

# Electronic Absorption Spectroscopy of Jet-Cooled Molecules

VERONICA VAIDA<sup>†</sup>

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

Received October 14, 1985 (Revised Manuscript Received February 21, 1986)

The interactions of light with matter provide our best probes into the structure and dynamics of molecules. Energy- and time-resolved spectroscopic techniques of increasing sophistication are being developed and applied to the characterization of various aspects of potential energy surfaces of polyatomic molecules. It is now possible to imagine obtaining an experimental and theoretical description for both the structure and reactivity of a molecular system, especially for light-induced processes such as unimolecular decomposition and isomerization.

This Account will focus on an experimental technique, namely "direct absorption of jet-cooled molecules"<sup>1-12</sup> which probes excited electronic states of polyatomic molecules. The unique possibilities of this method for the study of reactive potential energy surfaces will be discussed along with its use in obtaining a quantitative understanding of potential energy surfaces and reaction dynamics occurring on these surfaces.

One of the most important recent advances in optical spectroscopy has been the development of nozzle beam sources which allow preparation of spectroscopic samples consisting of isolated molecules at low temperature.<sup>13</sup> In the course of a supersonic expansion of a polyatomic molecule in an inert carrier gas through a nozzle, the polyatomic molecule cools its rotational and translational degrees of freedom by transfer of energy in two-body collisions with the carrier gas which itself reaches extremely low translational temperatures. Vibrational cooling can also be extensive, especially in molecules which possess low-frequency vibrational modes. As the expansion proceeds, the temperature and density of the gas decreases producing an ideal spectroscopic sample which consists of ensembles of molecules in defined quantum states and at sufficiently low density to eliminate spectroscopic effects due to intermolecular interactions. This procedure for preparing cold and isolated molecules results in the production of low sample densities and therefore spectroscopic studies of such samples have relied on indirect, extremely sensitive methods for detection of the absorption. Notably, laser-induced fluorescence (LIF)<sup>13</sup> and multiphoton ionization (MPI),<sup>14,15</sup> have been used in a variety of spectroscopic problems. The advantages of such indirect spectroscopic methods for studying jet-cooled samples have been illustrated and reviewed in the recent literature.<sup>13-15</sup>

The class of molecules of concern to us are those displaying an efficient reactive channel on an excited

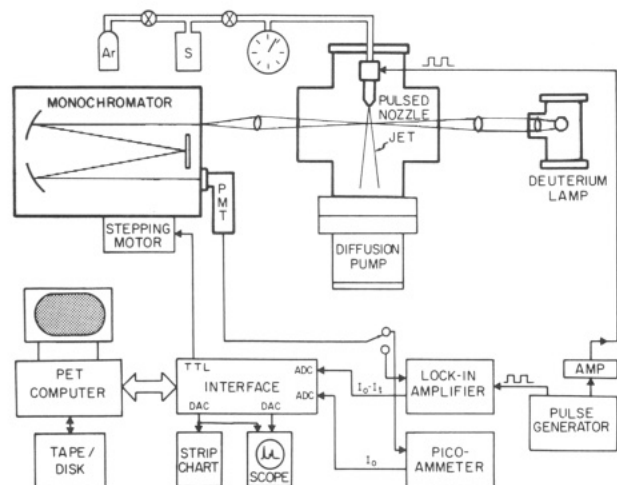
electronic surface. While chemically interesting, such reactive states have "unpleasant" spectroscopic consequences. The efficient reactive channel shortens the excited-state lifetime and gives rise to diffuse spectra with little or no rotational structure. Here, chemistry competes efficiently both with the emission and also with the up-pumping necessary for MPI so that these otherwise sensitive detection techniques are either not useful due to lack of signal or, at best, the results obtained are extremely difficult to interpret. These considerations have led us to the development of a direct absorption technique<sup>1</sup> for studying reactive excited states of samples prepared in supersonic expansions.<sup>16</sup> The examples to be discussed attempt to illustrate the power of a technique based on direct absorption of supersonically cooled molecules for studying reactive electronic states where the standard battery of indirect emission and ionization methods have not been successful.

The technique used in these absorption experiments has been described in the literature.<sup>4,6,10,11</sup> In our experiment (see Figure 1), the polyatomic sample is diluted in argon and expanded through a pulsed supersonic nozzle into a vacuum chamber, where it is crossed with continuum ultraviolet radiation produced by continuous<sup>1-10</sup> or pulsed<sup>11,12</sup> lamps. The light transmitted through the molecular jet is dispersed by a monochromator, then detected by a photomultiplier tube and a lock-in amplifier operated at the pulsed nozzle frequency. A microcomputer system is employed to perform signal averaging and normalize spectra with respect to incident light intensity. The ratio of transmitted light to incident light is proportional to absor-

<sup>†</sup> Camille and Henry Dreyfus Teacher-Scholar.

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Veronica Vaida was born in Transylvania in 1950. She carried out undergraduate studies at the University of Bucharest and Brown University. Following graduate work at Yale University, she went to Harvard as a Xerox postdoctoral fellow in 1978 and spent 6 years as an Assistant and Associate Professor of Chemistry. Dr. Vaida has been a Sloan Fellow and a Dreyfus Teacher-Scholar, and her research interests include spectroscopic studies of the reactive excited electronic states of small molecules, polyenes, and transition-metal cluster complexes.



**Figure 1.** Block diagram of the direct UV absorption supersonic jet apparatus. Abbreviations used: S = sample, PMT = photomultiplier tube, DAC = digital-to-analog converter, ADC = analog-to-digital converter, TTL = TTL output (0 V/5 V), AMP = amplifier. Reproduced with permission from ref 4. Copyright 1984 American Institute of Physics.

bance at the low light levels used.

Molecular jets are produced using argon rather than helium as the carrier gas in view of argon's superior efficiency in cooling the internal rotational and vibrational degrees of freedom of large molecules.<sup>17</sup> Sample vibrational temperatures, estimated from comparison of hot band intensities in room temperature and in jet-cooled spectra,<sup>18</sup> are typically 30–60 K. The terminal rotational temperatures of the jet-cooled samples are expected to be close to their terminal translational temperatures which are estimated to be below 10 K.

Under the conditions of the experiment, we estimate for a molecule like styrene a sample number density of about  $5 \times 10^{14}$  molecules/cm<sup>3</sup> at the focused light spot 1 cm from the nozzle, equivalent to a room temperature sample pressure of approximately 0.01 torr. With an estimated 1-cm pathlength and a typical peak extinction coefficient of  $1.5 \times 10^4$  L mol<sup>-1</sup> for these samples in the wavelength region monitored, maximum absorbances of about 0.01 are observed. The performance of this experiment is improved with extension of the pathlength by the use of planar jets.<sup>11,12</sup> Direct absorption is intrinsically less sensitive than indirect fluorescence excitation or MPI methods. In our laboratory, bands with a molar extinction coefficient  $\epsilon \geq 200$ , have been investigated.

The technique of direct ultraviolet absorption of jet-cooled samples has several features advantageous for the study of reactive excited states of polyatomic molecules. This experiment can be used to obtain spectroscopic information about photochemically active, nonemitting states, as well as higher excited states. In the version of the experiment described herein, a lamp is employed as a light source allowing this experiment to be performed over a wide energy range from the infrared<sup>19</sup> to the vacuum ultraviolet.<sup>20</sup> The use of a

low-intensity light source also allows easy and accurate normalization of spectra with respect to incident light intensity. In addition, these low-intensity light sources insure accurate relative intensities for all spectral features and eliminate saturation and other artifacts inherent with high-intensity laser sources. Indirect spectroscopic techniques (LIF, MPI, etc.) do, by and large, rely on intense laser sources and as a consequence spectra are plagued by nonlinear effects, saturation effects, difficulties associated with limited scanning range and normalization.

As with all spectroscopic techniques employing jet-cooled samples,<sup>13</sup> one obtains spectra that are free of thermal congestion, thus simplifying spectral analysis. It is particularly important for the reactive states we are studying that the measured vibrational line width is homogeneously broadened.

In photoactive molecules, characterization of the upper state relies on extracting a picture of the upper state by comparison with the ground state of the molecule by Franck–Condon analysis of the intensity profiles. It is therefore crucial to obtain extremely accurate Franck–Condon factors (i.e. relative areas under vibronic bands). We have discussed from a technical point of view, the way in which one can obtain accurate relative spectral bands intensities in absorption when employing a low-intensity lamp.<sup>1–12</sup> It is also important to cool the sample sufficiently so that all inhomogeneous contributions are excluded and homogeneous line widths can be measured.

An important effect observed in reactive excited states is the increase in homogeneous vibrational bandwidth with vibrational level. Clearly, the evaluation of theoretical methods by comparison of predicted to experimental spectra benefits from an optimum choice of line shapes to convolve with calculated Franck–Condon factors in the synthesis of model spectra. In the past, theorists have overwhelmingly chosen to model vibronic excitations in polyenes as Lorentzians and/or Gaussians whose line widths are fixed at a single value throughout the spectrum. However, our results for octatetraene<sup>4</sup> suggest that for this system, and possibly for many related systems as well, the assumption that all vibronic excitations in a given transition share a common bandwidth may itself introduce significant discrepancies between calculated and experimental spectra.

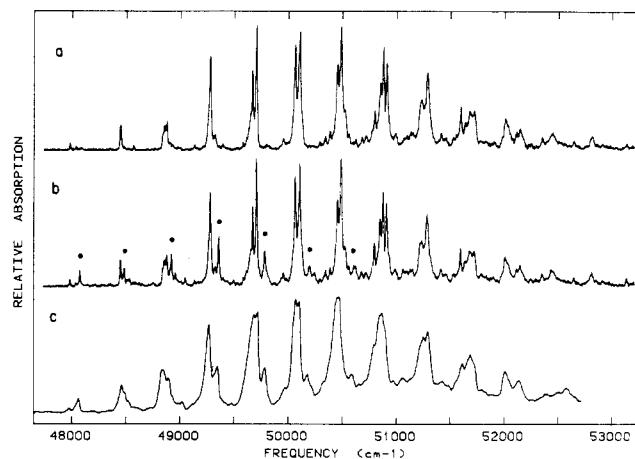
In the remainder of this account examples are presented of studies performed with direct absorption spectroscopy of jet-cooled samples. The results obtained are used in combination with other spectroscopic and theoretical studies to describe the excited state and its reactivity for polyatomic molecules. The examples consist of relatively small molecules such as CS<sub>2</sub> or NH<sub>3</sub> which, on excitation, undergo large changes in geometry and where the excited state dissociates efficiently. Effects of vibrational level coupling on the energy flow and consequently, on their chemistry, are manifested in these small molecules as spectroscopic perturbations

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**Figure 2.** CS<sub>2</sub> absorption spectra from 47 750 to 53 200 cm<sup>-1</sup>. (a) CS<sub>2</sub> coexpanded with argon and butane (rotationally cold/vibrationally cold). (b) CS<sub>2</sub> coexpanded with argon (rotationally cold/vibrationally hot). The dots identify transitions from excited vibrational levels of the ground electronic state, which are not observed in a. (c) Room temperature equilibrium vapor (rotationally hot/vibrationally hot). Reproduced with permission from ref 3. Copyright 1985 American Institute of Physics.

which can be unraveled from the jet-cooled spectra.<sup>21</sup> In the larger molecular systems discussed (the polyenes, styrene and stilbene) the spectra obtained shed light on both the upper state structure and the competition between internal vibrational relaxation and the characteristic photochemical reaction.

**Excited Electronic States of Small Dissociating Molecules.** The  ${}^1\Sigma_g^+ \rightarrow {}^1B_2({}^1\Sigma_u^+)$  transition of CS<sub>2</sub> occurring at 43 000–54 000 cm<sup>-1</sup>, provides an interesting model system where electronic excitation induces a large change in the geometry of the upper state and initiates efficient dissociation. Considerable interest in the photodissociation dynamics of the  ${}^1B_2({}^1\Sigma_u^+)$  state of CS<sub>2</sub> has led to several studies of its spectroscopy<sup>3,9,22–27</sup> and chemistry.<sup>28–32</sup> Although promising experimental methods<sup>33</sup> and theoretical techniques<sup>34–37</sup> have been

developed recently to treat the dynamics of small polyatomic molecules, a detailed understanding of the structure of the excited state is a prerequisite for building a dynamic picture. A partial rotational analysis by Douglas and Zanon<sup>25</sup> of the fine structure observed in a number of bands in the lower energy region of the  ${}^{12}\text{C} \text{ }^{32}\text{S}_2$  spectrum at 43 000–48 500 cm<sup>-1</sup>, has shown that upon excitation to the  ${}^1B_2({}^1\Sigma_u^+)$  state, the C–S bonds lengthen from 1.55 to 1.66 Å and the S–C–S angle decreases from 180° to 153°. This substantial change in both bond length and bond angle, combined with the prominence of the bending mode in the hot bands, indicates that both stretching and bending motion are likely to play a major role in the upper state vibrational progressions. Since symmetric stretching and bending vibrations have the same symmetry in the C<sub>2v</sub> excited state, their near degeneracy makes it possible for the two coordinates to couple in the  ${}^1B_2({}^1\Sigma_u^+)$  state.

The absorption spectrum of CS<sub>2</sub> cooled in supersonic expansions<sup>3,9</sup> is substantially simplified and therefore easier to interpret than the room temperature spectra, as much of the congestion due to inhomogeneous factors is eliminated (see Figure 2). The spectra of all three isotopes ( ${}^{12}\text{C}{}^{32}\text{S}_2$ ,  ${}^{12}\text{C}{}^{34}\text{S}_2$ ,  ${}^{13}\text{C}{}^{32}\text{S}_2$ ) studied in the jet arise from a transition from a linear ground state to a bent excited state at energies below 49 000 cm<sup>-1</sup>. Above this energy, at the Franck–Condon maximum, the K level structure and vibrational pattern are suggestive of a quasilinear excited state. The spectrum obtained for all three isotopes is characterized by clusters of bands separated by ~400–450 cm<sup>-1</sup>, with the structure within each cluster resulting from transitions to closely spaced vibrational levels of an upper state consisting of interacting  $\nu_1$  and  $\nu_2$ . The isotopic shifts for  ${}^{12}\text{C}{}^{34}\text{S}_2$  and  ${}^{13}\text{C}{}^{32}\text{S}_2$  as a function of band energy are interpreted to suggest that the active mode seen in the spectrum is the symmetric stretch perturbed by interactions with the bending mode.

The  $A \text{ } {}^1A_2'' \leftarrow X' A$  transition in ammonia provides, like CS<sub>2</sub>, an example of an excited state that undergoes a large change in geometry upon excitation: absorption of radiation at ~47 000 cm<sup>-1</sup> takes the pyramidal ground state into a planar excited state.<sup>38</sup> The characteristic chemistry<sup>39</sup> of this excited state is dissociation to NH<sub>2</sub> and H, a process occurring with a quantum yield of ~1.

Accurate spectroscopic information that can unambiguously be translated into a structural and dynamic picture of the excited electronic state is exceedingly difficult to obtain for reactive systems such as ammonia. Emission from the dissociating A state has not been observed from NH<sub>3</sub> although fluorescence<sup>40</sup> has been detected following excitation of ND<sub>3</sub>. Multiphoton ionization studies<sup>41</sup> have been used to explore the excited electronic states of NH<sub>3</sub>, yet the MPI spectra of the A state are complicated by the effect of predissociation: only weak features are observed with maximum

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signal at the  $\nu_2' = 2$  level and no signal for  $\nu_2' > 4$ . Vibrationally dependent predissociation is believed to be responsible for the peculiar intensities observed as MPI spectra reflect the competition between rapid predissociation and photoionization in the A state.

As a consequence, studies of the electronic states of dissociating molecules must rely on alternate techniques such as direct absorption<sup>2,42,43</sup> and resonance Raman spectroscopy.<sup>44</sup> The room-temperature absorption spectrum of ammonia has been used in connection with Franck-Condon model calculations.<sup>42,43</sup>

The absorption spectrum of jet-cooled ammonia<sup>2</sup> provides accurate experimental Franck-Condon factors as thermal inhomogeneous effects are largely eliminated. As a result of the efficient photodissociation, even in the low-temperature spectrum the FWHM of vibronic features are 70 to 283  $\text{cm}^{-1}$ , considerably broader than instrumental resolution. At room temperature where vibronic bands appear of equal width, relative peak heights are generally taken to be an accurate reflection of Franck-Condon factors and have been used to model the A state of ammonia.<sup>42,43</sup> However, in the spectrum of the jet-cooled molecule<sup>2</sup> as the homogeneous width of vibronic bands vary, the relative band intensities and relative band areas are different. The experimental Franck-Condon factors must be determined from integrated areas under vibronic bands. The spectroscopic information obtained indicate that the  $\nu_2'$  (bending) progression in the A state of ammonia maximizes at  $\nu_2' = 7$  while  $\nu_2 = 6$  is the most intense feature in the room temperature spectrum. No progression in  $\nu_1$  (symmetric stretch) is observed in the spectrum of the jet-cooled  $\text{NH}_3$  or  $\text{ND}_3$ . Motivated by this spectrum, an MCSCF approach has been used to calculate two-dimensional potential energy, dipole moment, and electronic moment surfaces for the X and A states of ammonia.<sup>45</sup> The ab initio data have been used to obtain anharmonic vibrational term values and wavefunctions as well as vibrational radiative transition probabilities for the symmetric stretch and bending modes. The calculated X  $\rightarrow$  A absorption Franck-Condon factors agree well with those deduced from the spectrum of jet-cooled ammonia.

In addition, the lowest dissociative pathway of ammonia has been mapped out by the MCSCF calculations.<sup>46</sup> Potential energy, dipole moment, and electronic transition moment surfaces of the X and A states have been calculated along an effective  $\text{H}_2\text{N-H}$  coordinate. The barrier in the A state is calculated to be planar and to increase for bent structures. This model gives a qualitative explanation for the homogeneous vibronic bandwidths observed in the jet-cooled absorption spectrum in light of the dissociation dynamics of this molecule.

**Excited Electronic States of Polyenes.** The study of the electronic structure and photodynamics of the linear polyenes has long been thought crucial to the development of our current understanding of electron delocalization, electron correlation, and other funda-

mental molecular quantum theoretical concepts.<sup>47-49</sup> The linear structure of these molecules allows the existence of geometrical isomers. In mapping out the mechanism for cis-trans isomerization in these molecules<sup>50</sup> (the discussion here will focus on butadiene, hexatriene, and octatetraene) particularly important is the description of the potential energy surfaces which control this photochemistry, namely the lowest  $1\text{B}_u^+$  and  $2\text{A}_g^-$  excited electronic states. The strategy employed is to describe the displacement along the double bond torsional coordinates of the equilibrium geometries of the excited states with respect to those of the planar ground state. These small polyenes can in principle accommodate any excited-state torsional geometry as, on one side, the V state of ethylene is twisted by  $90^\circ$  in contrast to planar geometries of the  $1\text{B}_u^+$  and  $2\text{A}_g^-$  state of octatetraene and longer polyenes.<sup>4,51-53</sup> Predictions of numerous theoretical calculations reported for the  $1\text{B}_u^+$  and  $2\text{A}_g^-$  states of butadiene and hexatriene span the same range.<sup>54</sup>

In addition, the ordering of the lowest excited states of the short polyenes is a subject of considerable controversy.<sup>49,55,56</sup> In octatetraene and several longer polyenes in the condensed phase,<sup>55,57</sup> a  $2\text{A}_g^-$  state, to which a one-photon transition from the ground state is parity forbidden, has been demonstrated to lie below the  $1\text{B}_1^+$  state. The  $2\text{A}_g^-$  state of butadiene and hexatriene has not been observed directly and its location is the subject of controversy.<sup>55-68</sup> Theoretical

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investigations have yielded conflicting results for the ordering of the  $2^1A_g$  and  $1^1B_u^+$  states of these systems and the energy gap between them.<sup>59</sup>

High-resolution spectroscopic data are needed to answer questions about the relative energies of excited states, and the equilibrium structures and photochemical dynamics associated with the lowest excited states of these polyenes. The difficulty in acquiring unambiguous data for these systems arises from the lack of detectable fluorescence<sup>60</sup> in butadiene and hexatriene, the lack of MPI resonance from this valence state<sup>61</sup> and the diffuseness of their absorption spectra<sup>62,65</sup> in low-temperature crystals. The absorption spectra of the room temperature vapor<sup>62</sup> are diffuse, partly because these large, flexible molecules possess a multiplicity of low-frequency vibrational levels with large Boltzmann populations at room temperature, resulting in considerable spectral broadening due to vibrational sequence band congestion. Hence, most of the available high-resolution data concerning the valence electronic transitions of the linear polyenes have been obtained by low-temperature matrix techniques.<sup>65</sup> However, matrix-induced line broadening and matrix site dependencies of vibronic band relative intensities limit the extent to which these results can be used to test theoretical predictions concerning excited-state geometries and force constants of the isolated molecule. A more ideal spectroscopic system is provided by the rotationally and vibrationally cold gas phase sample that can be prepared by supersonic molecular jet techniques. Such methods have been recently employed to obtain UV absorption spectra of these polyenes<sup>4,5</sup> and the fluorescence excitation spectrum of octatetraene<sup>52</sup> cooled in supersonic expansions.

Figure 3 shows comparative absorption spectra of the three unsubstituted jet-cooled polyenes.<sup>5</sup> Due to the alleviation of vibrational sequence band congestion on cooling, vibronic bands observed in the jet absorption spectra are significantly sharpened over their room temperature counterparts; the origin bandwidth is decreased by over  $100\text{ cm}^{-1}$  in all of the systems investigated. However, a dramatic increase in vibronic bandwidth with decreasing chain length is observed in these cold spectra. One of the broadening mechanisms considered to explain this effect is that arising from overlap of the  $1^1B_u^+ \leftarrow 1^1A_g^-$  spectrum by the nearby  $2^1A_g \leftarrow 1^1A_g$  transition that may attain significant

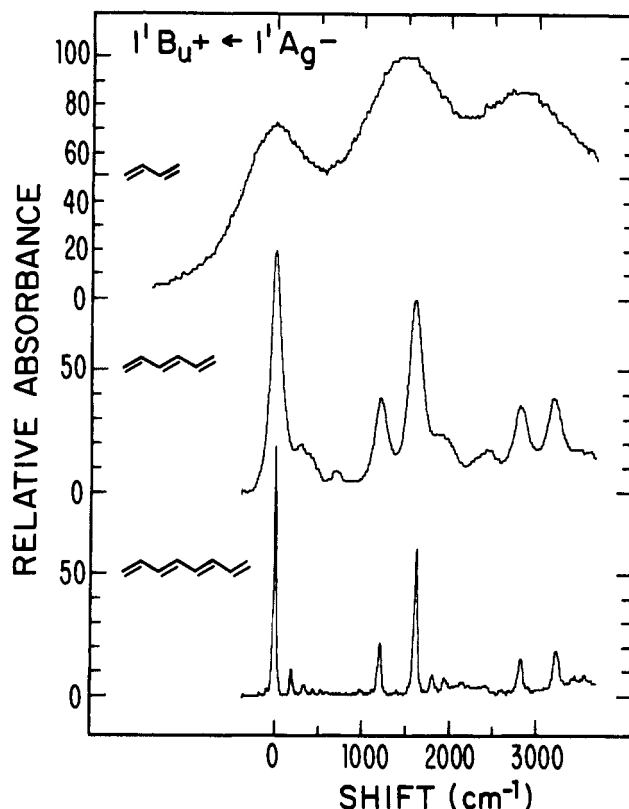


Figure 3. The  $1^1B_u^+ \leftarrow 1^1A_g^-$  absorption spectra of jet-cooled butadiene-*h*<sub>6</sub>, *trans*-1,3,5-hexatriene, and *trans,trans*-1,3,5,7-octatetraene. The spectra are plotted with the same maximum intensity for clarity. The origin bands of the transitions occur at  $46\,260\ (20)\text{ cm}^{-1}$ ,  $39\,786\ (3)\text{ cm}^{-1}$ , and  $35\,553\ (3)\text{ cm}^{-1}$  for butadiene, hexatriene, and octatetraene, respectively. Similar expansion conditions employing a 3–5% seeded argon jet at a stagnation pressure of  $\sim 0.1\text{ atm}$  behind a 1-mm diameter nozzle were used to obtain all three spectra. Reproduced with permission from ref. 5. Copyright 1984 American Institute of Physics.

oscillator strength via vibronic coupling.

A comparison of the vibronic structure observed in the jet spectrum of *trans*-hexatriene with that of *trans,trans*-octatetraene finds similar vibrational developments for the  $1^1B_u^+ \leftarrow 1^1A_g^-$  excitations of the two systems. In addition, bandwidths and intervals observed in the jet absorption spectra of the butadienes support the results of preresonance Raman studies<sup>63–65</sup> which have indicated normal mode displacements similar to those obtained for the longer polyenes. Thus, the jet absorption results provide no evidence for a substantially more distorted  $1^1B_u^+$  state in butadiene and hexatriene than in octatetraene, despite the dramatically different photophysical behavior of these systems.

**Phenyl-Substituted Ethylenes: Spectroscopy and Photochemistry.** Electronic spectra of aromatic and nonaromatic conjugated molecules can, in principle, be used to develop potential energy surfaces which in turn, describe the effects of electronic excitation on nuclear motion. Particularly important are the effects of electronic excitation on vibrational spectra and in inducing photochemical transformations (*cis*–*trans* isomerization for the examples discussed here). Styrene and stilbene are interesting models for study as they combine ground- and excited-state features of the vinyl (polyene-like) substituent and of the aromatic phenyl moiety. They provide simple systems where it is pos-

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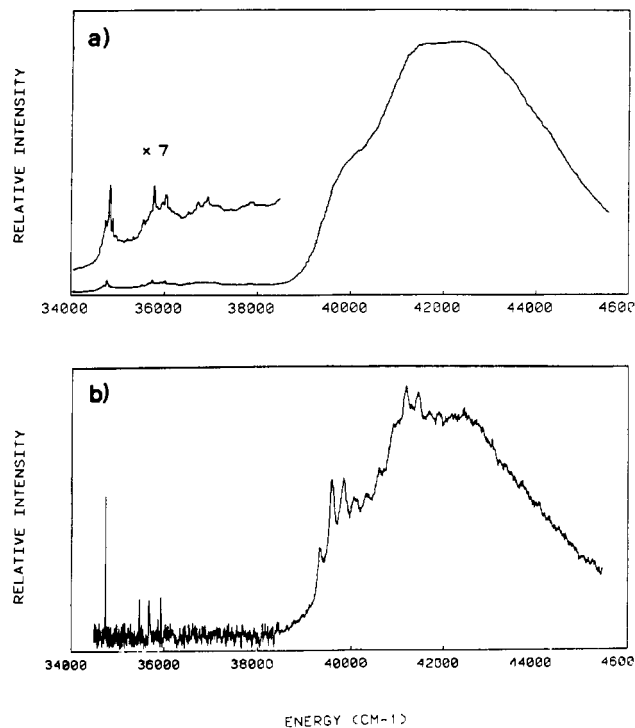
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sible to correlate the general properties of aromatic and nonaromatic  $\pi$ -electron systems. Not surprisingly, numerous photochemical studies have been performed on styrene<sup>66</sup> and stilbene.<sup>67</sup> Both models are well suited for the analysis of excited-state isomerization because the reaction occurs along a single well-defined spatial coordinate, namely the rotation about the ethylenic bond.

Controversy still surrounds the description of the photoactive states in *styrene*; for example,  $S_1$  has been described by an earlier model based on fluorescence excitation measurements,<sup>66b</sup> as twisted about the vinyl  $\text{CH}_2$  group. In contrast, recent investigations<sup>68</sup> of the  $S_0 \rightarrow S_1$  spectrum have shown that this state has a steep minimum at the planar configuration. This latter picture contradicts the results of earlier semiempirical calculations<sup>69</sup> but is supported by later *ab initio*<sup>70</sup> and semiempirical work.<sup>71</sup>

Spectroscopic studies on styrene include high-resolution absorption,<sup>67,68</sup> single vibronic level fluorescence measurements<sup>72</sup> and a multiphoton study of the  $S_1 \leftarrow S_0$  transition.<sup>73</sup> While many vibrational levels have been determined, the  $S_1 \leftarrow S_0$  band is highly congested at room temperature due to the population of levels of the low-frequency ring-substituent torsional mode which gives rise to a large degree of sequence hot-band activity. Recently, spectra have been obtained for this transition in jet-cooled styrene.<sup>72,73,74</sup> Absorption spectra of the jet-cooled molecule have also been obtained for the higher electronic states.<sup>6</sup> A comparison with the room temperature vapor<sup>75</sup> shows that in the spectra of the jet-cooled molecule a significant degree of simplification occurs as well as a significant change in the vibronic intensities relative to the absorption baseline (see Figure 4). Analysis of the singlet one-photon spectrum of the three lowest excited states has been made by means of Franck-Condon factors calculated in the harmonic approximation from an extended PPP-Cl model for the potential surfaces of the states involved.<sup>71,75</sup> Normal modes in the complete conformational space of the molecule were calculated for energy-minimized geometries and then used to evaluate the Franck-Condon factors. It was found that in the theoretical calculation,<sup>71</sup> the orbital structure and equilibrium geometry of the  $S_1$  state largely resembles that of the  $1^1\text{B}_{2u}$  of benzene, although it shows distinct displacements in both the ring and the substituent due to the activity of the substituent orbitals in the  $S_1 \leftarrow S_0$  transition. The leading configuration of the  $S_2$  state is the single excitation [HOMO, LUMO] transition. The  $S_2$  geometry is characterized by a considerable deformation of the phenyl ring as well as C-C bond inversion in the substituent. The  $S_3$  state has a large contribution from the [HOMO HOMO, LUMO LUMO] double excitation similar to that calculated for the  $2^1\text{A}_g$



**Figure 4.** Experimental absorption spectra for styrene. (a) Experimental absorption spectrum of styrene vapor at room temperature. (b) Experimental absorption spectrum of styrene cooled in a supersonic expansion. Reproduced with permission from ref 75. Copyright 1985 American Institute of Physics.

states of the linear polyenes. Like the polyene  $2^1\text{A}_g$  state, the equilibrium geometry of the  $S_3$  state is greatly displaced from that of the ground state. The  $S_3 \leftarrow S_0$  transition is calculated to be relatively intense and to be within 0.2 eV of  $S_2 \leftarrow S_0$ . There is very good overall agreement between theory and experiment concerning the narrow-lined and vertical  $S_1 \leftarrow S_0$  spectrum. This supports the contention that the one-photon transition is predominantly vertical. The measured vibronic pattern of the second band in the spectrum of the jet-cooled styrene molecule is consistent with the FC factors for the  $S_2 \leftarrow S_0$  transition calculated from the model, except for the calculated intensity in the low-frequency region being somewhat too small. The diffuse  $S_3 \leftarrow S_0$  transition is calculated to contribute to the one-photon spectrum in the region of the second absorption band but further spectroscopic work is necessary to more fully characterize this excited state, including its coupling with the other singlet state.

The vertical nature of the experimental  $S_1 \leftarrow S_0$  spectrum supports the conclusion drawn from the large barrier calculated for ethylenic bond torsion<sup>71,76</sup> that the transitions to the  $S_2$  and  $S_3$  states (and not  $S_1$ ) may in fact be responsible for *cis-trans* photoisomerization in this molecule.

**Stilbene** (a good emitter with distinguishable *cis* and *trans* isomers) is a molecule in which excited state dynamics can be followed for a photoinduced *cis-trans* isomerization reaction.<sup>67a,68b,76-78</sup> For ultra cold isolated stilbene both energy-resolved emission spectra and time-resolved emission data from photoselected states

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are available.<sup>10,12,79</sup> Attempts at elucidating isomerization dynamics have recently included LIF and direct absorption spectra of cold jets of stilbene providing fluorescence quantum yields for excess vibrational energies up to 5000  $\text{cm}^{-1}$  above the electronic origin of  $S_1$ .<sup>10,12</sup>

The spectra of jet-cooled stilbene provides new information about the upper state structure and dynamics. New, low-frequency spectral bands (assigned to the ethylenic carbon-phenyl torsional and out of plane bending modes) were directly seen and assigned from the jet spectra;<sup>10</sup> at room temperature thermal congestion masks these bands. Furthermore, information concerning the excited state dynamics was obtained from the onset of spectral congestion<sup>10,12</sup> in the  $S_1$  state at excess energies of  $\sim 900$  to  $1500 \text{ cm}^{-1}$ . This information is in agreement with energy-resolved emission data<sup>79</sup> that suggest that intramolecular vibrational energy redistribution in this system is fast at excess energies above  $1200 \text{ cm}^{-1}$ . Considerably more information is gleaned about the photochemical rearrangement from the spectra as a result of the comparison between the intensities of the fluorescence excitation and direct absorption spectra of the jet-cooled sample.<sup>10,12</sup> The fluorescence quantum yield measurements obtained as a function of excited vibronic level indicate that up to  $900 \text{ cm}^{-1}$  above the origin of  $S_1$ , the quantum yield for fluorescence is independent of the vibrational mode in the excited state. In the energy range  $900$ – $1500 \text{ cm}^{-1}$ , an onset type behavior is observed for the quantum yield for emission, while in the range  $1500$ – $5000 \text{ cm}^{-1}$  it exhibits an inverse dependence on excess energy. This decrease of the quantum yield in the range above  $900 \text{ cm}^{-1}$  reflects the onset of an effective nonradiative decay channel, presumably involving isomerization. The smooth energy dependence of the quantum yield on excess energy indicates that effective intramolecular vibrational redistribution is occurring in this system and

therefore the photoisomerization dynamics of the isolated molecule can be given in terms of conventional unimolecular kinetics.

### Concluding Remarks

The study of the photochemical dynamics of molecular excited states has significantly advanced with the development of modern experimental and theoretical techniques. The promise of a quantitative understanding of reactive polyatomic systems is only justified with the current development of theoretical tools<sup>34–37</sup> for predicting the spectroscopy of bound and unbound states. From a potential surface obtained by ab initio or semiempirical electronic structure theory, dynamics calculations can now be used to predict many spectral properties.

For photochemically active molecules one can calculate electronic and Raman spectra and compare them with experimental data. The power of experiment working in concert with theory is illustrated recently by the emission work<sup>33</sup> on the dissociating molecules  $\text{CH}_3\text{I}$  and  $\text{O}_3$ . For several of the reactive molecules discussed in this Account, resonance Raman data is available.<sup>43,65,80</sup> However such data is yet to be obtained<sup>81</sup> on the same jet-cooled molecules.

The technique of direct absorption of jet-cooled samples is but one of the methods now available to probe structure and dynamics in reactive polyatomic systems. Its development has been paralleled by that of complementary experimental and theoretical tools. Presently the spectroscopic study of reactive systems is an extremely promising endeavor.

*I would like to acknowledge the help of my collaborators Dr. G. M. McClelland, Professor J. L. Roebber, Dr. D. G. Geller-Leopold, and R. J. Hemley with the experiments discussed here. This work was supported by the National Science Foundation.*

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