

and the iterations were continued until

$$\max_r |b_{i+1}(r) - b_i(r)| \leq 10^{-5},$$

where $b_i(r)$ denotes the output of the i th iteration.

A straightforward application of bipolar coordinates in two dimensions causes the integrand to become singular at all points along the r axis. This difficulty was avoided by an integration by parts, as suggested by Ben-Naim.³ The integrations were performed using Simpson's rule with 120 intervals in the range $0 \leq r \leq 6\sigma$. The criterion for convergence was the same as above, but its magnitude was relaxed to 10^{-4} .

The reduced virial pressure $p_v/\rho kT$ and reduced energy E/NkT were obtained from $g(r; \rho^*, T^*)$ for various values of $T^* = kT/\epsilon$ and $\rho^* = \rho\sigma^2$ by the usual equations. For the PY case the compressibility pressure p_c was also obtained using the two-dimensional form of Baxter's equation.⁶ These calculations are listed in Table I.

Also given in Table I are some molecular-dynamics computer simulations of Fehder,⁷ Monte Carlo computer simulations of Tsien and Valleau,⁸ and PY calculations of Mandel.⁵ We note that our PY and HNC calculations agree only moderately well with the com-

puter simulations, as is the case with the three-dimensional Lennard-Jones fluid. The PY virial and compressibility pressures bracket the computer-simulation pressure for each of the states considered. We also note that our PY results disagree substantially with those of Mandel.⁵ Since we obtained identical results using two different procedures for solving the PY equation, we believe that our values in Table I are the correct ones.

A comparison of the PY and HNC radial distribution functions which we obtained with computer simulations and the utilization of these radial distribution functions in a statistical-mechanical perturbation theory will be the subject of a future article.

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Observation of radiationless processes in a molecular beam*

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Internal conversion is a radiationless process¹ involving the transition from an excited singlet state S_1 to isoenergetic vibrational levels of the ground singlet state, denoted by $S_0^\#$. The experimental evidence for internal conversion is usually indirect and is based on the measurement of the deviation from unity of the sum of the excited singlet state and triplet state quantum yields. Although the intramolecular nature of internal conversion in large aromatic molecules has long been suspected, the difficulty of separating intramolecular from intermolecular interactions has seriously impeded experimental investigations of this phenomena. Recently, Soep² has reported the first direct observation of internal conversion in isolated gaseous pentacene, $C_{22}H_{14}$. In this bulb experiment (36–360 mtorr), transient absorption was used to monitor the presence of $S_0^\#$ following pulsed excitation of the 0–0 band of the $A^1B_{3u} - X^1A_{1g}$ transition.³ We report here a study of internal conversion in pentacene with a more sensitive detection technique, namely laser-induced fluorescence,⁴ which allows us to repeat the above experiment under molecular beam conditions. The use of a molecular beam has the advantages of eliminating experimental artifacts caused by wall collisions, excimer formation, bulk heating, etc., and of permitting colli-

sion-free studies to be carried out for a longer period of time than is convenient in bulb experiments.

Figure 1 shows a schematic diagram of the experimental setup. An effusive beam of pentacene (Aldrich Chemical Co., mp 300 °C) from an oven at 530 °K (1.5×10^{-2} torr) enters a second separately-pumped vacuum chamber (2×10^{-5} torr). The pentacene beam

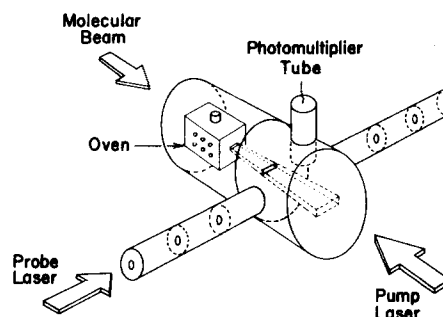


FIG. 1. Schematic diagram of the apparatus, showing the directions of the pump laser beam, the probe laser beam, and the pentacene molecular beam. An extensive system of light baffles in the entrance and exit arms of the vacuum chamber prevents stray laser light from reaching the photomultiplier.

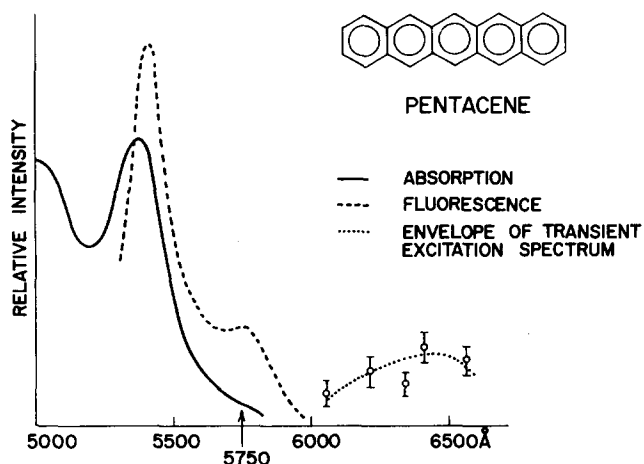


FIG. 2. The absorption spectrum (in the gas phase), the fluorescence spectrum (in solution), and the transient excitation spectrum (in a molecular beam) of pentacene. The arrow points to the wavelength of the pump beam for the transient excitation spectrum.

is collinear with a pump beam, which is the output of a flashlamp-driven dye laser (1 mJ per pulse, 2 pps, 300 nsec pulse width) tuned to the (1-0) transition of the S_1-S_0 absorption band (5750 Å). After a variable delay (1-10 μ sec) a probe beam from a nitrogen-laser-driven Molelectron tunable dye laser (0.1 mJ per pulse, 2 pps, 15 nsec pulse width) is directed into the excited pentacene beam in order to produce transient fluorescence, detected by a bare photomultiplier (RCA 7265 S-20 response) located directly above the intersection zone. The wavelength of the probe laser is scanned from 6000-6650 Å and the transient excitation spectrum is taken with a boxcar integrator (PAR Model 164) employing a 50 nsec observation window centered around the probe pulse.

Figure 2 shows the absorption and fluorescence spectrum of pentacene under thermal conditions as well as the transient excitation spectrum, normalized for the variation of probe beam power with wavelength. In addition, the latter has been corrected for scattered light from both the pump and probe beams, as well as for any direct fluorescence excited by the probe beam acting alone. Although it was not possible to determine what fraction of the excited pentacene molecules participate in the transient excitation spectrum, we estimate from the magnitude of the direct fluorescence that this fraction is a significant portion of all pentacene molecules excited.

The transient excitation spectrum is shifted to the red and appears much broader than the absorption spectrum. The transient species that can be produced by radiationless processes from initially excited S_1 are $T_1^\#$ or $S_0^\#$. However, solution and gas-phase studies have shown that the triplet-triplet absorption spectrum lies to the blue of the absorption spectrum.⁵ In addition, because the fluorescence spectrum is not much shifted from the absorption spectrum, pentacene mole-

cules that have undergone one fluorescence cycle cannot be responsible for absorption of the probe beam. Moreover, the intensity of the transient excitation spectrum is found to be proportional to the intensity of the pump beam. Thus we conclude that the transient excitation spectrum corresponds to absorption by $S_0^\#$. This result is reasonable since quantum yield measurements in solution indicate that the fluorescence quantum yield is 8%, intersystem crossing 16%, and internal conversion 76%.⁶

The initial excitation energy of S_1 is redistributed among 2.7×10^{14} vibrational levels per wavenumber,⁷ preferentially to high-frequency accepting modes such as the symmetric C-H stretch (≈ 3000 cm^{-1}) and, among others, the symmetric C-C optical mode (≈ 1400 cm^{-1}). Excitation of the C-H stretch can contribute little to the red shift of the transient excitation spectrum, while the C-C optical mode accounts for "hot bands" in the absorption spectrum (Fig. 2). Clearly, a model in which energy is randomly distributed among the 102 vibrational modes cannot account for the appearance of the observed transient excitation spectrum. Indeed, the red shift requires the preferential population of $v=2-3$ of the C-C optical mode, which evidently does not have sufficient anharmonicity for the vibrational modes to freely exchange energy on the experimental time scale of 1-10 μ sec.⁸

These preliminary results demonstrate the ability to follow time evolution of radiationless processes in the collision-free environment of molecular beams. Experiments with improved spectral and temporal resolution should now be possible, as well as comparative studies involving deuteration. Radiationless processes in molecular beams can be used to prepare selectively excited, isolated $S_0^\#$ or $T_1^\#$ molecules in high vibrational levels with known energy content so that the subsequent collisional, radiative, and/or intramolecular behavior of these molecules can be studied in a controlled manner.

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