Direct absorption spectra of higher excited states of jet-cooled monosubstituted benzenes: Phenylacetylene, styrene, benzaldehyde, and acetophenone

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(Received 2 March 1981; accepted 28 July 1981)

The second π → π* absorption bands of phenylacetylene, styrene, benzaldehyde, and acetophenone cooled in supersonic molecular jets are investigated by direct ultraviolet absorption spectroscopy. New vibronic structure is observed and vibronic assignments are discussed. The most prominent vibronic bands arise from motions centered in the substituent and from substituent-sensitive benzene modes. This contrasts with the spectra of the first π → π* transitions of these molecules, which exhibit structure involving ring-localized motions primarily. The spectra presented here demonstrate the utility of the direct absorption technique in the investigation of higher electronic transitions of jet-cooled molecules.

INTRODUCTION

Investigations of excited state structure and dynamics of large molecules are often hindered by the limited spectroscopic information available concerning their higher electronic states. Thermal inhomogeneous broadening effects, including sequence band congestion and the overlap of vibronic band rotational envelopes, combined with rapid photochemical and photophysical relaxation channels, frequently result in diffuse gas phase absorption spectra displaying little or no vibrational structure. The reduction of thermal effects by low-temperature matrix techniques can be offset by the additional broadening introduced by matrix interactions. The utility of matrix methods in the study of higher electronic states is further restricted by the lack of transparent matrices at high energies. In contrast, the technique of supersonic cooling provides a means of producing rotationally and vibrationally cold molecules in the gas phase, thus avoiding many of the problems associated with condensed phase methods.

Laser induced fluorescence (LIF) has been widely and successfully employed in studying the first excited singlet states of large molecules cooled in supersonic expansions.\textsuperscript{1} Recently, the second excited singlet states of several jet-cooled molecules have been investigated with this technique.\textsuperscript{2} However, higher excited states of many other large molecules undergo efficient radiationless relaxation, via internal conversion, intersystem crossing, isomerization, or predissociation, resulting in low fluorescence quantum yields; for these, alternative detection methods are required. A further limitation of the LIF technique is that, since the observed intensities depend on the fluorescence quantum yield of the excited state, accurate absorption intensities are not obtained. Multiphoton ionization (MPI) spectroscopy\textsuperscript{3} has recently been employed as a detection method in supersonic jet experiments,\textsuperscript{4–6} and furnishes a means of probing nonfluorescent states. However, the MPI technique demonstrates a selectivity toward Rydberg states and cannot be used to study many valence states.\textsuperscript{8}

Direct absorption spectroscopy of molecules cooled in supersonic expansions provides a method well suited to the study of higher excited states. In this experiment, the transmission of the exciting light through the sample is monitored, allowing the investigation of nonemitting systems. As the absorption intensities observed are independent of the fluorescence quantum yield or the ionization efficiency of the excited state, the direct absorption technique can provide spectroscopic information complementary to that obtained by the LIF and MPI methods. As is demonstrated below, gas phase sample molecules with extremely low internal temperatures can be produced in seeded supersonic jets at number densities sufficiently high to provide adequate direct absorption signal-to-noise ratios with a conventional deuterium lamp source. The combination of the classical direct absorption experiment with the more recently developed method of supersonic cooling provides a powerful spectroscopic technique whose applicability extends to a wide range of systems.

The present paper reports the results of the first application of this technique to the simplification of the ultraviolet absorption spectra of higher excited states.\textsuperscript{9} The subject of this study is the second π → π* transition of several simple aromatic hydrocarbons in which the phenyl group is conjugated with a chromophoric substituent: phenylacetylene, styrene, benzaldehyde, and acetophenone. These systems were chosen for the present investigation for two reasons. First, they provide a good illustration of the utility of the technique employed. Their efficient nonradiative relaxation pathways result in extremely diffuse room temperature spectra and low fluorescence quantum yields.\textsuperscript{10,11} By means of the direct absorption molecular jet technique, these uninformative spectra are sharpened considerably, providing information concerning the higher valence states of these molecules that would be difficult to obtain by any other method. Second, the importance of the photochem-

\textsuperscript{Alfred P. Sloan Fellow.}
istry and excited state structure of these model compounds renders the spectroscopic results of this study interesting in their own right.

Phenylacetylene, styrene, benzaldehyde, and acetophenone each display several absorption bands in the ultraviolet. Benzaldehyde and acetophenone have weak ($\epsilon_{\text{max}} \sim 30$ liter mole$^{-1}$ cm$^{-1}$) bands at 300–370 nm, which arise from an $\pi - \pi^*$ transition analogous to the $1A_1 - 1A_2(n, \pi^*)$ transition in formaldehyde. The benzaldehyde band shows well resolved structure in the room temperature vapor spectrum, and the acetophenone band, diffuse at room temperature, exhibits discrete structure in low-temperature matrices. The first $\pi - \pi^*$ excitations of all four molecules correlate with the $1A_1 - 1B_2g$ transitions of benzene and give rise to stronger ($\epsilon_{\text{max}} \sim 10^2$ liter mole$^{-1}$ cm$^{-1}$) bands between 250 and 300 nm. At room temperature, these bands contain well resolved vibrational structure involving ring-localized motions primarily. In addition, experimental evidence for the onset of new photophysical decay channels at these energies has recently been reported. Important for this absorption system also stems from its relevance to the well studied photochemistry of these compounds. Unfortunately, spectroscopic information concerning this absorption band is limited due to the extreme diffuseness. Cooling of phenylacetylene, styrene, benzaldehyde, and acetophenone in supersonic expansions reduces inhomogeneous broadening effects, producing a substantial sharpening of the absorption spectra of their second $\pi - \pi^*$ transitions.

**EXPERIMENTAL PROCEDURES**

The molecular jet absorption technique is described in detail below. Briefly, the polyatomic sample is diluted in argon and expanded through a pulsed supersonic nozzle into a vacuum chamber, where it is cross-illuminated with continuum ultraviolet radiation produced by a deuterium lamp. 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, programmed to perform signal averaging and other data manipulation tasks, also provides analog output of the absorption spectra.

Molecular jets were 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 under moderate expansion conditions. The flow of argon through the sample was adjusted to maintain a nozzle stagnation pressure of 175 Torr and the sample cell temperature was regulated to provide a sample vapor pressure of about 5 Torr, giving a 1:35 dilution ratio. A pulsed nozzle, consisting of a modified Bosch Porsche fuel injector valve with a 1 mm aperture diameter, was used to provide the molecular jet. Valve operation at 43 Hz with gas pulse widths of about 3 msec provided a gas pulse duty cycle of about 15%. A baffled Varian VHS-6 6 in. diffusion pump with a pumping speed of about 1200 liter/sec maintained the vacuum chamber pressure below 1 $\mu$ Torr during nozzle operation. A liquid nitrogen-cooled copper trap provided cryogenic pumping for the condensable polyatomic gases, reducing possible background absorption from scattered sample molecules.

The vibrational temperatures of the jet-cooled molecules were estimated from comparisons of hot band intensities observed in the room temperature and the jet spectra. For example, in the first $\pi - \pi^*$ transition of styrene, sequence bands involving the 38 cm$^{-1}$ ground state torsional mode were observed; from the intensities of these bands, a vibrational temperature below 40 K was determined. It should be noted, however, that since higher frequency vibrations are likely to have smaller relaxation cross sections, a non-Boltzmann distribution among the modes cannot be ruled out. 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.

Ultraviolet absorption spectra were obtained using a 60 W Oriel 6316 deuterium lamp as a light source. Suprasil optics focused the light to a spot 1 cm downstream from the nozzle, and the light transmitted through the molecular jet was dispersed by a 0.6 m, f/5.7 Jobin–Yvon HR825 monochromator equipped with a 1200 lines/mm holographic grating capable of 0.15 Å resolution. Scanning was controlled by a Commodore Business Machines PET 2001–32 computer via a stepping motor mounted on the monochromator. The dispersed light was detected by a Hamamatsu R106UH photomultiplier tube. Absorbed light intensity $I_0 - I_1$ was monitored by a Brookdeal 9501E lock-in amplifier operated at the pulsed nozzle frequency. Incident light intensity $I_0$ was measured directly from the photomultiplier tube output by a Keithley 414A picoammeter. The PET computer stored the digitized readings and computed their ratio, which, at the low signal levels observed, is proportional to absorbance. The signal-to-noise ratio was improved by signal averaging. The instrumental resolution of the recorded jet spectra is 1.4 Å ($\sim 25$ cm$^{-1}$).

Under the conditions of the experiment, we estimate a sample number density of about $5 \times 10^{14}$ molecules/cm$^3$ 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 $1.5 \times 10^{4}$ liter mole$^{-1}$ cm$^{-1}$ for these samples in the wavelength region monitored, maximum absorbances of about 0.01 are observed.

Styrene (98%) was supplied by Eastman and phenylacetylene (98%) by Aldrich. Benzaldehyde and acetophenone were Fisher Scientific Co. certified re-
FIG. 1. The second $\pi \to \pi^*$ transition of phenylacetylene. (A) represents the direct absorption spectrum of the sample cooled in a supersonic expansion to an estimated vibrational temperature $<40^\circ$K, and a rotational temperature $<10^\circ$K. The sample (pressure 5 Torr) was seeded in argon at a pressure of 175 Torr, and expanded through a pulsed nozzle with a 1 mm aperture diameter. The instrumental resolution is $\sim 25$ cm$^{-1}$. (a)-(f) indicate spacings observed in the jet spectrum, corresponding to the following excited state frequencies ($\pm 15$ cm$^{-1}$): (a) 1846 cm$^{-1}$, (b) 723 cm$^{-1}$, (c) 979 cm$^{-1}$, (d) 1175 cm$^{-1}$, (e) 1239 cm$^{-1}$, (f) 437 cm$^{-1}$. (B) represents the room temperature gas phase absorption spectrum.

FIG. 2. Absorption spectra of the second $\pi \to \pi^*$ transition of styrene. (A) Jet-cooled sample; conditions as in Fig. 1. Vibronic band intervals ($\pm 10$ cm$^{-1}$) observed are (a) 1577 cm$^{-1}$, and (b) 245 cm$^{-1}$. (B) Room temperature gas phase spectrum.
agents. Samples were used without further purification.

Room temperature gas phase spectra were recorded with a resolution of 2 Å on a GCA-McPherson model EU-707 double beam spectrometer, then converted to digital format by a Houston Instrument DT-11 HIPAD digitizer interfaced to the PET.

RESULTS

Direct absorption spectra of the second \( \pi \to \pi^* \) transitions of jet-cooled phenylacetylene, styrene, benzaldehyde, and acetophenone are presented in Figs. 1–4, where they are contrasted with the corresponding room temperature static gas absorption spectra. Spacings

![Absorption spectra of benzaldehyde](image1)

**FIG. 3.** Benzaldehyde absorption spectra in the region of the second \( \pi \to \pi^* \) transition. (A) Spectrum of the jet-cooled sample; conditions as in Fig. 1. Excited state vibrational frequencies (\( \pm 10 \text{ cm}^{-1} \)) corresponding to the observed spacings are (a) 780 cm\(^{-1}\), and (b) 213 cm\(^{-1}\). (B) Gas phase spectrum obtained at room temperature.

![Absorption spectra of acetoephone](image2)

**FIG. 4.** Absorption spectra of the second \( \pi \to \pi^* \) transition of acetophenone. (A) Jet-cooled sample; conditions as in Fig. 1. The following spacings are observed: (a) \( \sim 1000 \text{ cm}^{-1} \), (b) 341 \( \pm 10 \text{ cm}^{-1} \), (c) 198 \( \pm 10 \text{ cm}^{-1} \), (d) 46 \( \pm 10 \text{ cm}^{-1} \). (B) Room temperature gas phase spectrum.

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<th>Phenylacetylene</th>
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<td>$\nu$ (cm$^{-1}$)</td>
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$^a$Intensities (VS—very strong, S—strong, MS—moderately strong, W—weak) refer to the peak-to-valley ratios of the vibronic features observed in a given spectrum. The accuracies of band frequencies are estimated to be $\pm 10$ cm$^{-1}$ for the narrower bands, and $\pm 25$ cm$^{-1}$ for shoulders and relatively broad bands, labeled "B".

$^b$The symbol $\nu_2$ refers to a vibronic transition in $\nu_2$ from $\nu = 0$ in the ground state to $\nu = 1$ in the second ($\pi^* \pi^*$) state. Vibrational numberings are those used for the ground state frequencies of phenylacetylene, styrene, benzaldehyde, and acetophenone in Refs. 39, 37, 38, and 35, respectively.

$^c$The assignment of the origin band of the styrene transition is tentative. The symbol [248] denotes the vibrational mode whose excited state frequency is 248 $\pm 10$ cm$^{-1}$.

observed in the spectra of the jet-cooled molecules are indicated above each figure, with the corresponding excited state vibrational frequencies given in the captions. The frequencies of some of the vibronic bands observed in the jet spectra are recorded in Table I; the vibrational assignments indicated in that table will be discussed below.

Figures 1–4 demonstrate a substantial sharpening of vibronic structure in the second $\pi - \pi^*$ transitions of phenylacetylene, styrene, benzaldehyde, and acetophenone when the molecules are cooled in supersonic expansions. This can be attributed both to the narrowing of vibronic band rotational envelopes and to the alleviation of sequence band congestion upon cooling. The latter effect may be particularly significant in the present case. Figure 5 illustrates the Boltzmann populations at room temperature and at 40 K of the low frequency ground state vibrational levels of acetophenone and phenylacetylene. The numbers of levels with large thermal populations are most substantial for acetophenone$^{36,37}$ and styrene, each of which has a ground state torsional mode below 50 cm$^{-1}$; a calculation assuming harmonic potentials indicates that fewer than 5% of these molecules are in the ground state zero point level at room temperature. This problem, although less severe, is also significant for benzaldehyde$^{38}$ and phenylacetylene, whose lowest frequency modes occur at 111...
and 162 cm\(^{-1}\), respectively. If an electronic transition is accompanied by distortions along the normal coordinates corresponding to low frequency ground state modes, numerous sequence bands may be induced. Rotational band congestion, combined with the availability of rapid photophysical and photochemical relaxation channels at high energies, may broaden sequence bands sufficiently to obscure vibronic structure. When the molecules are cooled to below 40°K in the jet expansions, the populations of their ground state excited vibrational levels are substantially reduced, and sequence band congestion is largely eliminated. Figure 5 contrasts the cooled and room temperature Boltzmann populations of phenylacetylene, whose room temperature spectrum undergoes moderate sharpening upon cooling, with those of acetophenone, whose room temperature and jet spectra differ dramatically.

Contributions to linewidths from inhomogeneous broadening mechanisms are expected to be small at the estimated < 40°K vibrational and < 10°K rotational temperatures of the jet-cooled molecules. From a Gaussian fit of the discrete vibronic bands observed in the jet spectra, linewidths of ~ 100 cm\(^{-1}\) for styrene, benzaldehyde, and acetophenone, and ~ 200 cm\(^{-1}\) for phenylacetylene, are estimated. However, preliminary results of a normal mode analysis of the styrene spectrum indicate that, when all vibronic transitions likely to be active in the transition are considered, the estimated homogeneous linewidths of the features observed in the jet spectrum are somewhat reduced.

The absorption spectra of the second \(\pi - \pi^*\) transitions of phenylacetylene, styrene, benzaldehyde, and acetophenone are individually described below.

**Phenylacetylene**

Figure 1 displays the absorption spectra of the second \(\pi - \pi^*\) transition of phenylacetylene. This system has been investigated by other workers in the gas phase at room temperature.\(^\text{19}\) No additional structure was seen in high resolution studies.\(^\text{19}\) In the jet spectrum, the widths of the two strong bands prominent at room temperature are decreased by approximately 50%, and additional discrete structure is resolved out of the irregular continuum on which they are superimposed. As indicated in the figure and in Table I, the spacings of these bands suggest the activities of excited state modes with frequencies of 437, 723, 979, 1175, 1239, and 1846±15 cm\(^{-1}\). Excitation of more than one quantum of the respective vibrational mode is observed for the 723 and 1846 cm\(^{-1}\) intervals only.
Styrene

The absorption spectra of the second $\pi - \pi^*$ transition of styrene are presented in Fig. 2. The room temperature gas phase spectrum, as previously reported by Walsh, consists of two broad bands spaced by about 1515 cm$^{-1}$. In the spectrum of the jet-cooled molecule, progressions of 248 $\pm$ 10 cm$^{-1}$ intervals are observed in combination with the higher frequency interval of 1577 $\pm$ 10 cm$^{-1}$. The first 248 cm$^{-1}$ progression is observed to the sixth member, with an intensity maximum in the second member.

Benzaldehyde

The absorption spectrum of jet-cooled benzaldehyde, shown in Fig. 3, displays more distinctly the bands observed at room temperature,$^{14,42}$ as well as additional higher energy bands. As indicated in the figure, the most prominent features observed in the jet spectrum involve vibrational modes with excited state frequencies of 212 and 780 $\pm$ 10 cm$^{-1}$. Progressions of up to four members of the 212 cm$^{-1}$ interval, with intensity maxima at $v=1$, appear in combination with each member of the 780 cm$^{-1}$ progression.

Acetophenone

Figure 4 displays the absorption spectra of the second $\pi - \pi^*$ transition of acetophenone. The room temperature gas phase spectrum consists of two broad bands spaced about 1000 cm$^{-1}$ apart. In the jet spectrum, the first of these bands resolves into several vibronic features indicating the activities of vibrational modes with frequencies of 46, 198, and 341 $\pm$ 10 cm$^{-1}$ in the excited state. The activities of higher frequency vibrational modes are suggested by the increase in absorption intensity above about 42 700 cm$^{-1}$; however, corresponding vibronic bands are not observed. The possible significance of the loss of structure at higher energies in the acetophenone jet spectrum is discussed below.

VIBRATIONAL ANALYSIS

Due to the appreciable homogeneous widths of vibronic lines in the absorption spectra of the second $\pi - \pi^*$ transitions, and the lack of data concerning fluorescence directly from these states, the vibrational analyses presented below are necessarily tentative. Nevertheless, convincing vibrational assignments can be made for most of the observed vibronic bands on the basis of comparisons among the four jet spectra reported here and the previously reported spectra of related molecules, leading to important conclusions regarding the nature of the spectral systems under investigation.

Phenylacetylene

The strong origin band at 41 955 $\pm$ 10 cm$^{-1}$ and the lack of extended vibrational progressions in the jet absorption spectrum suggest that the phenylacetylene molecule retains its ground state planar C$_{2v}$ symmetry in the excited state. Therefore, vibronic bands are most likely to arise from totally symmetric vibrational modes.

The assignment of the prominent 1846 $\pm$ 15 cm$^{-1}$ inter-

val observed in the phenylacetylene spectrum can be made on the basis of a comparison with the spectrum of the second $\pi - \pi^*$ transition of the related molecule, phenylcyanide. The spectrum of this molecule is very similar in appearance to that of jet-cooled phenylacetylene, except that the prominent high frequency interval appears at about 1924 cm$^{-1}$. The ratio of the excited state intervals observed in the phenylacetylene and phenylcyanide spectra is very close to that of their ground state C=C and C=N stretching frequencies, which are 2120$^{33}$ and 2242 cm$^{-1}$. Therefore, it is likely that these excited state intervals arise from the triple bond stretching vibrations in both molecules.

The second most prominent interval observed in the phenylacetylene spectrum (723 $\pm$ 15 cm$^{-1}$) can be assigned to the substituent-sensitive in-plane ring deformation $\nu_{11}$, whose ground state frequency is 760 cm$^{-1}$. This mode is also prominent in the phenylcyanide spectrum (762 cm$^{-1}$ ground state, 721 cm$^{-1}$ excited state$^{41}$), and in the first excited state of phenylacetylene (717 cm$^{-1}$). A second totally symmetric substituent-sensitive in-plane ring deformation $\nu_{12}$ can be ascribed to the 437 $\pm$ 15 cm$^{-1}$ excited state interval appearing weakly in the jet absorption spectrum. This mode has a ground state frequency of 465 cm$^{-1}$, and gives rise to a moderately strong 410 cm$^{-1}$ interval in the first $\pi - \pi^*$ phenylacetylene transition.

Three additional excited state intervals of 979, 1175, and 1239 $\pm$ 15 cm$^{-1}$ are observed in the jet absorption spectrum. The last two intervals appear weakly in the spectrum, while the first is associated with a fairly prominent vibronic band. There are four totally symmetric vibrational modes of similar ground state frequencies$^{26}$ to which these can be assigned:

$\nu_9$, \(\phi\)-CCH stretch (1192 cm$^{-1}$),
$\nu_{10}$, in-plane C-H bend (1175 cm$^{-1}$),
$\nu_{11}$, in-plane C-H bend (1028 cm$^{-1}$),
$\nu_{14}$, ring breathing (908 cm$^{-1}$).

Of these, only $\nu_4$ is likely to increase in frequency upon excitation; this may occur if the $\pi$-bond contribution to the single bond between the ring and the substituent increases in the excited state. Therefore, the 1239 cm$^{-1}$ excited state interval can be assigned to $\nu_4$. The 1175 cm$^{-1}$ excited state interval can, then, confidently be assigned to $\nu_2$. A choice of assignment of the remaining 979 cm$^{-1}$ excited state interval to $\nu_{10}$ or $\nu_{14}$ can be made on the following grounds. Since ring hydrogens are not intimately involved in the $\pi$-electron system, skeletal vibrations are expected to be most prominent in the spectrum. Consistent with this prediction, the strongest bands observed in the first $\pi - \pi^*$ transition of phenylacetylene arise from skeletal vibrational modes$^{26,35}$ Since the 979 cm$^{-1}$ interval is fairly prominent in the spectrum of the second $\pi - \pi^*$ transition of phenylacetylene, it is most likely to be associated with $\nu_{14}$, the trigonal ring breathing mode.

**Styrene**

The first well-resolved vibronic band at 39,327 ± 10 cm⁻¹ can tentatively be assigned as the origin of the second π → π⁺ transition of styrene. Additional very weak features can be detected on the red edge of this band; however, their intensities suggest their association with the first π → π⁺ transition.

The styrene jet spectrum exhibits two excited state intervals, of 1577 ± 10 and 248 ± 10 cm⁻¹; progressions in the latter interval have their intensity maxima in the second observed member. The following comparisons to spectra of related molecules suggest the assignments of the 1577 cm⁻¹ interval to νₚ, the ethylenic double bond stretch (1630 cm⁻¹ in the ground state)⁴⁴, and the 248 cm⁻¹ interval to νₓ, the in-plane bending motion of the whole substituent [241 cm⁻¹ in the ground state, ²⁵ 250 cm⁻¹ in the first (π, π⁺) state]¹⁷.

(a) The absorption spectrum at 20°K of the analogous electronic transition⁴⁶ of the near relative trans-stilbene, which is the lowest allowed singlet transition in that system, displays as its most prominent features progressions of similar intervals: 1599 and 206 cm⁻¹. These assignments have been assigned to the ethylenic double bond stretch (1635 cm⁻¹ in the ground state) and to the predominant ethylene-like symmetrical in-plane skeletal bending mode (212 cm⁻¹ in the ground state), respectively.⁴⁵ These assignments are supported by the prominence of corresponding intervals in stilbene's fluorescence spectrum, and by semiempirical PPP-MO calculations.⁴⁷ Similarly, the absorption spectrum at 20°K of the analogous azobenze transition exhibits prominent progressions of 1342 and 220 cm⁻¹ intervals, which have been attributed to the N=N stretching vibration (1442 cm⁻¹ in the ground state) and the N=N bending mode (285 cm⁻¹ in the ground state), respectively.⁴⁸

(b) In the absorption spectrum of the first π → π⁺ transition of the more distant relative trans-hexatriene, the most intense peaks are separated by 1626 cm⁻¹, which has been assigned to the totally symmetric double bond stretching motion with a 1623 cm⁻¹ ground state frequency.⁴⁹ The strongest nonstretching mode contribution comes from an in-plane skeletal bending vibration, which is observed at 350 cm⁻¹ in the excited state and 347 cm⁻¹ in the ground state.⁴⁵ Semiempirical consistent force field calculations have confirmed this assignment.⁴⁸

(c) Further support for the assignment of the styrene 1577 cm⁻¹ interval comes from a comparison with the jet spectrum of phenylacetylene, which exhibits a prominent 1846 cm⁻¹ interval. These frequencies are close enough to be due to similar vibrational types, yet the difference between them is sufficient to suggest that they arise from the different substituents in the two molecules. The assignment of the phenylacetylene interval to the triple bond stretch, discussed above, suggests that the corresponding styrene interval be ascribed to the ethylenic double bond stretch.

(d) Finally, additional support for the assignment of the styrene 248 cm⁻¹ excited state interval comes from a comparison with the jet spectrum of the isoelectronic molecule, benzaldehyde. As shown in Fig. 3, the latter system also exhibits progressions of a similar interval (212 ± 10 cm⁻¹) which peak in the second member. As is discussed below, the assignment of the benzaldehyde 212 cm⁻¹ interval to the in-plane bending motion of the whole substituent, 224 cm⁻¹ in the ground state, is suggested by the activity of a hot band of similar frequency in the room temperature spectrum. The similarity between the styrene and benzaldehyde spectra suggests that the low-frequency excited state intervals observed may arise from the same vibrational mode in both systems.

Thus, comparisons with spectra of similar molecules strongly suggest the assignments of the 1577 and 248 cm⁻¹ excited state modes of styrene to the ethylenic double bond stretching vibration and the in-plane bending motion of the whole ethylene group, respectively. However, an alternate assignment for the low-frequency mode is suggested by preliminary results of semiempirical QCCF/P̄ calculations.⁴⁶ These indicate that the second (π, π⁺) state of styrene, the ethylene group is slightly twisted, and the height of the barrier to double bond torsion is significantly lower than in the ground state. As a result, ethylenic torsional progressions of 250–300 cm⁻¹ intervals with intensity maxima in the second or third members are expected to be prominent in the absorption spectrum.

It may be noted that jet absorption experiments on deuterated styrenes do not provide a straightforward means of determining the correct vibrational assignment in this case. In the ground state, νₓ, described as the ethylenic C=C torsional vibration, also involves considerable contribution from the out-of-plane bending vibration of the H atom on C(α), νₚₓ.⁴³ As a result, νₓ is reduced on deuteration of the CHₓ group by nothing like the factor of √2 which it would be if the vibration were purely CHₓ torsion. In fact, it is reduced by nearly the same relative amount (10% vs 11%) as is νₚ, the in-plane bending motion of the whole substituent.⁴⁵ These very slight differences could be even further reduced by excited state interactions. However, jet absorption experiments on derivatives of styrene in which double bond torsion is selectively hindered may help to determine the correct assignment; such experiments are in progress in our laboratory.

**Benzaldehyde**

The first vibronic band observed in the benzaldehyde jet spectrum, at 41,334 ± 10 cm⁻¹, can be assigned as the origin of the second π → π⁺ transition of that molecule. The room temperature spectrum displays a broad shoulder about 230 cm⁻¹ to the red of the assigned origin. This shoulder is not present in the jet spectrum, and its estimated intensity relative to that of the origin band in the room temperature spectrum is approximately that expected from the Boltzmann factor for a 230 cm⁻¹ hot band. The prominence of this hot band suggests the assignment of the 212 cm⁻¹ excited state interval to ν₂, the in-plane bending motion of the aldehyde group with respect to the ring, whose ground state frequency is 224 cm⁻¹.⁴⁸

The 780 ± 10 cm⁻¹ interval observed in the jet spectrum...
of benzaldehyde is similar in frequency to the 723 cm\(^{-1}\) interval prominent in the phenylacetylene spectrum, which has been assigned to the substituent-sensitive in-plane ring deformation of the latter molecule. Furthermore, the ratio of the 723 and the 780 cm\(^{-1}\) excited state frequencies is very close to that of the frequencies of this mode in the ground states of the two molecules.\(^{38,39}\) This suggests the assignment of the 780 cm\(^{-1}\) interval in the benzaldehyde spectrum to \(\nu_{21}\), the substituent-sensitive in-plane ring deformation vibration. This mode is mixed with the in-plane bending motion of the carbonyl group in the ground state.\(^{35}\)

**Acetophenone**

The first band observed in the jet spectrum of acetophenone, at 41 695 ± 10 cm\(^{-1}\), is likely to be the origin band. Shoulders centered 46 ± 10 cm\(^{-1}\) to the blue of the first two vibronic bands are likely to be associated with \(\nu_{56}\), the torsional motion of the ring-to-substituent single bond, whose ground state frequency is 48 cm\(^{-1}\).\(^{35}\) The 198 ± 10 cm\(^{-1}\) interval observed in the acetophenone spectrum is similar in frequency to the 212 cm\(^{-1}\) excited state interval of the related molecule, benzaldehyde.

The assignment, discussed above, of the latter interval to the in-plane bending motion of the substituent as a whole with respect to the ring suggests the corresponding assignment of the 198 cm\(^{-1}\) acetophenone interval to \(\nu_{53}\), whose ground state frequency is 225 cm\(^{-1}\).\(^{35}\) Finally, the 341 ± 10 cm\(^{-1}\) mode giving rise to a prominent progression of at least three members in the acetophenone jet spectrum is similar in frequency to the 437 cm\(^{-1}\) mode observed in the phenylacetylene spectrum. This mode has been assigned to a substituent-sensitive in-plane ring deformation motion in the latter molecule. The ratio of the 341 and 437 cm\(^{-1}\) excited state frequencies is very close to that of the frequencies of this mode in the ground states of the two molecules.\(^{32,33}\) This suggests the assignment of the acetophenone 341 cm\(^{-1}\) excited state interval to \(\nu_{34}\), a substituent-sensitive in-plane ring deformation whose ground state frequency is 386 cm\(^{-1}\).\(^{35}\)

The tentative conclusions of the foregoing vibrational analyses of the second \(\pi - \pi^*\) transitions of phenylacetylene, styrene, benzaldehyde, and acetophenone are indicated in Table II. The corresponding assignments of the individual vibronic bands observed in the four jet spectra are listed in Table I.

**DISCUSSION**

Table III compares the observed vibrational frequencies of the second excited state of phenylacetylene with those of the first \(\pi, \pi^*\) and the ground states. The following points are noteworthy:

(a) The stretching frequency of the acetylene triple bond decreases from its ground state value in the second excited state more than it does in the first.

(b) The stretching frequency of the single bond between the ring and the acetylene group increases from its ground state value in the second \(\pi, \pi^*\) state, but not in the first \(\pi, \pi^*\) state.

(c) The frequencies of the ring modes, \(\nu_9\) and \(\nu_{11} - \nu_{13}\), decrease from their ground state values in the first excited state more than they do in the second excited state.

(d) Ring modes give rise to the dominant features in

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**Table II. Vibrational frequencies of phenylacetylene, styrene, benzaldehyde, and acetophenone in the ground and second \(\pi, \pi^*\) states.**

<table>
<thead>
<tr>
<th>Phenylacetylene</th>
<th>Styrene</th>
<th>Benzaldehyde</th>
<th>Acetophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground state (^{a})</td>
<td>Excited state (^{a})</td>
<td>Ground state (^{d})</td>
<td>Excited state (^{d})</td>
</tr>
<tr>
<td>640 (^{b})</td>
<td>241 (^{b})</td>
<td>248 (^{d})</td>
<td>224</td>
</tr>
<tr>
<td>465</td>
<td>437</td>
<td></td>
<td></td>
</tr>
<tr>
<td>760</td>
<td>723</td>
<td></td>
<td>825</td>
</tr>
<tr>
<td>998</td>
<td>979</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1175</td>
<td>1175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1192</td>
<td>1239</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2120</td>
<td>1846</td>
<td>1630</td>
<td>1577</td>
</tr>
</tbody>
</table>

\(^{a}\)stretch; \(^{b}\)in-plane bend; \(^{c}\)in-plane ring angle bend; \(^{d}\)X-sens—substituent-sensitive ring mode.

\(^{a}\)In benzaldehyde, this vibration is spanned by two levels, at 823 and 649 cm\(^{-1}\) in the ground state, arising from the mixing of CO bending and ring deformation motions (Ref. 38).

\(^{d}\)Accuracies of excited state frequencies are estimated to be ±10 cm\(^{-1}\) for styrene, benzaldehyde, and acetophenone, and ±15 cm\(^{-1}\) for phenylacetylene.

\(^{b}\)The assignment of the 248 cm\(^{-1}\) interval observed in the styrene spectrum is uncertain.

\(^{*}\)References 35 and 36.

\(^{2}\)Reference 37.

\(^{3}\)Reference 38.

\(^{4}\)Reference 39.
TABLE III. Assignments of vibronic bands observed in the second absorption system of jet-cooled phenylacetylene.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Description</th>
<th>Ground State</th>
<th>First $\pi - \pi^*$</th>
<th>Second $\pi - \pi^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_{13}$</td>
<td>$X\text{-sens } \sigma(C\text{-}C\text{-}C)$</td>
<td>465</td>
<td>410</td>
<td>437</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>$X\text{-sens } \sigma(C\text{-}C\text{-}C)$</td>
<td>760</td>
<td>717*</td>
<td>723</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>Ring breathing</td>
<td>998</td>
<td>944*</td>
<td>979</td>
</tr>
<tr>
<td>$v_{9}$</td>
<td>$\pi\text{-sens } \pi(C\text{-}H)$</td>
<td>1175</td>
<td>1057</td>
<td>1175</td>
</tr>
<tr>
<td>$v_{8}$</td>
<td>$X\text{-sens } \sigma(C\text{-}C\text{-}C)$</td>
<td>1192</td>
<td>1191*</td>
<td>1239</td>
</tr>
<tr>
<td>$v_{5}$</td>
<td>$\sigma(C\text{-}C)$</td>
<td>2120</td>
<td>2016</td>
<td>1846*</td>
</tr>
</tbody>
</table>

$^a$ $\pi$-stretch; $^b$ in-plane bend; $^c$ $\sigma$-in-plane ring angle bend; $^d$ X-sens substituent-sensitive benzene mode.

The spectrum of the first $\pi - \pi^*$ transition; in the second $\pi - \pi^*$ transition, a substituent-localized mode is most prominent.

Analysis of the first $\pi - \pi^*$ absorption system of phenylacetylene has shown that this transition is primarily localized on the benzene ring. A greater involvement of the acetylene group in the second $\pi - \pi^*$ transition is indicated by the above observations. In particular, (a) and (b) suggest that the order of the acetylene triple bond decreases significantly in the second excited state, and that an increased delocalization of $\pi$-electron density occurs, causing the acetylene single bond to acquire some double bond character. However, it is clear that the degree of geometrical distortion of the acetylene group in the second ($\pi, \pi^*$) state of phenylacetylene is not nearly as great as in the first excited singlet state of acetylene itself. In the latter system, large geometrical changes occur, accompanied by a decrease of 30% in the frequency of the triple bond as well as extended vibrational progressions, not observed in the present spectrum.

Results of semiempirical CNDO/CI calculations of the excited states of phenylacetylene have predicted two electronic states with comparable transition intensities in this spectral region. The authors suggest that the absorption band under study is actually composed of transitions to both of these states, which are strongly perturbing each other vibronically. The foregoing vibrational analysis indicates that the discrete vibronic bands resolved in the jet spectrum can be plausibly explained in terms of transitions to a single electronic state. However, the diffuse background underlying these features, and the greater widths of vibronic bands in the phenylacetylene spectrum than those in the other jet spectra presented here, may indicate the proximity of a second electronic state broadening features in this region.

It has been shown that all discrete vibronic feature observed in the jet spectrum of styrene's second $\pi - \pi^*$ transition can be attributed to ethylenic vibrational modes. This contrasts markedly with the vibronic structure of the first $\pi - \pi^*$ system, which indicates the localization of that transition on the benzene ring. The difference in the localization of the two transitions is evident from a comparison of the first and second absorption bands of styrene and phenylacetylene. It has previously been noted that the spectra of the lower energy transitions of the two molecules are remarkably alike, with respect to the frequencies of their dominant vibrations, their lack of extended progressions, and their overall shapes. Comparison of Figs. 1 and 2 shows that the higher energy bands of styrene and phenylacetylene differ in all of these respects, and suggests the greater involvement of the different substituent groups in the second $\pi - \pi^*$ transitions of these molecules.

The assignment of the 1577 cm$^{-1}$ excited state interval observed in the styrene spectrum to the ethylenic double bond stretch, whose ground state value is 1630 cm$^{-1}$, suggests that the order of this bond changes only slightly in the second ($\pi, \pi^*$) state. Assuming that the total bond order varies linearly with the force constant for small changes, so that a fractional change in bond order is given by the fractional change in the square of the frequency, the observed decrease in the frequency of this mode on excitation indicates a decrease in total bond order of about 6%. This is similar to the 4% decrease in total bond order estimated from the analogous absorption band of stilbene, which corresponds to a change in $\pi$-bond order of about 10%–15%. This modest change in the $\pi$-bond order of the ethylenic bond, and the observed intensity profile of the 248 cm$^{-1}$ progressions, indicate that in the second ($\pi, \pi^*$) state of styrene the degree of geometrical distortion of the ethylene group is far less than in the $N - V$ transition of ethylene itself. In that molecule, the ground state is planar, while the first excited singlet state is thought to have an equilibrium conformation in which the planes of the two CH$_2$ groups are perpendicular to each other; this severe distortion produces a long torsional progression whose intensity increases strongly with frequency.

Several calculations of the excited states of styrene have indicated the presence of more than one electronic state in the region of the absorption band investigated here. An ab initio calculation has predicted that a doubly excited singlet state, which may be considered to be the analog of the 2$^1$A$_2$ state of polyenes, may lie to the red of the second ($\pi, \pi^*$) state. The transition to the doubly excited state is predicted to have an oscillator strength $\sim 10^3$ less than that to the nearby singlet state, and thus conceivably to be hidden beneath it. On the other hand, a semiempirical PPP-SCF-CI calculation has predicted a doubly excited state with high oscillator strength lying to the blue of the second ($\pi, \pi^*$) state. Although the vibrational analysis of the styrene jet spectrum indicates that all prominent vibronic features observed in the second absorption band can be attributed to transitions to a single electronic state, it is possible that part of the intense, diffuse background underlying these discrete features may arise from transitions to a second state.

The vibrational analysis of the previous section has indicated the activities of in-plane bending motions...
the aldehyde group, the carbonyl group, and the ring in the second $\pi \rightarrow \pi^*$ transition of benzaldehyde. In the corresponding acetophenone transition, similar modes are prominent; the greater activity of torsional motion in the acetophenone spectrum may be related to the nonplanarity of that molecule in its ground state. Thus, the vibronic structure associated with the second $\pi \rightarrow \pi^*$ transitions of benzaldehyde and acetophenone is dissimilar to that observed both in the first $\pi \rightarrow \pi^*$ systems of these molecules, in which ring-localized motions are the most prominent, and in the $\pi \rightarrow \pi^*$ absorption bands, which are dominated by progressions involving the carbonyl stretching vibration.

The acetophenone spectrum shows a rather sudden onset of diffuseness at about 42 700 cm$^{-1}$; in the region to the blue, individual vibronic bands cannot be distinguished. Undoubtedly, the higher density of vibronic transitions contributes to the increased diffuseness at higher energies. The increase in absorption intensity at about 42 700 cm$^{-1}$ may indicate the activity of additional vibrational mode(a) in that region. Combinations with the several low-frequency modes noted above would contribute to a severely overlapped spectrum. However, it is also possible that this loss of structure results in part from the opening of rapid photophysical or photochemical relaxation channels or the presence of another electronic state in this region, producing increased broadening of vibronic transitions. Such mechanisms find support in the results of optoacoustic studies, which have disclosed changes in rates of heat evolution at about 43 300 cm$^{-1}$, leading the authors to suggest the existence of unsuspected electronic states or the surmounting of energy barriers to photochemistry in this region.

CONCLUSION

In conclusion, this study demonstrates the utility of direct absorption spectroscopy of jet-cooled molecules in obtaining simplified spectra of higher singlet states. This technique has been employed to investigate the second $\pi \rightarrow \pi^*$ absorption bands of several simple aromatic hydrocarbons in which the phenyl group is conjugated with a chromophoric substituent: phenylacetylene, styrene, benzaldehyde, and acetophenone. Previously unobserved vibronic structure is revealed, for which tentative vibrational assignments are given. Although some evidence suggests the opening of new nonradiative channels and/or the presence of additional electronic states in this absorption region, all discrete vibronic bands observed in each system appear to be associated with a single electronic transition. The vibronic structure observed in the jet absorption spectra is dominated by substituent-localized vibrational modes and substituent-sensitive ring motions, indicating a greater involvement of the substituent groups in the second $\pi \rightarrow \pi^*$ transitions than at the first.

ACKNOWLEDGMENTS

Financial support from the National Science Foundation is gratefully acknowledged. We thank Professor M. Karplus and Dr. U. Dinur for their interest in this work, and for communicating the results of their calculations prior to publication.


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40. U. Dinur, R. Hemley, and M. Karplus (work in progress).
43. Unpublished work of the authors.