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# Analytical Applications of Supersonic Jet Spectroscopy

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**We report some applications of the techniques of laser spectroscopy of large molecules seeded in centrosymmetric supersonic expansions and in planar supersonic expansions of rare gases for the identification of large organic molecules, for the sensitive detection of minor amounts of organic molecules, and for isotopic analysis. Laser-induced fluorescence and energy-resolved emission in jets are useful for high-resolution ( $<3\text{ cm}^{-1}$ ) chemical analysis and for isotopic analysis. The utilization of planar supersonic expansions for the sensitive detection of minor traces of organic impurities allows for the detection of fluorescent large molecules whose vapor pressure at  $200^\circ\text{C}$  exceeds  $10^{-7}$  torr and for detection of impurities at concentrations exceeding 1 ppm.**

Fluorescent analysis of organic compounds provides a selective and sensitive analytical method (1-3). Traditional fluorescence excitation spectra and emission spectra of large organic molecules in solution at room temperature are extremely broad (4). Typical line widths of electronic-vibrational excitations of large molecules are  $100\text{--}1000\text{ cm}^{-1}$ . These huge magnitudes of line broadening, which are comparable to the vibrational spacings, originate from two major causes.

(1) Thermal vibrational sequence congestion (5). At room temperature the large molecules are thermally excited, occupying a multitude of vibrational levels. As the vibrational frequencies are different in the ground and in the excited electronic states, the thermally excited vibrational population of the electronic ground state will result in appreciable broadening of the electronic-vibrational transitions.

(2) Inhomogeneous broadening (6-8). Different solvent configurations around the large molecule will result in a statistical distribution of solvent shifts, leading to appreciable line broadening.

These thermal broadening and inhomogeneous broadening effects intrinsically limit the selectivity of fluorescent analytical methods. One can avoid inhomogeneous broadening effects in condensed phases by the utilization of the techniques of laser fluorescence line narrowing (7, 8). Alternatively, these effects can be circumvented by conducting fluorescence excitation in the low-pressure gas phase (9). However, the low volatility of large molecules requires high temperatures. Although fluorescence excitation and emission spectra of very large molecules, such as porphyrins (10), can be studied in the gas phase, the high temperatures required to obtain sufficient vapor pressure will result in drastic thermal vibrational sequence congestion effects. A powerful way to eliminate vibrational sequence congestion to obtain high-resolution vibrationally resolved spectra of large molecules rests on the use of supersonic expansions (11-13), sometimes referred to as jets, for effective internal cooling of large molecules (14-17). The recent use of such supersonic jets of rare gases seeded with large molecules provides a source of internally, cold, "isolated", large molecules, which can be interrogated by laser-induced fluorescence (LIF) (11-27) methods. The reduction of the line width in the LIF spectra of large molecules from  $100\text{ to }1000\text{ cm}^{-1}$  in solutions and in high-temperature gas phase to  $1\text{--}3\text{ cm}^{-1}$  in supersonic ex-

pansions allows for the increase of spectral resolution in supersonic expansions by 2 to 3 orders of magnitude over that accomplished in conventional spectroscopy of large molecules. These techniques were utilized extensively in the exploration of excited-state energetics and dynamics of large molecules (14-27). These novel techniques have exciting analytical applications. Small et al. (28-30) recently proposed and demonstrated the broad applicability of LIF in jets for the analysis of organic pollutants. In this paper we consider some of the implications and applications of laser spectroscopy in seeded supersonic jets to analytical chemistry. The following problems will be addressed:

(a) Identification of large organic molecules. The remarkable spectral resolution accomplished in seeded supersonic jets can readily be exploited for a highly selective identification method of molecules in a mixture. Small et al. have utilized the LIF method for the identification of chemical isomers of methylnaphthalenes (28-30). We shall show how the combination of LIF and energy-resolved fluorescence methods results in a selective and sensitive identification method. For this purpose conventional supersonic expansions, where the seeded gas is expanded through a pinhole, can be utilized.

(b) Sensitive detection of minor amounts of impurities of organic molecules. We have developed recently a pulsed, supersonic source for the production of planar jets, which involves expansion of a seeded gas through a long slit (31, 32). The use of planar jets makes it possible to enhance the detection sensitivity by LIF by 2 to 3 orders of magnitude over that accomplished with conventional supersonic sources, whereupon low impurity concentrations of fluorescent impurities are amenable to selective identification by LIF methods.

(c) Isotopic spectroscopic analysis. The high spectral resolution accomplished for fluorescence excitation spectroscopy in supersonic expansions can be extremely useful for the identification and quantitative determination of molecules which differ in their isotopic composition.

## EXPERIMENTAL SECTION

**Conventional Supersonic Jets.** The construction and operation of conventional supersonic sources utilized in this laboratory have been described previously (17, 23-30). Briefly, supersonic free expansion of seeded Ar was conducted through a circular nozzle of a diameter  $D = 150\text{ }\mu\text{m}$ . The supersonic nozzle is produced by mechanically drilling a  $150\text{-}\mu\text{m}$  hole in a  $100\text{ }\mu\text{m}$  tantalum or stainless steel disk. The disk is attached to a stainless steel sample chamber, which contains a solid sample of the molecule. The sample chamber could be heated up to  $400^\circ\text{C}$ . The temperature was chosen to obtain a vapor pressure of  $10^{-2}\text{--}1$  torr of the organic molecules. The Ar gas at stagnation pressures of  $p = 50\text{--}300$  torr was mixed in the sample chamber with the organic vapor and sent through the nozzle. We have demonstrated that effective internal rotational-vibrational cooling of large molecules can be accomplished at moderately low stagnation pressures of Ar,  $p = 150\text{--}300$  torr. Accordingly, a "poor man's" medium-sized simple pumping system, consisting of a 6 in. diffusion pump backed by a rotating pump (with a pumping speed of  $500\text{ L min}^{-1}$ ), was employed in the supersonic jet apparatus (17).

Fluorescence excitation of the large molecules in the supersonic expansion was induced by crossing the laser beam with the su-

personic expansion at a distance of  $x = 3\text{--}7$  mm down the nozzle.

**Planar Supersonic Expansions.** A nozzle slit source (31, 32) for the production of pulsed, planar supersonic jets was constructed from two concentric cylinders. Slits of dimensions 0.2 mm wide and 35 mm long were machined in the internal cylinder (length 70 mm, diameter 20 mm, wall thickness 0.5 mm) and in the external cylinder, whose inside diameter matched the outside diameter of the internal cylinder within a tolerance of 0.02 mm. The outer wall of the internal cylinder was lubricated with  $\text{MoS}_2$  powder. The internal cylinder was spun by a motor. The characteristics of the pulsed, supersonic, nozzle slit sources had a repetition rate of  $\sim 12$  Hz and a pulse width of  $\sim 150$   $\mu\text{s}$ . The source could be heated up to 200  $^\circ\text{C}$ . A sample of the molecule was placed near the inner cylinder, heated to give a vapor pressure of  $\sim 0.1$  torr, and mixed with Ar gas in the pressure range  $p = 20\text{--}100$  torr, which was fed into the inner cylinder. The pumping system consisted of two mechanical pumps, the pumping speed of the system being 700  $\text{L min}^{-1}$ . Light from a dye laser crossed the supersonic expansion parallel to the long axis of the slit at a distance of 4–15 mm from the source. The temporal coincidence between the laser pulses and the supersonic gas pulses was achieved by use of an IR optical switch (Spectronix 1874-14) and a homemade variable delay unit. The mechanical jitter was about 10  $\mu\text{s}$  and could be reduced further.

**Laser Spectroscopy.** The seeded supersonic beam was crossed by a nitrogen pumped dye laser (Moletron DL2), whose wavelength could be varied in the range 3600–7000  $\text{\AA}$ , while the frequency doubled (by an angle-tuned KDP crystal) laser radiation could be tuned in the range 2880–3000  $\text{\AA}$ . The characteristics of the laser were a pulse energetic width 0.3  $\text{cm}^{-1}$  (as determined by optogalvanic atomic spectroscopy), a temporal Gaussian pulse profile with a duration of 4 ns, output power of 10 kW, and repetition rate of 20 Hz. For elimination of effects of spurious daylight and of laser stray light, the laser beam was baffled at the entrance and at the exit tubes connected to the vacuum system. We have recorded:

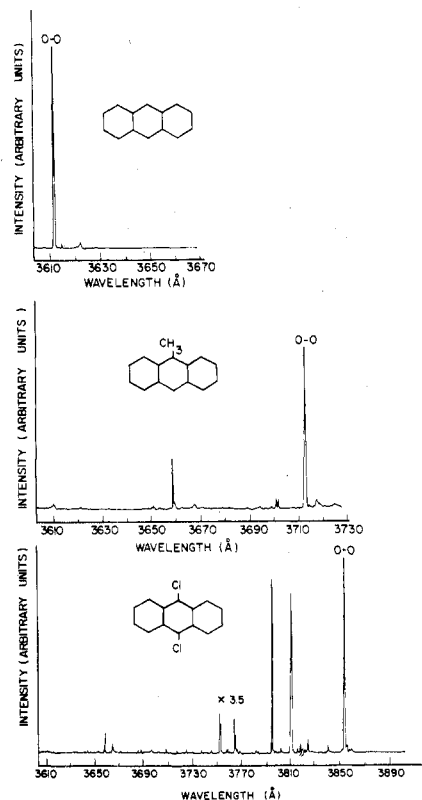
(1) Laser fluorescence excitation spectra. These correspond to the intensity of the total fluorescence vs. the laser wavelength, which was continuously scanned. The total emitted fluorescence was passed through appropriate glass filters and imaged by a lens (35 mm focal length) on a fast photomultiplier. The output of the photomultiplier was recorded by a boxcar integrator after normalization to the laser intensity. The spectral resolution is limited by the laser energetic width of 0.3  $\text{cm}^{-1}$ .

(2) Energy-resolved emission spectra. These correspond to the energy-resolved fluorescence resulting from excitation at a fixed laser wavelength. The emitted fluorescence was imaged by a lens onto the entrance slit of a monochromator (Jarrel-Ash  $1/4$  m) and detected by a photomultiplier. The spectral resolution in these spectra, determined by the monochromator, was 7  $\text{\AA}$  (30  $\text{cm}^{-1}$  at 4000  $\text{\AA}$ ).

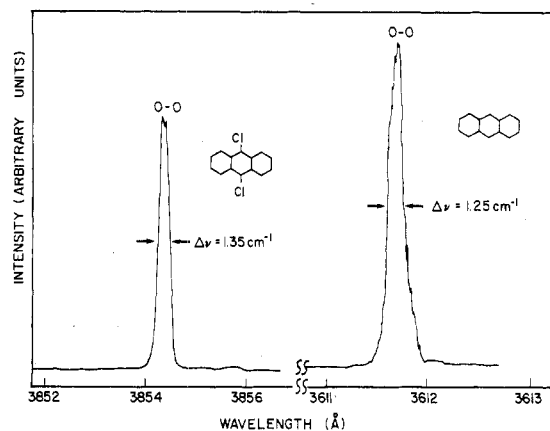
(3) Time-resolved emission, corresponding to the time-resolved fluorescence, excited at a fixed laser wavelength. The filtered total fluorescence was imaged by a lens on a fast photomultiplier. The output of the photomultiplier was measured by a Biomation (Model 6100) transient recorder (with a spacing 2 ns between consecutive channels) and averaged by a home-built signal averager or a PAR (Model 4200) averager. Decay lifetimes exceeding 5 ns could be obtained from the output without the necessity of performing any deconvolution procedures (24).

## RESULTS

**Identification of Large Aromatic Molecules.** Laser-induced fluorescence excitation spectroscopy in conventional supersonic expansions is expected to be extremely useful for the identification of specific organic molecules. In Figure 1 we present the fluorescence excitation spectra of anthracene and two of its derivatives, i.e., 9-methylantracene and 9,10-dichloroanthracene. These spectra reveal the electronic-vibrational transitions involving the first spin-allowed  $S_0 \rightarrow S_1$  electronic excitation of these molecules. Each distinct feature in the spectra corresponds to an individual electronic-vibrational transition. The lowest energy, longest wavelength, pronounced spectral feature in each spectrum corresponds to the (0–0) transition from the lowest vibrational level

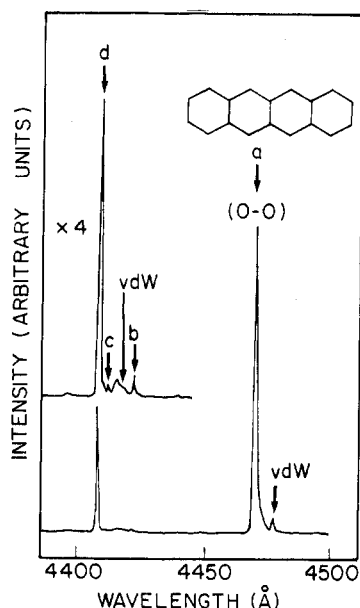


**Figure 1.** Fluorescence excitation spectra of (a) anthracene, (b) 9-methylantracene, and (c) 9,10-dichloroanthracene seeded in supersonic axisymmetric ( $D = 150$   $\mu\text{m}$ ) expansions of Ar. Anthracene was heated in the sample chamber to 130  $^\circ\text{C}$  and seeded in Ar at the pressure of  $p = 350$  torr. 9-Methylantracene was heated in the sample chamber to 130  $^\circ\text{C}$  and seeded in Ar at  $p = 180$  torr. 9,10-Dichloroanthracene was heated in the nozzle chamber to 180  $^\circ\text{C}$  and seeded in Ar at  $p = 200$  torr. This spectrum in the range 3605–3820  $\text{\AA}$  is scaled by a factor of 3.5. The exciting dye laser crossed the supersonic expansion 5 mm down the nozzle.



**Figure 2.** Medium resolution fluorescence excitation spectra (spectral resolution of 0.3  $\text{cm}^{-1}$ ) of the electronic origin of anthracene and of 9,10-dichloroanthracene in supersonic expansions of Ar. All experimental conditions are as in Figure 1. Each spectrum is displayed on a different relative intensity scale. Widths of the spectral features (fwhm) are marked.

of the ground electronic state  $S_0$  to the vibrationless level of the first electronically excited singlet state  $S_1$ . Spectral features at higher energies beyond the electronic origin correspond to vibrational excitations within the  $S_1$  manifold. The individual spectral features are remarkably narrow, as demonstrated in Figure 2, where we display the 0–0 electronic origins of anthracene and of 9,10-dichloroanthracene on an expanded wavelength scale. The width of individual spectral features is  $\sim 0.2$   $\text{\AA}$  ( $\sim 1.4$   $\text{cm}^{-1}$ ), originating essentially from



**Figure 3.** The fluorescence excitation spectrum in the range 4500–4400 Å of tetracene (heated in the sample chamber to 220 °C) seeded in Ar at the backing pressure of  $p = 180$  torr and expanded through a  $D = 150$   $\mu\text{m}$  circular nozzle. The laser crossed the supersonic expansion at 7 mm down the nozzle. The spectrum exhibits the electronic origin (band (a)) and the prominent 314  $\text{cm}^{-1}$  vibration of tetracene. Two weak features marked vdW were identified to correspond to tetracene–Ar van der Waals complexes (see text). The weak features marked (b) and (c) were identified by using the technique of energy-resolved emission.

unresolved rotational structure (16, 17, 24).

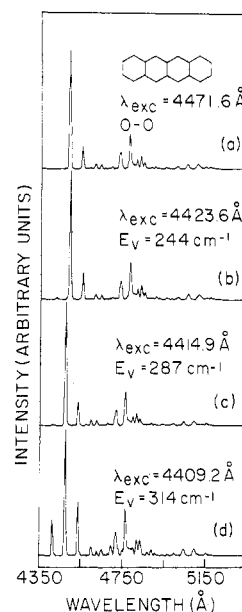
The internal vibrational temperature of the large molecules is sufficiently low ( $<30$  K) (17) so that only the lowest vibrational level of  $S_0$  is populated. Thus, each distinct spectral feature corresponds to an individual electronic–vibrational excitation from the lowest vibrational state of  $S_0$  to a vibronic level in the  $S_1$  manifold. Each vibrational excitation is broadened by rotational excitations. The moments of inertia of these large molecules are extremely large, characteristic rotational energies being  $\sim 10^{-2}$   $\text{cm}^{-1}$ , corresponding to an effective temperature of  $\sim 1.5 \times 10^{-2}$  K. Accordingly, the cooling of the rotational motion to a low rotational temperature of 5–10 K (17) achieved in the supersonic expansion is insufficient to accomplish effective rotational cooling and high rotational states will remain populated, so that rotational broadening will still prevail. Regarding the relative intensities of the individual vibronic features, we would like to point out that in these electronic–vibrational spectra the most intense vibrational feature involves the 0–0 transition, as these large aromatic molecules exhibit only a small change in their equilibrium nuclear configuration upon electronic excitation.

The remarkable spectral resolution achieved in the supersonic expansion makes it possible to distinguish between spectral features of distinct large molecules, whose positions differ by more than 3  $\text{cm}^{-1}$  ( $\sim 0.3$  Å at 3000 Å,  $\sim 0.5$  Å at 4000 Å or  $\sim 0.6$  Å at 6000 Å). The immediate analytical implications for identification of molecules are as follows:

(1) The position of the electronic origin and of the low-lying vibrational excitations of a large molecule provides a unique energetic “fingerprint” pattern for the identification of the molecule.

(2) The high specificity of the method is ensured by the energetic narrowness of the spectral features of an individual molecule.

In the analysis of a LIF excitation spectrum of a large aromatic molecule, it is easy to identify the intense molecular features, i.e., the 0–0 electronic origin and the intense low-lying



**Figure 4.** Energy-resolved fluorescence spectra of tetracene cooled in a supersonic expansion (180 torr Ar expanded through a 150  $\mu\text{m}$  circular nozzle). Photoselective excitation was conducted at the four energies which were marked in Figure 3: (a) band a of Figure 3 corresponding to the electronic origin; (b) band b of Figure 3 corresponding to a weak feature at excess vibrational energy  $E_v = 246$   $\text{cm}^{-1}$ ; (c) band (c) of Figure 3 corresponding to a weak feature at  $E_v = 288$   $\text{cm}^{-1}$ ; (d) band d of Figure 3 corresponding to a prominent 314  $\text{cm}^{-1}$  vibration of tetracene.

vibrational excitations. A typical example showing the fluorescence excitation spectrum of the tetracene molecule cooled in a supersonic expansion of Ar is portrayed in Figure 3. In addition, the LIF excitation spectrum reveals also some very weak spectral features, whose relative intensities, normalized to the intensity of the electronic origin, are  $5 \times 10^{-2}$  to  $5 \times 10^{-3}$  (see Figure 3). It is imperative to establish whether such weak spectral features originate from very weak vibrational excitations of the large molecule or are due to traces of impurities. Such an identification of these weak spectral features is of importance, both for diagnostic purposes and for the determination of the purity of the compound. One type of interesting esoteric molecules encountered in supersonic expansions involve van der Waals molecules formed between the aromatic molecule and rare gas atoms of the diluent carrier gas. The spectral features due to these van der Waals molecules can readily be identified (17, 24, 33, 34) on the basis of the dependence of their intensity on the stagnation pressure of the rare gas and by the dependence of their energetic location on the nature of the diluent. These fascinating van der Waals molecules are irrelevant for analytical applications and will not be considered further. The technique of energy-resolved emission spectroscopy provides a diagnostic tool to determine whether some weak spectral features in the fluorescence excitation spectrum originate from the bare molecule or are due to chemical impurities. Consider the excitation of a large molecule to a vibrationally excited level  $\bar{v}$  of the  $S_1$  electronic state, which will be denoted by  $S_1(\bar{v})$ . The large molecule does not appreciably change its equilibrium nuclear configuration upon electronic–vibrational excitation. We thus expect that the most intense transition in the fluorescence spectrum will be  $S_1(\bar{v}) \rightarrow S_0(\bar{v})$ , i.e., to the same vibrational level  $\bar{v}$  in the ground electronic state  $S_0$ . We shall refer to this transition, which does not change the vibrational state, as the  $\Delta v = 0$  transition. This expectation is borne out by the energy-resolved emission spectrum of tetracene (Figure 4) originating from the excitation of the electronic origin (band a in Figure 3) and of the intense 314- $\text{cm}^{-1}$  vibrational excitation

(band d in Figure 3). As is apparent from the emission spectra a and d in Figure 4, both for 0-0 and for 314-cm<sup>-1</sup> excitation, the general appearance of the energy-resolved emission spectrum is similar, being dominated by the  $\Delta v = 0$  transition. The only difference between the spectrum in Figure 4a and Figure 4d is the resonance emission exhibited at 314 cm<sup>-1</sup> above the  $\Delta v = 0$  transition in Figure 4d, which is expected. To determine whether some of the weak features in the fluorescence excitation spectrum of Figure 3 are intrinsic, we have examined the energy-resolved fluorescence originating from photoselective excitation of the weak bands located at 246 cm<sup>-1</sup> (band b, Figure 3) and at 288 cm<sup>-1</sup> (band c, Figure 3) above the S<sub>1</sub> origin of tetracene. If these weak features originate from some (unidentified) aromatic impurities, we would expect the energy-resolved spectrum to be dominated by a "resonance" emission band, which coincides with the energetic position of the weak band in the fluorescence excitation spectrum. In any case, the energy-resolved emission from an impurity should differ from the corresponding spectra of tetracene (Figure 4a,d). The energy-resolved emission spectra (Figure 4b,c) originating from photoselective excitation of these 246-cm<sup>-1</sup> and 288-cm<sup>-1</sup> weak features are "nonresonant", being dominated by the tetracene  $\Delta v = 0$  emission and showing the general features of the tetracene energy-resolved emission spectra (see Figure 4). We thus conclude that these two weak spectral features are intrinsic and are not due to impurities. This example demonstrates the potential of energy-resolved emission spectroscopy for the qualitative identification of organic impurities. The obvious disadvantage of the energy-resolved emission spectroscopy method is its relatively low sensitivity. As the emission spectra have to be dispersed by a monochromator, the sensitivity of this technique is lower by 2 to 3 orders of magnitude than the fluorescence excitation method, where the emitted photons at all wavelengths are simultaneously interrogated.

To consider the sensitivity of the laser-induced fluorescence excitation method in conventional supersonic expansions, one should evaluate the total number of photons emitted per laser pulse. In what follows we shall assess the sensitivity of the method by utilizing detailed experimental information concerning the intensity of the fluorescence of the tetracene (C<sub>18</sub>H<sub>14</sub>) molecule cooled in a supersonic expansion of Ar and excited by the dye laser (16, 23). In these experiments (16, 24) the nozzle diameter was  $D = 150 \mu\text{m}$  and the nozzle crossed the supersonic expansion at  $X = 5 \text{ mm}$  downstream. The nozzle chamber temperature was 220 °C corresponding to a partial pressure  $p_m^\circ$  of tetracene at the nozzle of  $p_m^\circ \simeq 0.1$  torr. Laser excitation of the 0-0 transition of tetracene (see Figure 3) resulted in the total number of  $2 \times 10^4$  photoelectrons per laser pulse detected by the photomultiplier before amplification. The laser repetition rate is 20 Hz, resulting in  $4 \times 10^5$  counts s<sup>-1</sup>. The main sources of noise are as follows: (a) Photomultiplier dark current. This source of noise is rather small, as we have used a boxcar integrator with a gating time shorter than 1  $\mu\text{s}$ , which reduces the dark current contribution to a value lower than 0.1 counts s<sup>-1</sup>. (b) Laser stray light and spurious background daylight. These can be reduced by the use of irises, light baffles, and appropriate long-pass optical filters. We have succeeded in reducing this source of noise to a value lower than 4 counts s<sup>-1</sup> implying a signal to background noise ratio of  $\sim 10^5$ .

When the vapor pressure of the large molecule at the nozzle was  $p_m^\circ = 0.1$  torr, the signal to background ratio was found to be  $10^5$ . Taking into account the proportionality of the fluorescence signal to the vapor pressure and the square root dependence of the number of counted photons, one arrives at a minimum detectable pressure of  $p_m^\circ = 10^{-4}$  torr (for a signal to noise ratio of 10). This analysis of our experimental

LIF data for tetracene demonstrates the potential of laser spectroscopy of molecules seeded in conventional axisymmetric jets expanded from a round orifice for the identification and detection of minor quantities of fluorescent molecules. The detection level of this technique requires a vapor pressure of  $10^{-4}$  torr of the large molecule in the heated nozzle chamber. A dramatic further improvement of the sensitivity of the technique can be accomplished by the use of pulsed planar supersonic jets.

**Detection of Organic Impurities in Pulsed Planar Jets.** Pulsed axisymmetric supersonic jets expanded from an orifice were originally developed by Gentry and Giese (35, 36). Such supersonic sources are typically characterized by a 100  $\mu\text{s}$  pulse duration and by a repetition rate of 10 pulses/s, so that the duty factor of the pulsed source is  $10^{-3}$  compared to an equivalent density continuous source. This allows for the instantaneous density of the pulsed source to be  $10^3$  times higher than that of a CW source, while the same pumping requirements and material consumption are maintained. The instantaneous density of the large molecule in the seeded pulse expansion also scales up by the same numerical factor, enhancing the sensitivity of the LIF method by 3 orders of magnitude relative to a CW source operated under equivalent conditions.

We have developed (31, 32) a pulsed nozzle slit source for the production of planar supersonic jets (37, 38). The planar supersonic jet is produced by the expansion of a seeded rare gas through a slit of width  $l$  and length  $L$ , where  $l \ll L$ . The characteristics of such a planar supersonic jet are as follows (31, 32):

(1) Long optical pathlength. The entire length  $L$  of the planar expansion can be irradiated by the laser beam directed parallel to the long axis. In our slit nozzle the optical pathlength is  $L = 35 \text{ mm}$ , being considerably larger than the optical pathlength  $a \simeq 2.5 \text{ mm}$  in a conventional centrosymmetric expansion from a pinhole, with  $D = 150 \mu\text{m}$ , at the distance 5 mm downstream, whereupon  $L/a = 14$ .

(2) High densities of the ultracold seeded molecules at the interrogation distance. In a planar supersonic expansion the density profile decreases as  $X^{-1}$  with the distance,  $X$ , for the nozzle (31, 32, 37, 38)

$$\rho = 0.4\rho_0\left(\frac{l}{X}\right) \quad (1)$$

while for a circular nozzle the density decreases as  $X^{-2}$ , i.e., (39)

$$\rho = 0.16\rho_0\left(\frac{D}{X}\right)^2 \quad (2)$$

The density of the large molecule at the interrogation distances  $X = 5\text{--}7 \text{ mm}$  in the planar jet is higher by about a numerical factor of  $10^2$  than the density of the seeded molecule at the same distance from our conventional circular nozzle.

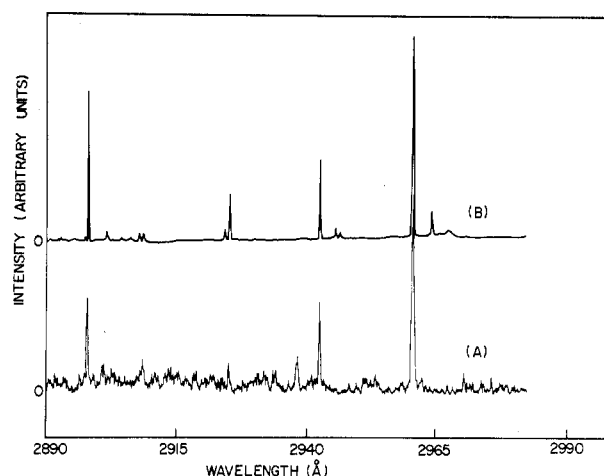
(3) The nozzle can withstand high temperatures up to 200 °C. The gas pulse length is 150  $\mu\text{s}$  accomplished over the entire temperature range of 25–200 °C.

Information concerning the quantitative aspects of internal cooling of large molecules in planar jets is crucial for the assessment of their spectroscopic and analytical applications. The efficiency of vibrational (31, 32) and rotational (32) cooling in planar jets has recently been explored. For the aniline molecule, which serves as a useful "rotational temperature thermometer", we have determined (32) a rotational temperature  $T_R = 10 \text{ K}$ , when expanded in Ar through the nozzle slit at  $p = 15$  torr. The same rotational temperature was accomplished for aniline expanded in Ar through a  $D = 150 \mu\text{m}$  conventional circular nozzle at  $p = 450$  torr. As  $T_R$  in a centrosymmetric jet is roughly proportional to  $(pD)^{-\gamma}$  (with

$\eta = 0.8\text{--}1.0$ ) (32), the rotational temperature in the nozzle slit at  $p = 15$  torr Ar is equivalent to that accomplished at the same value of  $p$  in a conventional circular nozzle with an effective diameter of  $\bar{D} \approx 4.5$  mm. The area  $\pi\bar{D}^2/4 = 16$  mm<sup>2</sup> of the conventional effective nozzle somewhat exceeds the area  $LL = 7$  mm<sup>2</sup> of our nozzle slit. From this analysis three conclusions emerge. First, the effective diameter of a circular nozzle  $\bar{D} \approx (4LL/\pi)^{1/2}$  provides a reasonable rough estimate for the efficiency of internal cooling in the planar jet under equivalent expansion conditions. Second, effective internal cooling can be accomplished in planar jets. Third, comparable conditions of internal cooling of large molecules can be accomplished in our planar jets and in our conventional centrosymmetric jets. We thus infer that long optical pathlengths and the high local densities prevailing in the planar jets allow for a considerable increase in the sensitivity for LIF detection of molecules seeded in supersonic expansions from a nozzle slit.

To demonstrate the increased sensitivity of the LIF method in planar expansions, some quantitative experimental information (31, 32) will be pertinent. For large molecules, such as aniline or 9,10-dichloroanthracene expanded in Ar at  $p = 20\text{--}100$  torr, we have recorded up to 10% absorption of the laser light. Taking 1% absorption when the partial pressure in the nozzle chamber is  $p_m^0 = 1$  torr and the planar expansion is irradiated by laser pulses of 100  $\mu$ J, we estimate that  $10^{12}$  photons are absorbed per laser pulse. Taking the light collection efficiency of 1%, the photomultiplier quantum yield of 10%, and molecular fluorescence quantum yield  $Y = 0.4$ , we estimate the photon counting to be  $4 \times 10^8$  photons per laser pulse. The repetition rate of the pulsed nozzle is 12 Hz, so that we estimate the photon counting rate to be  $5 \times 10^9$  counts s<sup>-1</sup>. We may compare this result with the estimate presented in the previous section for the fluorescence intensity from the conventional CW expansion through a  $D = 150$   $\mu$ m nozzle, where for a molecular pressure of  $p_m^0 = 1$  torr we have estimated  $4 \times 10^6$  counts s<sup>-1</sup> for the photon counting rate. Accordingly, the use of the pulsed planar supersonic expansions through our  $0.2 \times 35$  mm nozzle slit allows for the increase of the sensitivity in LIF studies by about 3 orders of magnitude over that accomplished with conventional CW supersonic sources with  $D = 100\text{--}200$   $\mu$ m. To assess the sensitivity of the fluorescence detection method in seeded planar supersonic expansions, we can utilize again the estimates of the noise sources presented in a previous section, which result in noise due mainly to stray light in the level of 4 counts s<sup>-1</sup>. Thus the signal to noise ratio for fluorescence from the planar expansion with  $p_m^0 = 1$  torr is  $10^9$ . One can monitor the fluorescence excitation spectrum of a large molecule excited by a pulsed dye laser in the planar jet with a signal to noise ratio of 10 when the pressure of the large molecule at the nozzle is as low as  $10^7$  torr. This is obviously an optimistic estimate of the lower limit of the molecular vapor pressure required for LIF detection. Two conclusions emerge from this discussion. Firstly, from the technical point of view extreme care must be exerted to ensure the absence of any undesired volatile impurities in the nozzle slit system to eliminate spurious fluorescence. Secondly, this technique provides a highly sensitive detection method for large molecules.

To demonstrate the applicability of planar seeded supersonic expansions for the sensitive detection of minute traces of impurities in organic materials, we have observed and analyzed an extremely weak fluorescence excitation spectrum due to traces of fluorene in biphenyl. The chemically pure biphenyl sample was analyzed mass spectrometrically and the amount of impurities of heavier molecular weight, including fluorene, was found to be lower than 1000 ppm, being limited



**Figure 5.** Fluorescence excitation spectroscopy in seeded, pulsed, planar supersonic jets in the ultraviolet 2890–2990 Å spectral range. The lower LIF spectrum was obtained from a biphenyl sample heated to 100 °C, seeded into Ar at  $p = 40$  torr, and expanded through the nozzle slit. The upper LIF spectrum was obtained from fluorene at 25 °C seeded into Ar at  $p = 76$  torr. The seeded gas was expanded through the  $0.20$  mm  $\times$   $35$  mm slit nozzle. The dye laser crossed the supersonic expansion parallel to the long axis of the slit at the distance of 6 mm from the nozzle. Spectra are normalized to the laser intensity.

**Table I.** Identification of Fluorene Impurity in Biphenyl, by Laser-Induced Fluorescence Excitation and Time-Resolved Spectroscopy in a Planar Supersonic Jet

biphenyl sample temp 100 °C $p(\text{Ar}) = 30$ torr		pure fluorene sample temp 25 °C $p(\text{Ar}) = 30$ torr		assignment
wave- length, Å	life- time, ns	wavelength, Å	life- time, ns	
2960.2	$22 \pm 2$	2960.0	$23 \pm 2$	fluorene (0-0)
2942.1	$22 \pm 2$	2941.9		fluorene
2938.0	$13 \pm 2$	(2837.8 <sup>a</sup> )		aniline (0-0)
2924.8	$22 \pm 2$	2924.7		fluorene
2897.7	$22 \pm 2$	2897.6		fluorene

<sup>a</sup> This peak was not observed in the pure fluorene sample. It was observed for pure aniline (ref 42, 43, and 45). Thus this impurity band is assigned to aniline impurity.

by the vacuum background. The biphenyl sample was heated to 100 °C, mixed with Ar at  $p = 30$  torr and expanded through the planar slit. The fluorescence excitation spectrum in the spectral range 2890–2990 Å is presented in Figure 5A. Five spectral features with signal to noise ratio 3–20 were observed. The fluorescence decay lifetimes of each of these spectral features were determined by time-resolved spectroscopy and are summarized in Table I. Four out of the five spectral features are assigned to the fluorene molecule. Figure 5B presents the fluorescence excitation spectrum of pure fluorene. The fluorene solid sample was maintained at room temperature, where the vapor pressure (40) is  $10^{-2}$  torr, mixed with Ar at  $p = 30$  torr and expanded through the slit nozzle. Decay lifetimes of the spectral features, corresponding to the vibrational excitations of fluorene, were determined. The identification of the four spectral features in the spectrum of Figure 5A to fluorene rests on (a) energetic positions of spectral features (Figure 5 and Table I), (b) relative intensities (Figure 5), and (c) decay lifetimes (Table I).

The only alien spectral feature appearing in the impurity fluorescence excitation spectrum of Figure 5A is the weak band at 2938.0 Å, which is due to traces of aniline in the nozzle system (Table I).

To provide an assessment of the sensitivity of these impurity detection methods, we have compared the intensities of the fluorescence excitation spectra in Figure 5, which were excited by the same laser intensity. The fluorescence excitation spectrum of fluorene at the nozzle pressure of  $p_m^\circ = 10^{-2}$  torr (Figure 5B) is more intense by a numerical factor of  $10^4$  than the impurity spectrum of Figure 5A. Accordingly, the nozzle pressure of fluorene for the impurity spectrum was  $p_m^\circ/10^4 \approx 10^{-6}$  torr. We are now able to make a rough estimate of the concentration of the fluorene impurity in the biphenyl sample. The biphenyl sample was heated to 100 °C beyond the melting point of biphenyl. The vapor pressure of pure fluorene at 100 °C is  $\sim 1$  torr (36) and using Rault's law the mole fraction of fluorene in biphenyl is roughly  $10^{-6}$ . This low impurity level of  $\sim 1$  ppm is amenable to experimental interrogation in the planar supersonic expansion.

To provide a dramatic demonstration of the sensitivity of laser fluorescence excitation in planar supersonic jets, we note that the nozzle pressure of  $10^{-6}$  torr of the impurity organic molecule, which was required to obtain the LIF spectrum of Figure 5, corresponds to a density of  $\rho_0 \approx 2 \times 10^{10} \text{ cm}^{-3}$  at the nozzle, while the density at the interrogation region is as low as  $\rho \approx 10^9 \text{ cm}^{-3}$ .

To conclude, the advantages of the planar supersonic expansions for analytical implications are (A) very low vapor pressures of the impurity molecule just exceeding  $\sim 10^{-7}$  torr are sufficient, (b) low impurity concentrations ( $\sim 1$  ppm) are amenable to detection, (C) small amounts of material ( $\sim 1$  mg) are sufficient to obtain fluorescence excitation spectra, (D) sufficient vapor pressure can be obtained by heating the solid sample to moderately low temperatures, and (E) low pressures of Ar gas are required for effective intramolecular cooling.

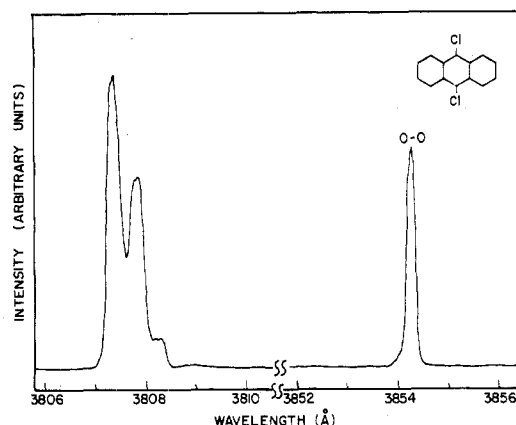
**Isotopic Analysis.** Up to this point, we have been concerned with problems pertaining to chemical analysis. Another interesting application of laser spectroscopy in supersonic jets involves isotopic analysis. The main requirement for the identification of two isotopically distinct large molecules by LIF spectroscopy in jets is

$$\Delta\nu < \delta\nu_I \quad (3)$$

where  $\Delta\nu$  is the width of an individual vibrational feature in the spectrum due to rotational broadening, a typical value being  $\Delta\nu \approx 1\text{--}3 \text{ cm}^{-1}$ , while  $\delta\nu_I$  is the isotopic spectral shift in the electronic-vibrational spectrum. The isotopic spectral shift  $\delta\nu_{10}$  of the electronic origin is due to the differences in all the vibrational zero-point energies occurring upon electronic excitation. Let  $\omega_\mu^{(a)}(S_j)$  denote the frequency of the  $\mu$ th normal mode of the molecule containing the isotope (a) in the electronic state  $S_j$  ( $j = 0$  for the  $S_0$  ground state and  $j = 1$  for the  $S_1$  electronically excited state). The isotopic spectral shift for the electronic origin,  $\delta\nu_{10}$ , between the isotopes (a) and (b) is given by the second difference

$$\delta\nu_{10} = \frac{1}{2} \sum_\mu (\hbar\omega_\mu^{(a)}(S_1) - \hbar\omega_\mu^{(a)}(S_0)) - \sum_\mu (\hbar\omega_\mu^{(b)}(S_1) - \hbar\omega_\mu^{(b)}(S_0)) \quad (4)$$

where the sums are taken over all the vibrational modes. To provide some quantitative data concerning the isotopic shift of an electronic origin, we would like to mention that for a single substitution of a hydrogen atom by a deuterium atom in an aromatic molecule  $\delta\nu_{10} = 10 \text{ cm}^{-1}$  (41), whereupon condition 3 is obeyed and the electronic origin of deuterated molecules can easily be distinguished by LIF spectroscopy in jets. For the substitution of a  $^{12}\text{C}$  atom by a  $^{13}\text{C}$  atom in aromatic molecules, the spectral shift for the electronic origin (42, 43)  $\delta\nu_{10} \approx 2 \text{ cm}^{-1}$  is small, whereupon condition 3 is violated making LIF spectroscopy of the 0-0 electronic origin inapplicable for the isotopic analysis of molecules containing



**Figure 6.** Medium-resolution fluorescence excitation spectra (spectral resolution  $3 \text{ cm}^{-1}$ ) in the ranges 3852–3856 Å at 3805–3810 Å of 9,10-dichloroanthracene in a pulsed planar supersonic expansion. The 9,10-dichloroanthracene was heated to 110 °C, seeded into Ar at  $p = 25$  torr, and expanded through the 0.20 mm  $\times$  35 mm slit. The dye laser crossed the supersonic expansion parallel to the long axis of the nozzle slit at the distance of 17 mm from the slit.

$^{13}\text{C}$ . In this case, photoselective molecular ionization detection methods (42–45), as discussed previously, will be applicable for  $^{13}\text{C}$  isotopic analysis.

For the majority of isotopic substitutions, except that of deuterium, the isotopic spectral shifts in the electronic origin of the  $S_0 \rightarrow S_1$  transitions are modest, being comparable to or smaller than the rotational broadening  $\Delta\nu$ . Appreciably larger isotopic spectral shifts are exhibited for electronic-vibrational excitations in the  $S_1$  manifold. Let  $\omega_\kappa^{(a)}(S_1)$  and  $\omega_\kappa^{(b)}(S_1)$  denote the vibrational frequencies in the  $S_1$  state for the  $\kappa$  mode, which contain isotope (a) and isotope (b), respectively. The isotopic spectral shift  $\delta\nu_{1\kappa}$  accompanying the vibrational excitation of the  $\kappa$  mode is

$$\delta\nu_{1\kappa} = \delta\nu_{10} + [\hbar\omega_\kappa^{(a)}(S_1) - \hbar\omega_\kappa^{(b)}(S_1)] \quad (5)$$

For a vibrational model which involves a substantial contribution from nuclear displacement of the isotopic atom, the isotopic spectral shift, eq 5, accompanying this vibrational excitation is expected to be large even for heavy atoms. We note that  $\delta\nu_{10}$  involves a sum of second-order differences, while  $\delta\nu_{1\kappa}$  contains a first-order difference in frequency shifts. Accordingly, for those vibrations involving nuclear displacement of the isotope, we expect that  $|\delta\nu_{1\kappa}| \gg |\delta\nu_{10}|$ .

To demonstrate the applicability of LIF techniques for isotopic analysis of large molecules, we have studied the excitation spectrum of 9,10-dichloroanthracene ( $\text{C}_{14}\text{H}_8\text{Cl}_2$ ), where the  $^{37}\text{Cl}/^{35}\text{Cl}$  natural abundance is 0.33. Figure 1 portrays the general vibrational structure of the  $S_0 \rightarrow S_1$  electronic transition, while Figure 6 presents the details of the fluorescence excitation spectrum on an expanded scale, both for the 0-0 electronic origin peaking at 3854.3 Å and for a low vibrational excitation in the range 3807.5–3808.5 Å. The electronic origin exhibits a single peak devoid of any structure, whose width (fwhm) is  $1.4 \text{ cm}^{-1}$ . This line broadening of the origin band originates from rotational structure (which has already been discussed in this paper), as well as from overlapping of 0-0 excitations of molecules with different isotopic compositions. From our failure to resolve the individual isotopic components for  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in the electronic origin of 9,10-dichloroanthracene, we can safely conclude that  $\delta\nu_{10} < 1.4 \text{ cm}^{-1}$ .

The vibrational excitation in the spectral range 3807.0–3808.5 Å (Figure 6) is entirely different from the electronic origin. This vibrational excitation exhibits three nearly equidistant peaks located at  $313.3 \pm 0.2 \text{ cm}^{-1}$ ,  $316.1 \pm 0.2 \text{ cm}^{-1}$ , and  $319.3 \pm 0.2 \text{ cm}^{-1}$  above the electronic origin. These three peaks are assigned by us to the vibrational excitation of the distinct molecules containing ( $^{35}\text{Cl}$ ,  $^{35}\text{Cl}$ ), ( $^{35}\text{Cl}$ ,



Table II. Isotopic Analysis of Cl in 9,10-Dichloroanthracene by Laser-Induced Fluorescence Spectroscopy

wavelength, <sup>a</sup> Å	energy, <sup>b</sup> cm <sup>-1</sup>	spacing from 0-0 transi- tion, <sup>c</sup> cm <sup>-1</sup>	assignment	rel intens (exptl)	rel intens (from Cl isotopic abundance)
3854.25	25 945.3	0	0-0 (all isotopic species)		
3808.31	26 258.3	313.3	<sup>37</sup> Cl, <sup>37</sup> Cl	0.10	0.11
3807.87	26 261.4	316.1	<sup>35</sup> Cl, <sup>37</sup> Cl	0.66	0.67
3807.40	26 264.6	319.3	<sup>35</sup> Cl, <sup>35</sup> Cl	1.00	1.00

<sup>a</sup> Absolute accuracy of wavelength scale  $\pm 3$  cm<sup>-1</sup> due to uncertainty in laser calibration. <sup>b</sup> Accuracy  $\pm 0.15$  cm<sup>-1</sup>. <sup>c</sup> Accuracy  $\pm 0.3$  cm<sup>-1</sup>.

<sup>37</sup>Cl), and (<sup>37</sup>Cl, <sup>37</sup>Cl). On the basis of Teller's theorem (46) the highest frequency excitation can be attributed to the molecule containing (<sup>35</sup>Cl, <sup>35</sup>Cl). From the analysis of the three vibrational features of the distinct isotopic species (Table II), we can assert that:

(a) The low frequency vibration, corresponding to  $319.3 \pm 0.2$  cm<sup>-1</sup> for (<sup>35</sup>Cl, <sup>35</sup>Cl),  $316.1 \pm 0.2$  cm<sup>-1</sup> for (<sup>35</sup>Cl, <sup>37</sup>Cl), and  $313.3 \pm 0.2$  cm<sup>-1</sup> for (<sup>37</sup>Cl, <sup>37</sup>Cl), exhibits a large isotopic spectral shift, so that condition (3) is applicable and an isotopic analysis can be conducted by LIF techniques.

(b) The appearance of three distinct vibrational features for isotopically substituted Cl atoms in 9,10-dichloroanthracene implies that the low frequency vibration involves the excitation of a normal mode, where both Cl atoms participate in the nuclear motion. The other alternative would involve a bond mode (46), where the C-Cl motions are essentially uncorrelated and independent. In the latter case, we would expect the appearance of two isotopically distinct spectral vibrational features, one corresponding to the C-<sup>35</sup>Cl bond and the second one to the C-<sup>37</sup>Cl bond. The qualitative features of the spectrum preclude the bond-made picture for this low vibrational excitation.

(c) The relative intensities of the three vibrationally excited features corresponding to the three isotopically distant molecules (Table II) are in accord with the natural abundance. This result provides quantitative support to the normal mode picture for this low vibrational excitation. Furthermore, this result clearly demonstrates that quantitative determination of the abundance of heavy isotopes in large molecules can be conducted.

(d) The equidistant spacing of the low vibrational frequency for the three distinct isotopes is also in accord with the normal mode picture for the vibrational motion.

We have demonstrated that for vibrational excitations involving the nuclear motion of heavy isotopes  $\delta\nu_{1x} > \delta\nu_{10}$ , so that these vibrational excitations are recommended as candidates for isotopic analysis by LIF. The interrogation of vibrational excitations of ultracold molecules containing heavy isotopes provides a powerful method for the identification and for the quantitative determination of the isotopic species.

## DISCUSSION

Laser spectroscopy in supersonic jets is expected to provide novel, highly selective, and sensitive techniques for the chemical and isotopic identification and detection of minor amounts of organic molecules. In this context, the analytical applications of planar supersonic expansions are very promising. Large molecules can be interrogated by laser fluorescence excitation techniques in supersonic jets provided they fulfill some basic requirements.

(A) **Emission Efficiency.** The quantum yield for fluorescence should be reasonably high, exceeding  $10^{-3}$ .

(B) **Volatility.** For identification of molecules in conventional supersonic expansions, vapor pressures of  $10^{-5}$  torr

should be attainable at temperatures below 400 °C. For identification and detection of molecules in planar supersonic expansions the current techniques require that a vapor pressure of  $10^{-7}$  torr should prevail at temperatures below 200 °C.

(C) **Chemical Stability.** The molecule should be stable in the vapor phase at the temperatures employed.

It is apparent that these techniques are not limited to organic molecules and can also be applied to adequate inorganic compounds. However, as the technique is restricted by the volatility requirement, a variety of inorganic ions are not amenable to interrogation by this method, whereupon the main applications will probably be directed toward organic molecules.

We have been concerned in our examples, which are representative rather than exhaustive, with the applications of energy-resolved LIF spectroscopy and of time-resolved spectroscopy. Other interrogation techniques can be utilized for the specific and selective identification and detection of large molecules in supersonic jets. Among these, the following should be mentioned:

(a) **Absorption spectroscopy** (31, 32, 48, 49). Absorption studies on ultracold large molecules can conveniently and effectively be conducted with the planar supersonic jet source developed by us (31, 32). The long optical pathlength and the high density in the linear jet result in high levels of optical absorption of  $\sim 10\%$  (31, 32). From the technical point of view, such absorption studies in planar supersonic sources can be conducted with a conventional lamp and a monochromator replacing the laser light source. From the point of view of general methodology, absorption studies can be used to explore "dark" molecules, whose excited states are characterized by low ( $Y = 10^{-4}$ ) emission quantum yields, so that requirement (A) is eliminated. Absorption studies in seeded planar supersonic expansions will provide a high-resolution "finger print" pattern for the spectroscopic identification of large molecules. At the risk of triviality, we point out that the obvious disadvantage of the absorption techniques is their lower sensitivity, as compared with the fluorescence excitation method, whenever the latter is applicable.

(b) **Molecular ionization detection** (42-45). A novel approach to the interrogation of excited state energetics of molecules cooled in supersonic expansions involves molecular photoionization followed by the measurement of the ion current (42-45). The ion signal spectra, i.e., the dependence of the ion current on the laser wavelength, probe essentially the excitation probability to the bound intermediate molecular state. These ion signal spectra have an appearance that is qualitatively similar to the fluorescence action spectra. The advantage of the ion current spectra lies in (i) interrogating excited states of "dark" molecules (44) and (ii) performing mass analysis of the produced ions by time of flight mass spectrometry (42, 43), which enables the identification of the isotopic composition of the produced ions.



The molecular ionization method in conjunction with time of flight mass spectroscopy will be extremely useful for the production and detection of isotopically distinct molecular ions. The identification of the isotopic composition of the produced ions makes it possible to separate distinct isotopic molecules, whose spectral features overlap. A relevant example involves the  $^{13}\text{C}/^{12}\text{C}$  substitution in aromatics where the spectral shift of the electronic origin  $\delta\nu_{10} \approx 2\text{ cm}^{-1}$  is small and, as already pointed out herein, the LIF method is inapplicable. Recently, it was demonstrated that the laser molecular ionization, combined with time of flight mass spectrometry techniques, can be used by the isotopically selective production of aniline ions containing  $^{13}\text{C}$  and  $^{12}\text{C}$ , i.e.,  $^{12}\text{C}_6\text{H}_5\text{NH}_2$  and  $^{13}\text{C}^{12}\text{C}_5\text{NH}_2$ , respectively (42, 43). This was accomplished by photoselective excitation at different energies along the rotational contour of the electronic origin of aniline. This isotopically selective ion production method will be of interest in isotopic analysis.

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### LITERATURE CITED

- (1) Bauer, H. H.; Christian, G. D.; O'Reilly, J. E. "Instrumental Analysis"; Allyn and Bacon: Boston, MA, 1978.
- (2) Barnes, R. M. *Anal. Chem.* **1972**, *44*, 122R.
- (3) Barnes, R. M. *Anal. Chem.* **1974**, *46*, 150R.
- (4) Jortner, J.; Levine, R. D. "Photoselective Chemistry"; Jortner, J.; Levine, R. D.; Rice, S. A., Eds.; Wiley-Interscience: New York, 1981; *Advances in Chemical Physics*, Vol. 47, p 1.
- (5) Byrne, J. P.; Ross, I. G. *Can. J. Chem.* **1965**, *43*, 3253.
- (6) Rebane, K. K. "Impurity Spectra in Solids"; Plenum: New York, 1970.
- (7) Brown, J. C.; Duncanson, J. A.; Small, G. J. *Anal. Chem.* **1980**, *52*, 1711.
- (8) Yang, Y.; D'Silva, A. P.; Fassal, V. A. *Anal. Chem.* **1981**, *53*, 894.
- (9) Birks, J. "Photophysics of Aromatic Molecules".
- (10) Gouterman, M. "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, p 1.
- (11) Levy, D. H.; Wharton, L.; Smalley, R. E. "Chemical and Biochemical Applications of Laser"; Academic Press: New York, 1977; Vol. 2.
- (12) Levy, D. H.; Wharton, L.; Smalley, R. E. *Acc. Chem. Res.* **1977**, *10*, 134.
- (13) Levy, D. H. *Annu. Rev. Phys. Chem.* **1980**, *31*, 197.
- (14) Fitch, P. S. H.; Wharton, L.; Levy, D. H. *Chem. Phys.* **1979**, *70*, 2019.
- (15) Fitch, P. S. H.; Hayman, C. A.; Levy, D. H. *J. Chem. Phys.* **1980**, *73*, 1064.
- (16) Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1979**, *71*, 2319.
- (17) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys.* **1980**, *51*, 31.
- (18) Beck, S. M.; Liverman, M. G.; Mouts, D. L.; Smalley, R. E. *J. Chem. Phys.* **1979**, *70*, 232.
- (19) Hopkins, J. B.; Powers, D. E.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039.
- (20) Beck, S. M.; Powers, D. E.; Hopkins, J. B.; Smalley, R. E. *J. Chem. Phys.* **1980**, *73*, 2019.
- (21) Beck, S. M.; Powers, D. E.; Hopkins, J. B.; Smalley, R. E. *J. Chem. Phys.* **1981**, *74*, 43.
- (22) Hays, T. R.; Henke, W.; Selzle, H. L.; Schlag, E. W. *Chem. Phys. Lett.* **1981**, *77*, 19.
- (23) Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1981**, *75*, 3770.
- (24) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys. Lett.* **1980**, *72*, 21.
- (25) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys. Lett.* **1979**, *69*, 14.
- (26) Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1981**, *74*, 3745.
- (27) Even, U.; Magen, J.; Jortner, J.; Levanon, C. *J. Am. Chem. Soc.* **1981**, *103*, 4583.
- (28) Brown, J. C.; Hayes, J. M.; Warren, J. A.; Small, G. J. "Lasers in Chemical Analysis"; Hieftje, G. M.; Travis, J. M.; Lytle, F. E., Eds.; The Humana Press: Clifton, NJ, 1981; p 237.
- (29) Hayes, J. M.; Chiang, I.; McGlade, M. J.; Warren, J. A.; Small, G. J. *J. Soc. Photo-Opt. Instrum. Eng.* **1981**, *286*, 117.
- (30) Warren, J. M.; Hayes, J. A.; Small, G. J. *Anal. Chem.* **1982**, *54*, 138.
- (31) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys. Lett.* **1981**, *83*, 1.
- (32) Amirav, A.; Even, U.; Jortner, J.; Birss, F. A.; Ramsay, D. A. "Rotational Temperatures of Aniline in Pulsed Axisymmetric and Planar Jets"; to be submitted for publication.
- (33) Amirav, A.; Even, U.; Jortner, J. *Chem. Phys. Lett.* **1979**, *67*, 9.
- (34) Amirav, A.; Even, U.; Jortner, J. *J. Chem. Phys.* **1981**, *75*, 2489.
- (35) Gentry, W. R.; Glese, C. F. *Rev. Sci. Instrum.* **1978**, *49*, 595.
- (36) Gentry, W. R.; Glese, C. F. *J. Chem. Phys.* **1977**, *67*, 5389.
- (37) Beylich, A. E. Paper 111 on the 12th Symposium on Rarefied Gas Dynamics, Charlottesville, 1980.
- (38) Beylich, A. E. *Z. Flugwiss. Weltraumforsch.* **1979**, *3*, 48.
- (39) Ashkenas, A.; Sherman, F. S. "Rarefied Gas Dynamics"; de Leeuw, J. H., Ed.; Academic Press: New York, 1966; Vol. 2, p 84.
- (40) "International Critical Tables"; McGraw-Hill: New York, 1929.
- (41) Craig, D. P.; Philpott, M. R. *Proc. R. Soc. London, Ser. A* **1966**, *A290*, 583.
- (42) Leutwyler, S.; Even, U. *Chem. Phys. Lett.*, in press.
- (43) Amirav, A.; Leutwyler, S.; Even, U.; Jortner, J. *Ann. Isr. Phys. Soc.* **1981**, *4*, 3.
- (44) Dietz, T. G.; Duncan, M.; Liverman, M. G.; Smalley, R. E. *J. Chem. Phys.* **1980**, *73*, 4816.
- (45) Dietz, T. G.; Duncan, M. A.; Liverman, M. G.; Smalley, R. E. *Chem. Phys. Lett.* **1980**, *70*, 246.
- (46) Teller, E. *Handb. Jahrb. Phys. Chem.* **1934**, *9*, 141.
- (47) Sage, M. L.; Jortner, J. "Advances in Chemical Physics"; Wiley-Interscience: New York, 1981; Vol. 47, p 293.
- (48) Valda, V.; McClelland, G. M. *Chem. Phys. Lett.* **1980**, *71*, 436.
- (49) Henley, R. J.; Leopold, D. G.; Valda, V.; Roebber, J. L. *J. Phys. Chem.* **1981**, *85*, 134.

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## Shpol'skii Effect in the Analysis of Sulfur-Containing Heterocyclic Aromatic Compounds

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A number of sulfur heterocyclic polyaromatic compounds (S-PAC) have been studied with respect to their ability to emit well-resolved fluorescence spectra at cryo temperatures (Shpol'skii fluorescence). It has been observed that there is a high probability that a bay region sulfur substituted polyaromatic hydrocarbon will exhibit Shpol'skii fluorescence if the corresponding parent compound shows the same ability under identical conditions. The 0-0' transition of those spectra can in many cases be regarded as being blue shifted in a regular manner with respect to the 0-0' transition of the PAH analogue. These types of compounds are also detected in carbon black samples.

The utility of the Shpol'skii effect as an analytical technique

has during the last decade been proved by the efficiency of the method for the qualitative analysis of certain chemical compounds at trace levels of concentration (1-5, 7). The type of substances studied with this low-temperature fluorescence technique has mostly been pure hydrocarbons due to the fact that the well-resolved spectra derived from polyaromatic hydrocarbons (PAHs) in *n*-alkane solutions usually become drastically less well resolved when more polar atoms are introduced in the fluorescing molecule. This problem can partially be overcome by the aid of laser-excited spectroscopy if the band broadening is dependent only on an increased number of sites of the fluorescing molecule in the solvent crystal (5). However, if the band broadening is dependent basically on an increase in the phonon-wing, i.e., an increase in the interaction with the solvent at an electronic transition,