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# Spectroscopic manifestation of intramolecular relaxation of azulene in supersonic jets

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In this paper we report on the line profiles in the absorption spectra for the  $S_0 \rightarrow S_1$  electronic origin and for the 659 and 1394  $\text{cm}^{-1}$  vibrational excitations in the  $S_1$  manifold of azulene in pulsed, planar, supersonic expansions. The  $S_1$  electronic origin exhibits a Lorentzian line shape, whose homogeneous linewidth results in the lifetime  $\tau = 0.8 \pm 0.2$  ps for interstate electronic relaxation in the isolated molecule.

## I. INTRODUCTION

The anomalous fluorescence from the  $S_1$  and  $S_2$  electronic states of azulene<sup>1</sup> provides the best-known example for the violation of the Kasha rules.<sup>2</sup> The vibronic levels of the  $S_1$  state of azulene exhibit effective nonradiative coupling to the isoenergetic vibronic manifold of the  $S_0$  state, which results in internal conversion on the ps time scale. Hunt and Ross<sup>3</sup> and McCoy<sup>4</sup> noted that the most striking feature of the  $S_0 \rightarrow S_1$  high-temperature (100–150 °C) vapor spectrum of azulene is its diffusiveness, the individual vibronic components being 5–10  $\text{cm}^{-1}$  wide. Ross and his colleagues<sup>3,5</sup> proposed that diffusiveness in the  $S_1$  state of azulene, as well as in higher electronically excited states of other large molecules, originates from internal conversion. Subsequent theoretical work<sup>6</sup> showed that relaxation broadening in a bound level structure, which corresponds to the statistical limit, results in a Lorentzian line shape. The verification of the Ross concept<sup>3,5</sup> of spectral diffusiveness, which originates from interstate electronic relaxation in bound electronic-vibrational excitations of isolated large molecules, was fraught with experimental difficulties, as high-temperature gas-phase spectra contain a large thermal inhomogeneous contribution due to broad rotational contours and vibrational sequence congestions, so that the homogeneous contribution to the linewidth could not be disentangled. With the advent of the techniques of spectroscopy in seeded supersonic expansions, rotational broadening would drastically be reduced, while vibrational sequence congestion would practically be eliminated, revealing narrow (1–3  $\text{cm}^{-1}$  wide) rotational contours of vibrational-electronic excitations of isolated large molecules.<sup>7</sup> Recent interesting information emerging from fluorescence excitation<sup>8,9</sup> and absorption studies<sup>10</sup> in jets pertains to the Lorentzian homogeneous line broadening of the electronic origin of the second electronically excited singlet state of several isolated large molecules, i.e., the  $Q_y$  state of free-base porphine,<sup>9</sup> the Soret band of several porphyrins<sup>8</sup> and the  $S_2$  state of phenanthrene,<sup>10</sup> all of which correspond to the statistical limit of fast (ps and sub-ps) electronic relaxation.

The quantitative interrogation of the homogeneous line broadening of the vibronic component of the  $S_1$  state of the isolated azulene molecule is of considerable methodological interest within the general context of spectroscopic manifestations of fast intramolecular electronic relaxation from the

$S_1$  state.<sup>1–4</sup> Several unsuccessful attempts were made in this laboratory to observe laser-induced fluorescence (LIF) from the  $S_1$  state of azulene in axisymmetric and in planar supersonic jets. This failure is not surprising in view of the low fluorescence quantum yield ( $Y \approx 5 \times 10^{-6}$ )<sup>11</sup> from the thermally inhomogeneously broadened  $S_1$  origin and the low oscillator strength ( $f \approx 0.009$ )<sup>3</sup> for the  $S_0 \rightarrow S_1$  transition. Accordingly, the LIF intensity from the  $S_1$  origin of azulene is expected to be reduced by  $\sim 10^{-7}$ – $10^{-8}$  relative to that observed for the  $S_1$  origin of “conventional” large molecules (with  $Y \approx 0.1$ – $1$  and  $f \approx 0.5$ – $0.1$ ) in jets. We have applied the technique of absorption spectroscopy of large molecules in pulsed, planar, supersonic jets<sup>12,13</sup> to record the  $S_0 \rightarrow S_1$  transition of the isolated ultracold azulene. The spectral features corresponding to individual vibronic excitations within the  $S_1$  manifold exhibit excessive homogeneous broadening, which is in accord with the Ross spectral diffusiveness hypothesis. We have observed Lorentzian line broadening of the electronic origin and low-energy vibronic components within the  $S_1$  manifold, providing quantitative information on the dynamics of electronic relaxation.

## II. EXPERIMENTAL DETAILS

Absorption spectra of azulene cooled in pulsed planar supersonic jets were determined using a pulsed Xe lamp and monochromator.<sup>12,13</sup> Pulsed planar jets were produced by expansion of seeded Ar through the nozzle slit (dimensions 0.27 × 90 mm, repetition rate 9 Hz and temporal width of the gas pulse 300  $\mu\text{s}$ ). Azulene was heated in the nozzle chamber to 90–110 °C (vapor pressure  $p_M = 1$ –2 Torr<sup>14</sup>) and mixed with Ar at the stagnation pressure of 50–100 Torr. Light from a pulsed simmered Xe flashbulb (pulse duration 20  $\mu\text{s}$ ) was passed through an 0.3 mm monochromator equipped with a 1200 lines/mm grating. The spectral resolution of the monochromator (FWHM) with 10–60  $\mu$  slits was determined using an Hg lamp and an He/Ne laser. The monochromator wavelength was calibrated within an accuracy of  $\pm 0.5$  Å ( $\pm 1.0$   $\text{cm}^{-1}$ ) using an Hg lamp and an Hg/Ne laser. The light from the exit slit of the monochromator was focused onto the jet parallel to the slit at a distance of  $x = 10$  mm from it. The light beam was split and monitored by two photodiodes. The attenuation  $\Delta I$  of the light beam due to absorption was determined from the difference in the light intensity before and after crossing the planar jet, and was

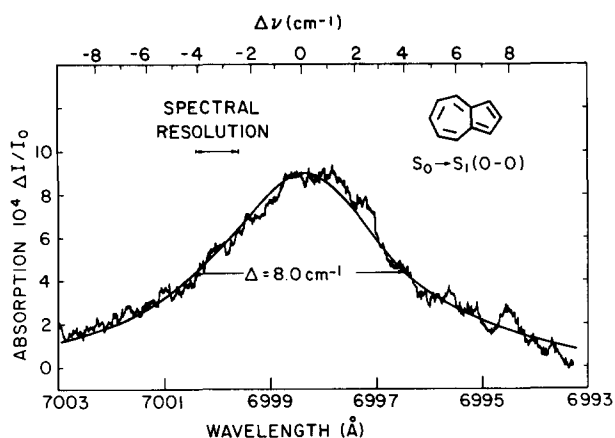


FIG. 1. Absorption spectrum in the region 6993–7003 Å of azulene in planar supersonic jets of Ar. Azulene was heated in the nozzle chamber to 110 °C, mixed with Ar and expanded through the 0.27 × 90 mm nozzle slit. The spectral resolution was 1.5 cm<sup>−1</sup> and is marked on the figure. The solid line represents the Lorentzian fit of the absorption line shape, which corresponds to the  $S_0 \rightarrow S_1$  electronic origin.

normalized by the incident light intensity  $I_0$  to give the absorption  $\Delta I/I_0$ . The signals were recorded when temporal matching of the gas pulse from the nozzle and the light pulse occurred. In view of the low oscillator strength<sup>3</sup> ( $f \approx 0.009$ ) for the  $S_0 \rightarrow S_1$  transition, which is manifested in a low absorption coefficient in the bulb (e.g.,  $\epsilon \sim 100 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>11</sup> and the homogeneous broadening of the  $S_1$  electronic origin of azulene, high experimental sensitivity was required. The noise level accomplished in these experiments was  $10^{-4} I_0$ . The absorption signals recorded were in the range  $\Delta I/I_0 = (1\text{--}25) \times 10^{-4}$ . These values of absorption for the  $S_0 \rightarrow S_1$  transition of azulene were lower by about two orders of magnitude than those recorded for the  $S_0 \rightarrow S_2$  transition of this molecule (in the range 3480–3250 Å) or for  $S_0 \rightarrow S_1$  transitions of anthracene<sup>12</sup> and tetracene<sup>15</sup> measured in the same experimental setup. Because of the high material consumption rates and long integration times utilized in the measurement of the  $S_0 \rightarrow S_1$  absorption of azulene, we were unable to record simultaneously the entire vibronic manifold and individual vibronic components had to be recorded separately.

### III. RESULTS AND ANALYSIS

The absorption spectrum of azulene in planar jets of Ar exhibits in the spectral range 6900–7200 Å a single prominent broad absorption band peaking at  $6998.2 \pm 1.0 \text{ Å}$  (Fig. 1). This spectral feature is due to the bare azulene molecule. No spectroscopic evidence for the appearance of azulene-Ar van der Waals molecules and of azulene dimers could be obtained under our experimental conditions. The  $6998.2 \pm 1.0 \text{ Å}$  ( $\nu_0 = 14\,289 \pm 2 \text{ cm}^{-1}$ ) feature is attributed to the 0–0 electronic origin of the first spin-allowed  $S_0 \rightarrow S_1$  ( $^1A_1 \rightarrow ^1B_1$ ) transition of azulene. Converting the wavelength in air to vacuum results in the corrected energy  $\bar{\nu}_0 = 14\,285 \pm 2 \text{ cm}^{-1}$  for the  $S_0 \rightarrow S_1$  electronic origin of azulene in jets. The location of the origin agrees with the energy  $\bar{\nu}_0 = 14\,284 \text{ cm}^{-1}$  measured by McCoy<sup>4</sup> for this transition of gaseous azulene.

Environmental medium shifts of the  $S_1$  origin of azulene are of some interest. The relevant energetic data for the peak energies are summarized in Table I. This transition exhibits a blue spectral shift,<sup>4</sup> in contrast to the trend of dispersive red medium-induced spectral shifts, which were documented for the  $S_0 \rightarrow S_1$  transitions of a variety of nonpolar aromatic molecules in solid state hosts and in van der Waals complexes.<sup>16</sup> In view of the low oscillator strength of the azulene  $S_0 \rightarrow S_1$  transition ( $f \approx 0.009$ ), the contribution of dispersive excited-state stabilization interactions is small and the major contribution to the blue spectral shift originates from electrostatic interactions induced by the large change in the permanent dipole moment  $|\Delta\mu| \approx 2 \text{ D}$  between the  $S_1$  and  $S_0$  states.<sup>4</sup> In this context, it will be extremely interesting to study the absorption spectra of van der Waals complexes of azulene with nonpolar and polar solvents. However, in view of the excessive line broadening, this is by no means an easy task.

The most striking feature of the  $S_1$  origin band (Fig. 1) is its appreciable line broadening. The line profile of the  $S_0 \rightarrow S_1$  origin was found to be independent on the stagnation pressure of Ar and on the vapor pressure of azulene in the nozzle chamber. This line profile could be fitted into a Lorentzian. As is apparent from Fig. 1, the Lorentzian fit is adequate over approximately four linewidths. The Lorentzian line profile of the  $S_0 \rightarrow S_1$  origin qualitatively differs

TABLE I. Energetics of the  $S_0 \rightarrow S_1$  origin of azulene.

Medium	Peak energy (cm <sup>−1</sup> )	Spectral shift (cm <sup>−1</sup> )	Width (cm <sup>−1</sup> )	Comments	Reference
Planar supersonic jet	14 285	0	8.0	Lorentzian line shape spectral resolution 1.6 cm <sup>−1</sup> rotational contour $\sim 3.4 \text{ cm}^{-1}$	Present work
Gas phase 40 °C 0.08 Torr	14 284	...	$\sim 10$	Bands poorly defined due to vibrational congestion	McCoy (Ref. 4)
Naphthalene 4 K	14 652	+ 365	2.1	Lorentzian line shape inhomogeneous broadening 0.47 cm <sup>−1</sup>	Hochstrasser and Li (Ref. 23)
Naphthalene- <i>d</i> <sub>8</sub> 4 K	14 657	+ 360	2.1	Lorentzian line shape inhomogeneous broadening $\sim 0.5 \text{ cm}^{-1}$	Hochstrasser and Li (Ref. 23)
Crystalline azulene 4 K	$14\,630 \pm 20$	+ 340	$\sim 100$	Inhomogeneous broadening due to disordered orientation of dipoles	Hunt and Ross (Ref. 4)

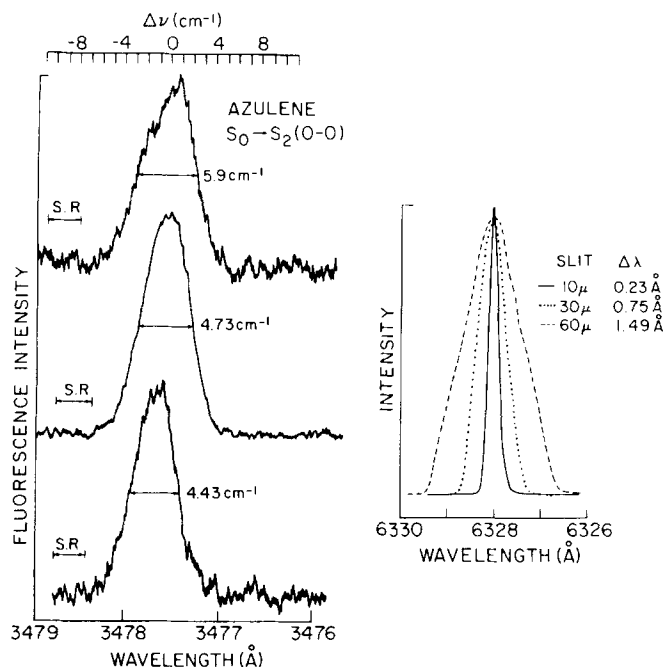


FIG. 2. Fluorescence excitation spectra of the  $S_0 \rightarrow S_2$  electronic origin of azulene in planar supersonic jets of Ar in the spectral range 3476–3479 Å. Azulene was heated in the nozzle chamber to 105 °C. The three spectra were obtained under different experimental conditions: (a) Top spectrum  $p(\text{Ar}) = 50$  Torr,  $\Delta\nu(\text{SR}) = 2.9 \text{ cm}^{-1}$ , (b) Middle spectrum  $p(\text{Ar}) = 80$  Torr,  $\Delta\nu(\text{SR}) = 3.3 \text{ cm}^{-1}$ , and (c) Lower spectrum  $p(\text{Ar}) = 80$  Torr,  $\Delta\nu(\text{SR}) = 2.9 \text{ cm}^{-1}$ . The spectral resolution (SR) is marked by horizontal arrows. The widths  $\Delta_2$  of the spectral features (FWHM) are also marked. The insert on the right-hand side of the figure represents a calibration of the spectral resolution using an He/Ne laser. The slit widths and the width (FWHM) of the signals (in Å) are marked in this insert.

from the asymmetric quasi-Gaussian line shape exhibited by the  $S_0 \rightarrow S_2$  origin of azulene, which is located at 3478 Å (Fig. 2). The Lorentzian profile of the broad  $S_0 \rightarrow S_1$  origin points towards a substantial homogeneous broadening of this spectral feature. In order to demonstrate the occurrence of homogeneous line broadening, we have shown that the linewidth  $\Delta_1$  of the  $S_0 \rightarrow S_1$  origin (Table II) considerably exceeds the spectral resolution and the rotational broadening. In order to provide an estimate of the rotationally broadened line width  $\Delta_2$  of the  $S_0 \rightarrow S_2$  origin, which are summarized in Table II. The spectral resolution

$\Delta\nu(\text{SR})$  was determined independently by calibrating the spectrograph using an Hg lamp and an He/Ne laser. The rotational broadening  $\Delta\nu(\text{ROT})$  was extracted using a Gaussian deconvolution procedure

$$\Delta\nu(\text{ROT}) = [\Delta_2^2 - \Delta\nu(\text{SR})^2]^{1/2}. \quad (3.1)$$

The value of  $\Delta\nu(\text{ROT})$  for the  $S_2$  origin (Table II) was found to be independent of the spectral resolution, inspiring confidence in our procedure. We have found that  $\Delta\nu(\text{ROT})$  decreases with increasing stagnation pressure due to the decrease in the rotational temperature (Table II). In the absence of direct experimental information on the rotational width of the  $S_0 \rightarrow S_1$  origin, we have assumed that the rotational broadening of the  $S_1$  and  $S_2$  origins are equal. Although the changes in the rotational contours of the  $S_0 \rightarrow S_2$  transition ( $\Delta A \sim 0$  and  $\Delta B \sim -0006 \text{ cm}^{-1}$ )<sup>17</sup> differ from those for the  $S_0 \rightarrow S_1$  transition ( $\Delta A \sim 0.00065 \text{ cm}^{-1}$  and  $\Delta B \sim -0.0007 \text{ cm}^{-1}$ ),<sup>17</sup> we expect that at the low temperature conditions ( $T_R = 10\text{--}15 \text{ K}$ ), employed herein, the widths of the rotational contours of *a*-type and *b*-type origins are similar. Accordingly, we take  $\Delta\nu(\text{ROT}) = 3.4 \text{ cm}^{-1}$  for the  $S_0 \rightarrow S_1$  origin of azulene, under the experimental conditions of Fig. 1 and Table II. As is apparent from the data of Table II, we have for the linewidth of the  $S_1$  origin

$$\Delta_1^2 \gg \Delta\nu(\text{ROT})^2, \quad \Delta\nu(\text{SR})^2. \quad (3.2)$$

The observation of a broad Lorentzian line shape for the  $S_1$  electronic origin, whose width exceeds the spectral resolution and the inhomogeneous rotational broadening, provides strong evidence for homogeneous broadening. For the  $S_1$  electronic origin of the isolated molecule, the homogeneous broadening does originate from electronic relaxation.

To provide a quantitative estimate of the homogeneous Lorentzian linewidth, we have deconvoluted from the experimental Lorentzian linewidth two quasi-Gaussian contributions, which are due to the spectral resolution and to the rotational broadening. The width (FWHM),  $\Gamma$ , of the homogeneous contribution is given by

$$\Gamma = \frac{\Delta_1^2 - \{[\Delta\nu(\text{ROT})^2 + \Delta\nu(\text{SR})^2]/2 \ln 2\}}{\Delta_1}. \quad (3.3)$$

The data of Table II result in the homogeneous width  $\Gamma = 6.8 \text{ cm}^{-1}$ . The electronic relaxation lifetime for the  $S_1$  electronic origin of isolated azulene is  $\tau = \hbar/\Gamma \simeq 0.8 \text{ ps}$ . As a

TABLE II. Line broadening data for the electronic origins of the  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  origins of azulene in jets.

Transition	Experimental conditions <sup>a</sup>	Lineshape <sup>b</sup>	Linewidth <sup>c</sup> $\Delta$ (cm <sup>-1</sup> )	Spectral resolution $\Delta\nu(\text{SR})$ (cm <sup>-1</sup> )	Half-width of rotational contour $\Delta\nu(\text{ROT})$ (cm <sup>-1</sup> )	Homogeneous width <sup>e</sup> $\Gamma$ (cm <sup>-1</sup> )
$S_0 \rightarrow S_1(0)$	$p = 80$ Torr	L	8.0	1.53	(3.4) <sup>d</sup>	6.7
	$p = 80$ Torr	L	8.7	3.06	(3.4) <sup>d</sup>	6.9
	$p = 50$ Torr	L	8.8	3.06	(4.4) <sup>d</sup>	6.5
$S_0 \rightarrow S_2(0)$	$p = 50$ Torr	NL	5.29	2.90	4.42	...
	$p = 80$ Torr	NL	4.43	2.90	3.35	...
	$p = 80$ Torr	NL	4.73	3.31	3.38	...

<sup>a</sup>  $p$ —stagnation pressure of Ar.

<sup>b</sup> L—Lorentzian. NL—nonLorentzian.

<sup>c</sup> All linewidths given for FWHM.

<sup>d</sup> Assumed to be equal to  $\Delta\nu(\text{ROT})$  of the  $S_2$  origin obtained under the same experimental conditions.

<sup>e</sup> Calculated from Eq. (3.3).

conservative estimate for the uncertainty range for  $\tau$ , we take as a lower limit the value  $\hbar/\Delta_1$ , while for the upper limit we assert that  $\Delta\nu(\text{ROT})$  has been underestimated by 50%. These considerations result in  $\tau = 0.8 \pm 0.2$  ps for electronic relaxation from the  $S_1$  origin of isolated azulene.

We have observed two additional broad spectral features in the  $S_0 \rightarrow S_1$  transition of azulene, whose peaks are located at the energies 659 and 1394  $\text{cm}^{-1}$  above the  $S_1$  origin (Fig. 3). As is apparent from Table III, the energies of these two spectral features are in excellent agreement with the most intense vibrations in the  $S_1$  manifold recorded in the gas phase<sup>4</sup> and in the mixed crystal.<sup>18</sup> The 659  $\text{cm}^{-1}$  spectral feature in the range 6684.5–6694.5 Å reveals a Lorentzian line shape (Fig. 3) with a width  $\Delta = 11.1$   $\text{cm}^{-1}$  which, after corrections for spectral resolution and rotational broadening (Table III), results in  $\Gamma = 9.6$   $\text{cm}^{-1}$ . The 659  $\text{cm}^{-1}$  vibration is sufficiently low in energy so that intrastate coupling effects, which result in intramolecular vibrational redistribution, are not expected to be severe. Accordingly, the lifetime  $\tau = 0.6$  ps of the  $S_1$  (659  $\text{cm}^{-1}$ ) vibration is attributed to interstate electronic relaxation. The situation is different for the spectral feature in the range 6363.0–6383.5 Å, which exhibits a compound line shape (Fig. 3). This spectral feature could be resolved into a broad Lorentzian profile peaking at 6376.3 Å, together with an additional broad band on its high energy side (Fig. 3). At this relatively high excess vibrational energy of 1394  $\text{cm}^{-1}$  in the  $S_1$  manifold of this large molecule intrastate coupling prevails, being manifested by the appearance of Fermi resonances and/or by extra line broadening.<sup>7</sup> The width of the Lorentzian profile is 15.4  $\text{cm}^{-1}$  which, after correction to spectroscopic resolution and rotational broadening, results in  $\Gamma = 14.3$   $\text{cm}^{-1}$ . The homogeneous width of this high 1394  $\text{cm}^{-1}$  vibrational excitation cannot be attributed to interstate electronic relaxation, as the decay rate may contain a contribution from intrastate vibrational energy redistribution. Accordingly, the value of  $\tau = 0.4$  ps at this energy constitutes a lower limit for the electronic relaxation lifetime.

#### IV. DISCUSSION

The observation of homogeneous line broadening of individual vibronic excitations within the  $S_1$  manifold of jet-cooled azulene is of methodological interest, providing a quantitative verification for the concept of Lorentzian relaxation line broadening within a bound level structure of an isolated large molecule. The Lorentzian line profiles of the  $S_1$  electronic origin and the 694  $\text{cm}^{-1}$   $S_1$  vibrational excitation in isolated azulene manifest the consequences of interstate coupling and electronic relaxation in the statistical limit. From the practical point of view, quantitative information has been inferred concerning the ultrafast intramolecular electronic process in isolated azulene. The lifetimes for electronic relaxation from the  $S_1$  manifold were found to be  $\tau = 0.8 \pm 0.2$  ps for the origin,  $\tau = 0.6 \pm 0.2$  ps for the 694  $\text{cm}^{-1}$  vibration and  $\tau > 0.4$  ps for the 1394  $\text{cm}^{-1}$  vibrational excitation. The lifetimes are somewhat shorter than the corresponding ps lifetimes reported for the  $S_1$  state of azulene in condensed phases.<sup>19–24</sup> Following the pioneering work of Rentzepis,<sup>19</sup> several time-resolved measurements of the de-

cay of the  $S_1$  state of azulene in solution were conducted,<sup>20–24</sup> where excitation was performed at the excess vibrational energy  $E_V$  above the electronic origin. Huppert *et al.*<sup>24</sup> reported  $\tau = 4 \pm 3$  ps at  $E_V \approx 4800$   $\text{cm}^{-1}$  and  $\tau = 3 \pm 2$  ps at  $E_V \approx 2000$   $\text{cm}^{-1}$ , while Ippen *et al.* observed<sup>22</sup>  $\tau = 1.9 \pm 0.2$  ps at  $E_V \approx 1800$   $\text{cm}^{-1}$ . These solution data do not interrogate the electronic relaxation from a well-defined initial  $E_V$

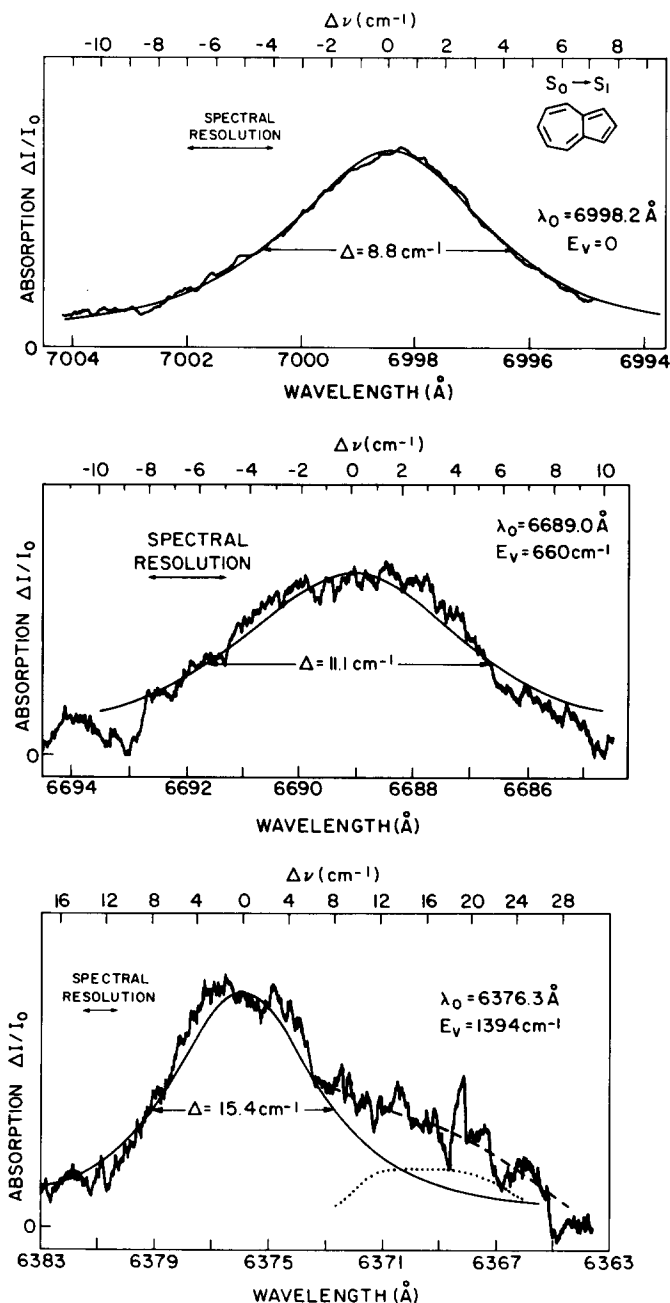


FIG. 3. Absorption features of the azulene molecule in planar supersonic jets of Ar in the ranges 7004–6994, 6694–6685, and 6383–6363 Å. Azulene was heated in the nozzle chamber to 105 °C. The stagnation pressure of Ar was  $p(\text{Ar}) = 80$  Torr. The spectral resolution was 3.1  $\text{cm}^{-1}$  and is marked by horizontal arrows. The wavelengths  $\lambda_0$  of the peak positions and their energies  $E_V$  above the  $S_1$  origin are marked. The solid lines represent the Lorentzian fits of the absorption features. The absorption line profiles for the  $S_1$  electronic origin and for the  $S_1$  (660  $\text{cm}^{-1}$ ) excitation correspond to a single Lorentzian. The  $S_1$  (1394  $\text{cm}^{-1}$ ) excitation exhibits a compound line profile consisting of a Lorentzian (solid line) and an extra contribution (dashed line).

TABLE III. Energetics and line broadening of some spectral features for the  $S_0 \rightarrow S_1$  transition of isolated azulene.

Position <sup>a,b</sup> (Å)	$E_\nu$ <sup>a,c</sup> (cm <sup>-1</sup> )	$E_\nu$ (cm <sup>-1</sup> )		$\Delta$ <sup>a,b</sup> (cm <sup>-1</sup> )	$\Gamma$ <sup>a,f</sup> (cm <sup>-1</sup> )	$\tau$ <sup>a</sup> (ps)
		Gas phase <sup>d</sup>	Mixed crystal <sup>e</sup>			
6998.2	0	0	0	8.7	6.8	0.8 <sup>h</sup>
6689.0	660	659	662	11.1	9.6	0.6
6376.3 <sup>g</sup>	1394	1395	1388	(15.4)	(14.3)	(0.4) <sup>i</sup>

<sup>a</sup> Present work.<sup>b</sup> Experimental conditions for jet spectroscopy:  $p = 80$  Torr,  $\Delta\nu(\text{SR}) = 3.1 \text{ cm}^{-1}$ .<sup>c</sup>  $E_\nu$ —peak energy with respect to the electronic origin.<sup>d</sup> Hunt and Ross, Ref. 4.<sup>e</sup> Small and Kuserov, Ref. 18.<sup>f</sup> Estimated from Eq. (3.3) with  $\Delta\nu(\text{SR}) = 3.1 \text{ cm}^{-1}$  and  $\Delta\nu(\text{ROT}) = 3.4 \text{ cm}^{-1}$ .<sup>g</sup> Compound line shape. Spectral data given for the major component.<sup>h</sup> Lifetime for electronic relaxation from the electronic origin.<sup>i</sup> Lifetime may contain contribution from Fermi resonances and vibrational redistribution.

range, as it is impossible to separate interstate electronic relaxation and medium-induced vibrational relaxation.<sup>24</sup> This difficulty can be overcome in a dense medium by interrogating the relaxation from the electronic origin, which was explored by Hochstrasser and Li,<sup>23</sup> whose spectroscopic line broadening data result in  $\Gamma = 1.61 \text{ cm}^{-1}$  and  $\tau = 3 \text{ ps}$  for the  $S_1$  origin of azulene in naphthalene. The value of  $\tau = 0.8 \pm 0.2 \text{ ps}$  obtained herein for the lifetime of the electronic origin of the isolated molecule is shorter by a numerical factor of  $\sim 3\text{--}4$  for the lifetime of this state in the mixed crystal. This medium effect on the lifetime for electronic relaxation is intriguing, as the standard theory of electronic radiationless transitions<sup>25</sup> implies that in an "inert" medium, which does not modify the intramolecular coupling and the energy levels, the relaxation rate from the electronic origin is invariant with respect to medium perturbations. The enhancement of the decay rate of the  $S_1$  origin of bare azulene may be at least partially rationalized in terms of the energy gap law for electronic relaxation. The reduction of the  $S_1 \rightarrow S_0$  electronic energy gap  $\Delta E$  in the bare molecule relative to  $\Delta E$  in the mixed crystal (Table I) will result in the increase of the internal conversion rate in the former case. However, the medium-induced change of  $\Delta E$  by  $365 \text{ cm}^{-1}$  appears to be too small to account for the medium effect on the electronic relaxation rate. We conjecture that the retardation of the nonradiative decay rate in the mixed crystal, relative to the isolated molecule, may originate from the clamping of some vibrational modes in the condensed phase. Spectroscopic evidence demonstrates the occurrence of medium-induced clamping of out-of-plane molecular modes of a guest molecule.<sup>26</sup> Provided that these modes act as accepting or promoting modes for the intramolecular internal conversion process, the unique medium-induced retardation of this radiationless transition process can be rationalized.

This work has been concerned with spectroscopic implications of ultrafast intramolecular electronic relaxation. In order to extract quantitative information from line broadening on the dynamics of interstate relaxation in isolated large molecules in jets, the following necessary conditions must be fulfilled:

(1) The occurrence of homogeneous broadening has to be inferred. The width of the spectral features exceeds the rotational envelope.

(2) A proper deconvolution of the homogeneous line shape by correction for rotational broadening and instrumental resolution has to be performed.

(3) A Lorentzian line shape of the deconvoluted width has to be demonstrated.

(4) Separation between electronic relaxation and intramolecular vibrational relaxation has to be ensured. Only homogeneous broadening of the 0-0 origin and possibly of low vibrational excitations, which do not suffer from intrastate coupling and intramolecular vibrational energy redistribution, can be utilized to extract quantitative information on electronic relaxation.

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