  $38\text{ cm}^{-1}$  in styrene. Numerous studies of indene spectroscopy have been published,<sup>9,13,14,23</sup> but to our knowledge, no complete normal-mode analysis has been performed, either in the ground or in the first excited state. The structure of the molecule is known from a microwave study,<sup>15</sup> and its photoelectron spectrum was compared with semiempirical quantum chemical calculations.<sup>16</sup> The  $S_0 \rightarrow S_1$  absorption spectrum shows sharp vibronic bands, while the  $S_0 \rightarrow S_2$  spectrum is diffuse,<sup>17</sup> indicating some efficient nonradiative transition. Recently, the formation of hydrogen atoms from the unimolecular dissociation of indene upon irradiation at 193 nm was studied by Yi et al.<sup>18</sup> The calculation of the unimolecular rate constant by the Rice–Ramsberger–Kassel–Marcus theory requires a full set of vibrational frequencies; in the absence of a better choice, they were estimated from the known frequencies of the isoelectronic and structurally similar molecule indole.

Extensive studies on the solution and gas phase photochemistry upon irradiation at the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  of indene and some of its alkyl substituted derivatives have been reported by Morrison's group.<sup>19</sup> Two different mechanisms for the low-pressure gas phase translocation of a substituent group positioned initially on carbon C1 (e.g., methyl, or a deuterium atom) were observed: C1/C2 transposition (see Figure 1 for atom numbering) and a net 1,2 shift. Similar mechanisms were proposed for substitution at the other positions on the five-membered ring. In solution, or when a foreign gas was added, the second mechanism was effectively suppressed. Using a variety of experimental methods, including isotopic labeling and photosensitization, it was shown that the methyl group (or deuterium) migration reactions take place either on the  $S_2$  surface or from vibrationally excited  $S_1$  ( $S_1^{\text{vib}}$ ). A mechanism based on the initial formation of a biradical intermediate formed at the location of the vinyl double bond and transforming to other biradicals around the five-membered ring (see Scheme V in ref 19c)). The substituent group migrates around the ring as the biradical changes its location, the net result being effective scrambling of the substituent's position. These results were correlated with a bulk gas phase fluorescence studies on styrene and indene,<sup>20</sup> in which biexponential decay was observed from the molecules upon excitation to  $S_2$ . The longer component was assigned to a twisted  $\pi$ -bond singlet species formed from the initially populated Franck–Condon  $S_2$  state. In this work we set out to explore theoretically the properties of the singlet states of indene, in an attempt to rationalize these results.

We have recently reported an experimental and theoretical study of the  $S_0 \leftrightarrow S_1$  ( $X(^1A') \leftrightarrow A(^1A')$ ) transitions of styrene and *trans*- $\beta$ -methylstyrene (BMS).<sup>4,5</sup> The correlation between the vibrational frequencies in  $S_1$  and  $S_0$  has been established, and it was found that, in general, out-of-plane modes are lowered in energy upon this electronic excitation, while in-plane ones are not changed significantly. This was tentatively accounted for by the changes in the  $\pi$ -electron density incurred by the

excitation: the main change is a decrease in the  $\pi$ -electronic density above and below the aromatic ring. One in-plane vibration underwent a dramatic frequency *increase*—it is the Kekulé type distortive vibration akin to the  $\nu_{14}(\text{b}_{2u})$  of benzene that shows a similar change on the transition from the  $A_{1g}$  ground state to the  $S_1(\text{B}_{2u})$  state.<sup>21,24,25</sup>

The frequency exaltation turns out to be a natural result of the fact that the  $1^1A_{1g}$  and the  $S_1(\text{B}_{2u})$  state may be considered as covalent twin states arising from the in- and out-of-phase combinations of the two Kekulé structures of benzene. The valence bond method is the natural one for qualitatively discussing the frequency exaltation effect, which can be shown to arise from an avoided crossing of the two twin states along the  $\text{b}_{2u}$  vibrational coordinate that interchanges the two structures.<sup>26–28</sup> The same effect is found experimentally for naphthalene,<sup>25</sup> and more recently for anthracene,<sup>28,29</sup> and has been explained in a similar fashion. Quantitative estimates and comparisons with experimental data are much more easily made by molecular orbital based calculations, which have been extended to include naphthalene and anthracene.<sup>27</sup> Our work on styrene<sup>4</sup> showed that the  $S_1$  state of this molecule is very similar to the  $1^1\text{B}_{2u}$  state of benzene, and therefore it is reasonable to assume that the avoided crossing model can be extended to substituted molecules. This means that the two lowest singlet states may be regarded as covalent twin states also arising from in- and out-of-phase combinations of the Kekulé structures of these molecules.

It is interesting to compare the photophysics and photochemistry of indene and its clusters to those of styrene, and we have recently measured some properties of indene clusters in a supersonic jet.<sup>8</sup> We hereby report our calculations on indene in  $S_0$  and some low-lying electronically excited states; they are compared with available infrared and Raman spectra, as well as with the jet data obtained in our laboratory.

## II. Experimental and Computational Details

The jet apparatus was previously described in detail,<sup>7</sup> so only a brief reminder is given. Indene was seeded into helium, and the mixture expanded through a 0.35 mm nozzle into a vacuum chamber. Resonance-enhanced multiphoton ionization was performed by passing the jet through a 2 mm skimmer and irradiating the resulting molecular beam with a pulsed tunable dye laser. Ions were separated by a time-of-flight mass spectrometer and detected by a Daly-type detector.

Calculations were performed using the Gaussian 92 program package,<sup>2</sup> run on a Silicon Graphics Indigo R4000/48 MB/2 GB HD 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,<sup>1</sup> also using the 4-31G basis set.<sup>6</sup> In this procedure, all singly excited configurations are considered.

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 negative 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.<sup>22</sup> The same factors (0.89 for the in-plane, and 0.85 for the out-of-plane modes) were used for all electronic states.

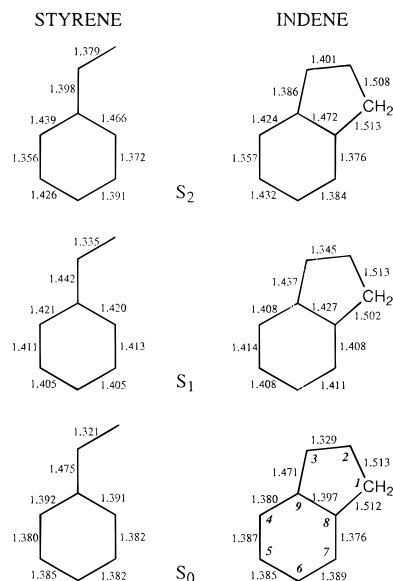
## III. Results

In the CIS approximation, the electronic structure of the  $S_1$  and  $S_2$  states of indene was found to be similar to that of

**TABLE 1: Calculated (CIS/4-31G) and Experimental Properties of Indene in  $S_0$ ,  $S_1$ , and  $S_2$** 

rotational const (MHz)	exp			calc		
	$S_0$	$S_1$	$S_2$	$S_0$	$S_1$	$S_2$
A	3775.0 <sup>a</sup>	3671.0 <sup>b</sup>		3842.6	3727.3	
B	1580.9	1568.5		1596.4	1582.2	
C	1122.2	1103.0		1135.7	1118.3	
dipole moment (D)	0.62 <sup>c</sup>			0.631	0.766	0.118
oscillator strength ( $S_0 \rightarrow S_1$ )		0.003 <sup>d</sup>	0.19 <sup>d</sup>		0.0138	0.265
ionization potential	8.143 <sup>e</sup>			8.08 <sup>f</sup>		

<sup>a</sup> Reference 15. <sup>b</sup> Reference 13. <sup>c</sup> Reference 12. <sup>d</sup> Evleth, E. M. *Theor. Chim. Acta* **1970**, 16, 22. <sup>e</sup> Reference 8. <sup>f</sup> Single-point calculation with a 6-31\*G+ basis set. With the 4-31G basis set the ionization potential is 7.96 eV.



**Figure 1.** Calculated structures of indene in the  $S_0$ ,  $S_1$  states at their respective energy minima and in the  $S_2$  state at the location for which the first derivative of the potential energy for all normal coordinates vanishes, and the second derivative is positive for all except one. The same geometry was obtained for the fully deuterated molecule, for which all second derivatives were positive. The calculated structures of styrene in the lowest three singlet states<sup>4</sup> are shown for comparison.

styrene.<sup>4</sup> The dominant contribution in the case of  $S_2$  comes from the configuration arising from the HOMO to LUMO excitation, whereas *two* singly excited configurations are the principal structures leading to the  $S_1$  state, those arising from a single electron excitation from the HOMO-1 orbital to the LUMO one and from the HOMO to the LUMO+1. In many benzene derivatives, singly excited configurations alone do not reproduce the correct excited states level order, while addition of doubly and triply excited configurations suffices to reconstruct it (see ref 4 and references therein). Application of second-order perturbation theory (MP2) to the CIS/4-31G calculation led to the correct level ordering, as indicated by the magnitude of the oscillator strengths for the  $S_0 \rightarrow S_1$  transitions. The MP2 correction does not significantly affect the vibrational calculations (normal-mode shapes, force constants, and frequencies) and we therefore used the potential surfaces computed by the CIS method to compute the vibrational frequencies in  $S_1$  and  $S_2$ .

Table 1 lists some of the calculated properties of the three lowest lying singlet states of indene. As in the case of styrene, the  $S_0 \rightarrow S_1$  transition affects mainly the aromatic ring: Figure 1 shows that the ring expands rather uniformly, all CC bond lengths being about 1.41 Å, except the C8C9 bond which in  $S_1$  is a bit longer (1.427 Å). In the side ring, all bonds largely

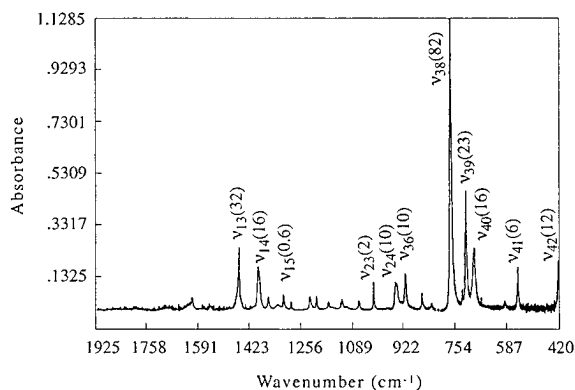
**TABLE 2: Vibrational Frequencies of Indene in  $S_0$** 

mode	exp <sup>a</sup>	exp <sup>b</sup>	calc <sup>c</sup>	approx descriptn <sup>d</sup>
in-plane modes				
$\nu_1$			3036	vinyl $\nu_{CH}$
$\nu_2$			3009	vinyl $\nu_{CH}$
$\nu_3$			3002	aromatic $\nu_{CH}$
$\nu_4$			2988	aromatic $\nu_{CH}$
$\nu_5$			2976	aromatic $\nu_{CH}$
$\nu_6$			2969	aromatic $\nu_{CH}$
$\nu_7$			2832	$\nu_{CH_2}$
$\nu_8$	1610	1609	1620	ring $\nu_{CC}$
$\nu_9$			1601	ring $\nu_{CC}$
$\nu_{10}$	1550		1571	ring $\nu_{CC}$
$\nu_{11}$			1464	ring $\nu_{CC} + \beta_{CH}$
$\nu_{12}$	1457	1457	1460	ring $\nu_{CC} + \beta_{CH}$
$\nu_{13}$	1394	1394	1433	CH <sub>2</sub> scissors
$\nu_{14}$	1362	1362	1349	vinyl $\beta_{CH}$
$\nu_{15}$	1312	1312	1309	aryl $\beta_{CH}$
$\nu_{16}$			1253	Kekulé
$\nu_{17}$	1226	1226	1227	aryl $\beta_{CH}$
$\nu_{18}$	1206	1206	1180	aryl $\beta_{CH}$
$\nu_{19}$	1160	1160	1161	aryl $\alpha_{CC}$
$\nu_{20}$			1146	Kekulé
$\nu_{21}$	1127	1123	1115	ring $\beta_{CH}$
$\nu_{22}$	1068	1068	1072	ring $\beta_{CH}$
$\nu_{23}$	1019	1019	1006	aryl $\alpha_{CC}$
$\nu_{24}$			946	$\nu_{C1C2}$
$\nu_{25}$	861		850	$\beta_{CC}$
$\nu_{26}$	830	830	821	$\beta_{CC}$
$\nu_{27}$	730		723	$\beta_{CC}$
$\nu_{28}$			724	$\beta_{CC}$
$\nu_{29}$			596	ring deform
$\nu_{30}$			528	ring deform
			377	ring deform
out-of-plane modes				
$\nu_{31}$			2730	$\nu_{CH_2}$
$\nu_{32}$			1098	$\beta_{CH_2}$
$\nu_{33}$			999	aryl $\gamma_{CH}$
$\nu_{34}$			968	vinyl $\gamma_{CH}$
$\nu_{35}$		942	945	aryl $\gamma_{CH}$
$\nu_{36}$		915	922	aryl $\gamma_{CH}$
$\nu_{37}$		861	862	aryl $\gamma_{CH}$
$\nu_{38}$		766	768	aryl $\gamma_{CH}$
$\nu_{39}$		718	715	aryl $\gamma_{CH}$
$\nu_{40}$		690	690	vinyl $\gamma_{CH}$
$\nu_{41}$		550	539	ring pucker
$\nu_{42}$	415 <sup>e</sup>	419	417	ring deform
$\nu_{43}$	388 <sup>e</sup>		380	ring deform
$\nu_{44}$	206 <sup>e</sup>		201	butterfly + torsion
$\nu_{45}$	188 <sup>e</sup>		186	skeletal bend

<sup>a</sup> From ref 23. The frequencies were obtained from Figure 2 of the paper, an error of  $\pm 5$  cm<sup>-1</sup> is estimated. <sup>b</sup> Infrared spectrum taken in a KBr pellet, this work. <sup>c</sup> In-plane frequencies scaled by 0.89, out-of-plane frequencies by 0.85. <sup>d</sup>  $\nu$ , stretch;  $\alpha$ , in-plane ring angle bend;  $\beta$ , in-plane bend;  $\gamma$ , out-of-plane bend. <sup>e</sup> Reference 11.

maintain their character, the C2C3 bond remaining a double bond, while the C3C9 one shortens from 1.471 to 1.437 Å. In the  $S_2$  state, no stable minimum is found for the protonated molecule and a very shallow one is found for the fully deuterated one. The structure shown in Figure 1 is the one calculated for the minimax conditions; for details, see the caption of the figure. The implications of these results are further dealt with in the discussion section.

The calculated vibrational frequencies of the electronic ground state of indene are listed in Table 2, along with available experimental information. The agreement between the calculated and experimental results is reasonably good. Figure 2 shows a part of the IR spectrum, along with selected assignments and the calculated intensities; it is evident that the IR transition intensities are reasonably well reproduced by the calculation. Experimental information for the  $S_1$  levels is less extensive, since the  $S_0 \rightarrow S_1$  transition is in-plane polarized and transitions from the totally symmetric vibronic ground state are of  $a'$



**Figure 2.** Part of the IR spectrum of indene, with assignment based on the calculation. The calculated IR intensities (in km/mol) are shown in parentheses.

symmetry and can only lead to  $a'$  vibronic levels of  $S_1$ . Therefore, only in-plane modes or even combinations of out-of-plane ones can be observed in the absorption spectrum. Table 3 lists the calculated vibrational frequencies in  $S_1$ , along with available experimental data. Harmonic frequencies were calculated for several isotopomers; these data may be obtained from the authors on request and will be used in subsequent work when the experimental values will become available.

#### IV. Discussion

The electronic structure of indene is found to be very similar to that of styrene, in both experiment and calculations. However, some photophysical and photochemical features of these molecules are expected to be different. The absence of a very low frequency vibration in  $S_0$  and  $S_1$  results in the observation of less congested absorption and emission spectra. The second excited state of indene is calculated to be unbound, in contrast with the corresponding state of styrene, which is calculated to be bound (and found experimentally to be predissociative). This result concurs with the diffuse nature of the absorption spectrum and the absence of emission from the  $S_2$  state at low pressure. The possible relation to the gas phase photochemistry is discussed below.

**IVa. Vibrational Modes.  $S_0$  Modes.** The similarity between indene and styrene extends also to the vibrational structure, and many of the vibrational modes of the two molecules can be correlated. It is found that the low-frequency modes of indene, both in- and out-of-plane, are somewhat higher in energy than the corresponding styrene modes. The higher frequency modes, CH bending as well as CC ring and vinyl bending and stretching, have essentially the same frequency. Figure 3 shows a correlation diagram relating the out-of-plane modes of the two molecules. The  $\text{CH}_2$  wag mode, calculated frequency  $1098\text{ cm}^{-1}$  ( $\nu_{32}$ ), has no analog in styrene, but of the others,  $\nu_{33}$  through  $\nu_{39}$  have very similar shapes and frequencies as their styrene counterpart. The two mainly vinyl modes  $\nu_{40}$  and  $\nu_{43}$  ( $\omega_{\text{calc}}$  690 and  $380\text{ cm}^{-1}$ , respectively) along with the  $\nu_{41}$  mode correlate with the two styrene modes  $\nu_{38}$  and  $\nu_{39}$  (at 626 and  $435\text{ cm}^{-1}$ ); the average frequency of these two groups remains the same at about  $530\text{ cm}^{-1}$ . The lowest bending mode,  $\nu_{45}$ , is virtually unchanged from the  $\nu_{41}$  mode of styrene: the frequencies are very similar (calculated 186 vs 188, experimental 189 vs  $199\text{ cm}^{-1}$ ). According to Caminati,<sup>12</sup> the  $189\text{ cm}^{-1}$  mode is due to the 1,3 twisting motion, analogous to the torsion in styrene, and the stronger IR band at  $206\text{ cm}^{-1}$  to the butterfly mode. The calculation reproduces the experimental IR intensity ratio (4:1) but shows that the lower frequency mode involves a skeletal bending in which most of the carbon atoms participate (see Figure 7 in the next subsection). The higher frequency one may have some features of a nonsymmetric butterfly mode

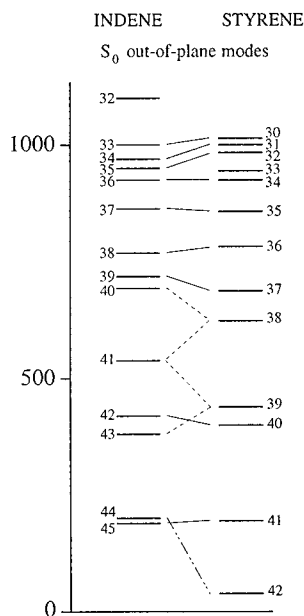
**TABLE 3: Vibrational Frequencies of Indene in  $S_1$**

mode <sup>a</sup>	exp		calcd <sup>b</sup>
	ref 9	ref 8	
in-plane modes			
$\nu_1$			3038
$\nu_2$			3022
$\nu_3$			3012
$\nu_4$			3011
$\nu_5$			3000
$\nu_6$			2990
$\nu_7$	2814		2791
$\nu_{16}$			1623
$\nu_8$			1586
$\nu_9$	1534		1521
$\nu_{10}$			1500
$\nu_{13}$	1432		1438
$\nu_{12}$			1419
$\nu_{11}$	1370		1398
$\nu_{14}$	1343		1347
$\nu_{15}$			1289
$\nu_{17}$			1220
$\nu_{19}$			1190
$\nu_{20}$			1161
$\nu_{18}$			1147
$\nu_{21}$			1098
$\nu_{22}$	1066	1066	1041
$\nu_{23}$			955
$\nu_{24}$		946	902
$\nu_{25}$	842	843	847
$\nu_{26}$		805	811
$\nu_{27}$	674	674	690
$\nu_{28}$	545	545	560
$\nu_{29}$	479	479	485
$\nu_{30}$	354	359	365
out-of-plane modes			
$\nu_{31}$			2674
$\nu_{32}$			1065
$\nu_{34}$			934
$\nu_{36}$			892
$\nu_{33}$			840
$\nu_{35}$			750
$\nu_{40}$			694
$\nu_{37}$			658
$\nu_{38}$			602
$\nu_{39}$			547
$\nu_{41}$			385
$\nu_{43}$			325
$\nu_{42}$		264	288
$\nu_{44}$			148
$\nu_{45}$		133	135

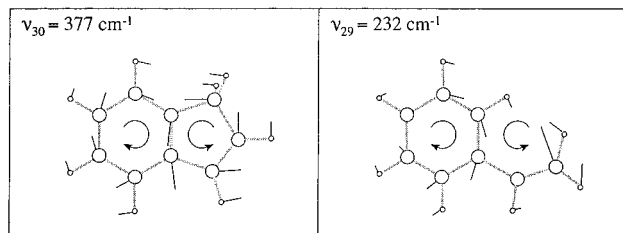
<sup>a</sup> Assignments are according to the  $S_0$  notation; see Figure 6 for correlation between  $S_0$  and  $S_1$ . <sup>b</sup> In-plane frequencies scaled by 0.89, out-of-plane frequencies by 0.85.

but is better described as a frustrated torsional mode of styrene, and inspection shows that the two correlated with each other (see the atomic displacements in Figure 7 and in Figure 5 of ref 4).

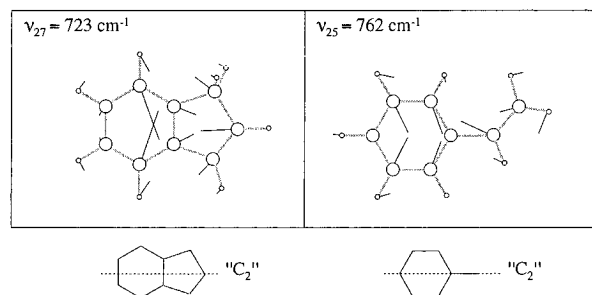
The stiffening of the "soft" low-frequency vibrations induced by the ring closure in indene as compared to styrene is also found in the in-plane modes: the lowest frequency ones are calculated at  $377$  and  $528\text{ cm}^{-1}$  for indene, as compared to  $232$  and  $431\text{ cm}^{-1}$  for styrene (experimental values are similar). Figure 4 shows the form of the two lowest lying in-plane modes of the two molecules: a remarkable similarity is evident. The main cause for the lower frequency is the reduced force constant in styrene ( $0.12\text{ mdyn/\AA}$ ) as compared to indene ( $0.38\text{ mdyn/\AA}$ ); the reduced masses are 3.1 and 3.6 amu, respectively. A one to one correlation for in-plane vibrations is not feasible for modes involving atomic motions in both rings, since the approximate symmetry of the molecules is different: a  $C_2$  axis in indene bisects the aromatic ring in the middle of the C5C6 and C8C9 bonds, while the analogous axis in styrene passes through the ring atoms C1 and C4. The in-plane modes of the



**Figure 3.** A correlation diagram connecting the out-of-plane modes of indene and styrene. Note the higher frequency of the lowest lying mode of indene.



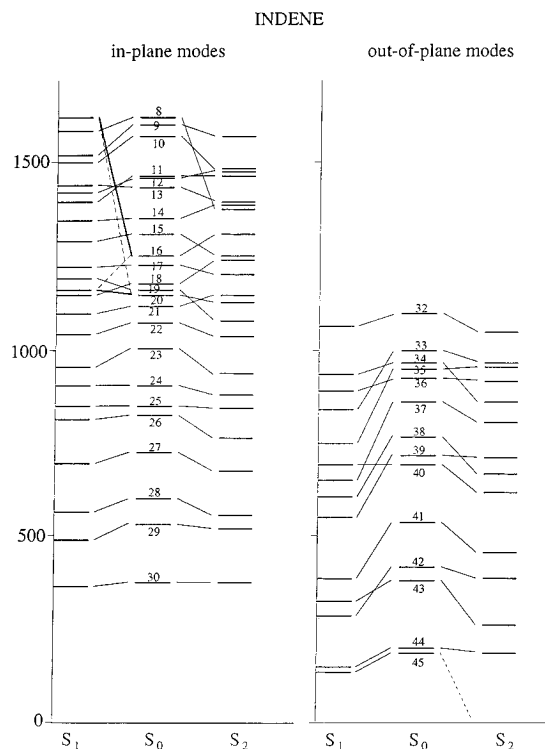
**Figure 4.** Form of the two lowest in-plane vibrational modes of indene ( $\nu_{30}$ , left) and of styrene ( $\nu_{29}$ , right) showing the similarity in the atomic displacements. The curved arrows, indicating the overall sense of the carbon atoms, are shown as a guidance to the eye.



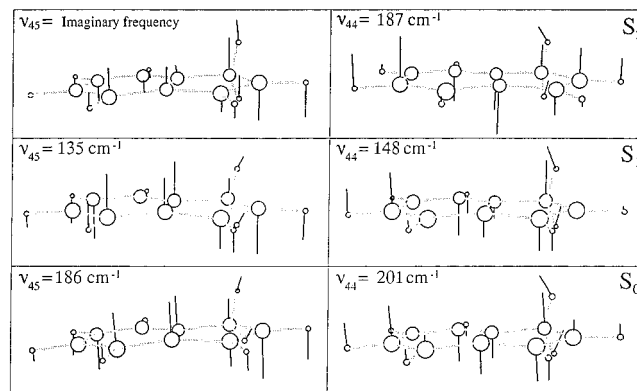
**Figure 5.** Atomic displacements of in-plane vibrational mode  $\nu_{27}$  of indene (left) and  $\nu_{25}$  of styrene (right) showing the symmetry with respect to the approximate  $C_2$  symmetry axis, which passes between atoms in indene and through atoms in styrene.

molecule tend to be symmetric with respect to these respective axes, as shown for two similar modes in Figure 5. Predominantly aromatic-ring modes, however, are well correlated; for instance, the Kekulé-type modes  $\nu_{16}$  and  $\nu_{20}$  of indene are calculated to have essentially the same frequencies in the corresponding modes in styrene ( $\nu_{17}$  and  $\nu_{20}$ ).

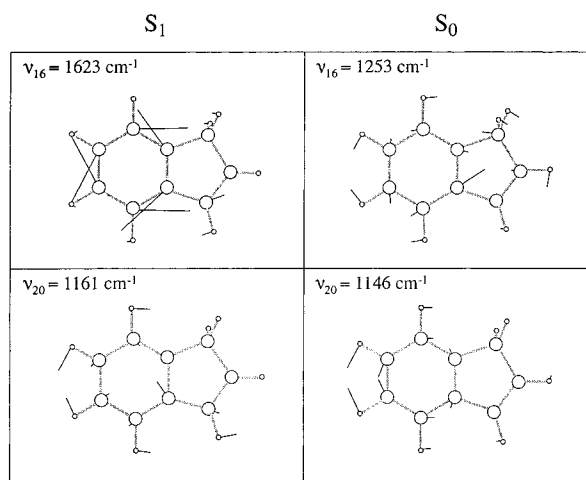
**Excited States.** Figure 6 shows the correlation between the modes of the ground state and those of the first two excited singlet states. The calculation shows that the lowest frequency mode,  $\nu_{45}$ , transforms to an unbound motion in  $S_2$  in the fully protonated molecule. The fully deuterated one is found to have a very shallow minimum, and the frequency of the  $\nu_{45}$  is calculated to be only  $9\text{ cm}^{-1}$ . The form of this vibration in  $S_0$ ,  $S_1$ , and  $S_2$  is shown in Figure 7, together with that of the other low-energy mode,  $\nu_{44}$ .



**Figure 6.** Correlation diagram between the vibrational modes of indene in the  $S_0$ ,  $S_1$ , and  $S_2$  states. The  $\nu_{45}$  mode of  $S_0$  has no counterpart in  $S_2$  and leads to an unbound motion.

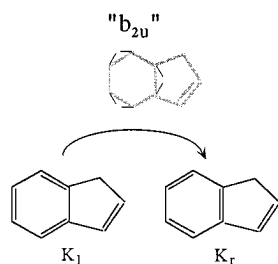


**Figure 7.** Form of the two lowest frequency modes of indene in the three first singlet states. In  $S_2$ , mode  $\nu_{45}$  transforms to an unbound motion for the fully protonated molecule.



**Figure 8.** Kekulé-type modes of indene in  $S_0$  and  $S_1$ .

Figure 8 shows the Kekulé-type vibrations of indene in  $S_0$  and in  $S_1$ . A large frequency increase is calculated for the  $\nu_{16}$

**SCHEME 1: Two Kekulé Structures of Indene and the Vibrational Mode that Interchanges Them**


mode, which in  $S_1$  involves almost pure carbon atom motions. This result is very similar to that obtained for styrene and BMS.<sup>4</sup> The frequency up-shift observed for the analogous modes in the  $1^1B_{2u}$  state of benzene,<sup>24</sup> naphthalene,<sup>25</sup> and anthracene<sup>26,29</sup> is also observed in indene. This implies that as in the case of styrene, the avoided crossing model involving the two Kekulé structures of unsubstituted acenes (benzene, naphthalene, and anthracene)<sup>28</sup> applies also to indene. The fact that the frequency exaltation is found also for the low-symmetry molecules styrene and indene indicates that the *local symmetry* of the aromatic ring is important in determining the properties of the Kekulé twin states derived from the  $1^1A_{1g}$  and  $1^1B_{2u}$  of benzene. Scheme 1 shows the two Kekulé structures of indene and the form of the motion that interchanges them. Comparison with Figure 8 that this motion is essentially a Kekulé-type mode.

**Vlb. Photochemical Implications.** The  $S_2$  state can collisionally couple to  $S_1$ , as shown by the fact that in liquid solution and in the presence of a foreign gas, fluorescence from  $S_1$  is observed following  $S_2$  excitation. However, at low pressures, hydrogen (or methyl, for methyl-substituted indene) scrambling is found, which was assigned<sup>19</sup> to 1,2 shifts within diradical-like intermediates. The reaction was shown to proceed on the  $S_2$  or a vibrationally excited  $S_1$  surface.

The first alternative is compatible with our computations; the  $\nu_{45}$  mode, whose frequency is drastically reduced in  $S_2$ , involves a strong twisting motion atomic displacements of the C1, C2, and C3 out of the molecular plane. This makes the formation of a C2C3 biradical possible, a species that can proceed to isomerize to the C1C3 biradical and then to the C1C2 one, which in turn will stabilize to the final product in which the hydrogen atoms have shifted (cf. Scheme II in ref 19c). The biradical mechanism is expected to lead to complete scrambling of the hydrogen atoms in the side ring, as indeed found experimentally for the reaction when conducted at low pressure.<sup>19b</sup> This result is also compatible with the experimentally observed diffuseness of the  $S_0 \rightarrow S_2$  absorption spectrum<sup>17</sup> and the absence of fluorescence from  $S_2$  in the gas phase. Thus, the  $\nu_{45}$  mode is suggested as a major component of the reaction coordinate. However, internal conversion to a highly excited vibrational level of either  $S_0$  or  $S_1$ , followed by reaction on one of these energy surfaces, which has not been studied in this work, is a possibility that cannot be excluded at the present time.

**V. Conclusions**

The CIS method has been criticized for relatively large errors in the calculated excitation energies. However, its performance for excited state geometries and vibrational frequencies has been checked recently and compared (for smaller molecules than indene) with higher level methods.<sup>30–32</sup> The results appear to be sufficiently encouraging to warrant its application for large molecules, where more sophisticated methods are not feasible. As seen from this paper, the CIS-MP2/4-31G level of theory appears to account well for available experimental information on indene, providing insight to the photophysics of the system.

It is found that a close, almost quantitative correlation with the properties of styrene can be worked out. The increased rigidness of the molecule is expressed by the increase in the low-lying vibrational frequencies, whereas for modes with a frequency exceeding  $\sim 600\text{ cm}^{-1}$  the calculated frequencies are essentially the same as those of styrene. The frequency exaltation of the Kekulé-type mode in the  $S_1$  state is found also in this molecule, as expected if this state is the covalent twin-state of the ground state.<sup>21,27,28</sup> A possible explanation for the gas phase photolysis hydrogen shift reaction taking place upon excitation of the  $S_2$  state<sup>19</sup> is offered.

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