

LETTERS TO THE EDITOR

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area. (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 January 1981 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Observation of intracavity absorption of molecules in supersonic beams^{a)}

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The techniques of fluorescence excitation spectroscopy have proven to be useful in obtaining transition frequencies for large molecules cooled by supersonic expansion in a beam apparatus.^{1,2} The determination of oscillator strengths and radiative decay rates obtained from the analysis of fluorescence excitation spectra are complicated by the fact that knowledge of the fluorescence quantum yields, the branching ratios, and the nonradiative decay rates are necessary for accurate evaluations. Furthermore, it is obvious that non- or weakly fluorescent transitions cannot be investigated by the excitation method. Conventional transmission experiments have recently been performed³; however, because of the small absorption, there are inherent limitations on the sensitivity. Intracavity absorption (ICA) spectroscopy has been demonstrated to be a sensitive means for directly studying the absorptive properties of low density samples and transitions with small oscillator strengths. Most previous studies have been concerned with the spectroscopy of atomic and small polyatomic species in the gas phase,⁴ and with molecules in solution.⁵

In this communication we wish to report on the observation of ICA of ultracold large molecules in a super-

sonic molecular beam. We observe intracavity absorption for the molecule dimethyl-*s*-tetrazine (DMT) at rotational and vibrational temperatures of < 0.1 and 16 °K, respectively. We also report on the ICA of I_2 at comparable rotational and vibrational temperatures. The results indicate that the sensitivity of the method is very high, enabling absorption measurements to be made, even though the molecular density and optical path length are small in the supersonic beam. For the study of non-fluorescing molecules this technique will be very important. Also, with a good ICA theory one will be able to determine absorption cross sections and relative quantum yields.

The experimental apparatus consisted of an argon ion-pumped dye laser modified to have a 1 m cavity length. The cw molecular beam chamber (designed to have a high throughput, 40 Torr liter/sec, at 10^{-2} Torr) with AR coated Brewster angle wedged windows was located within the laser cavity (see Fig. 1). The 30' wedged Brewster windows prevented interference fringes from developing in the laser output. The laser crossed the supersonic jet 3 mm from the nozzle, thereby defining an interaction region with approximate dimensions $0.1 \times 0.1 \times 1$ cm. ICA measurements were accomplished by

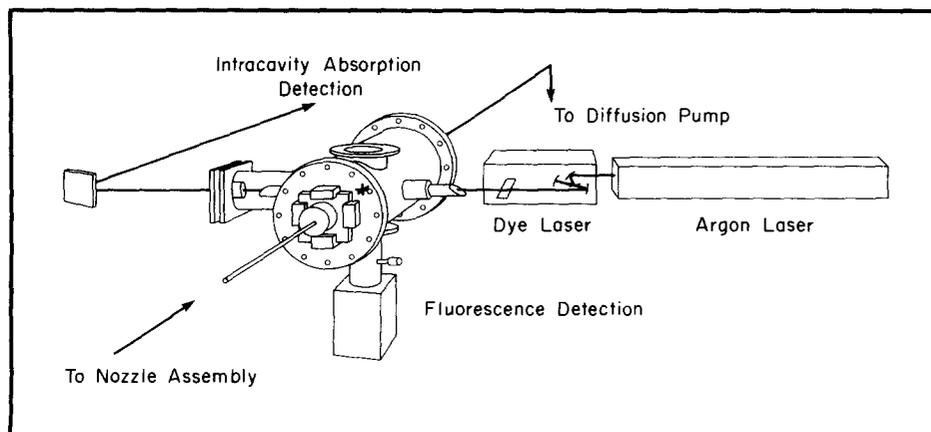


FIG. 1. The experimental arrangement for ICA spectroscopy in a molecular beam. ICA and fluorescence spectra can be obtained simultaneously.

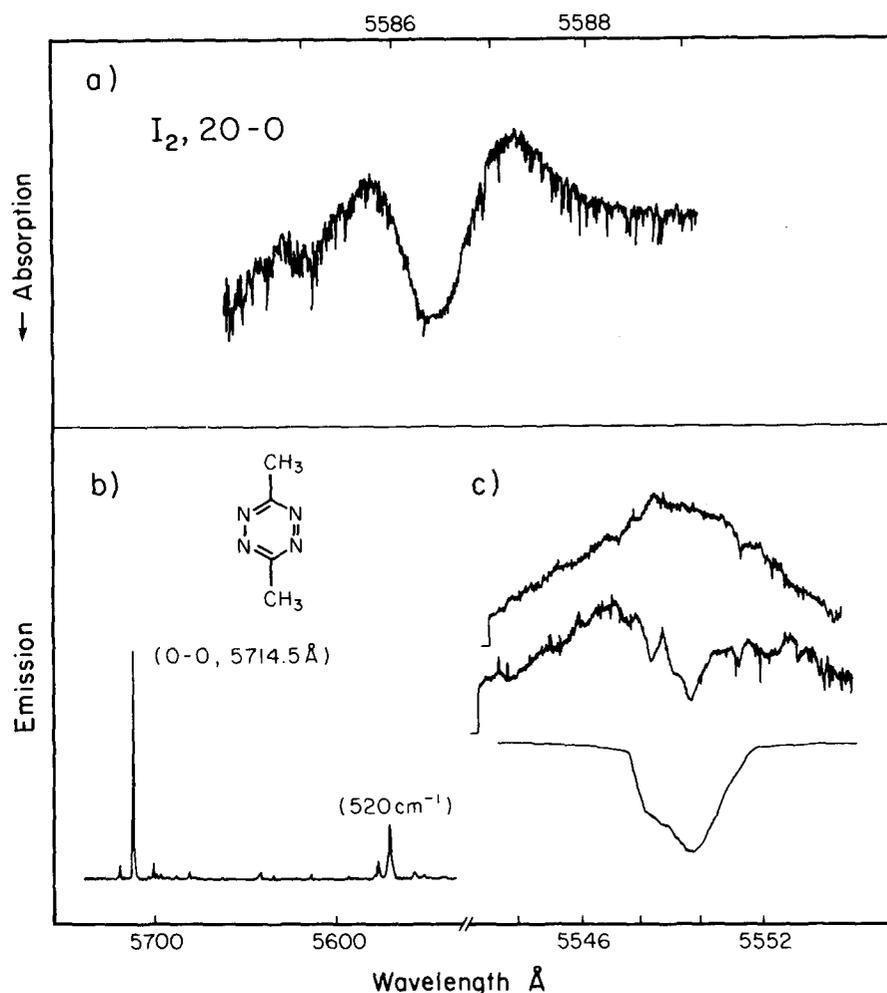


FIG. 2. (a) The ICA spectrum of I₂ in a supersonic molecular beam. The experimental conditions are described in the text. (b) A portion of the fluorescence excitation spectrum of DMT in a supersonic molecular beam, showing the 0-0 and the 520 cm⁻¹ vibrational mode. (c) The intracavity absorption and the fluorescence excitation spectrum of the 0-1 vibrational transition of DMT. The top spectrum shows the system response in the absence of DMT. The center trace shows the ICA spectrum. The lower spectrum portrays the fluorescence excitation taken under identical experimental conditions. The laser bandwidth for fluorescence excitation was 0.75 Å.

spectrally resolving (0.3 Å resolution) the light transmitted by the end mirror (reflectance 99.5%) of the laser cavity. The laser bandwidth was approximately 12 Å and the wavelength could be tuned throughout a 150 Å region centered about the dye gain maximum by adjusting the mirror alignment of the dye laser, and by changing the dye concentration. The intracavity laser power was estimated to be 1.5 W in the TEM₀₀ mode. Operating the dye laser above threshold, although reducing the inherent sensitivity of the ICA technique,⁶ improved the stability of the system. In order to obtain the fluorescence excitation spectra, a two-plate birefringent Lyot filter (0.75 Å bandwidth) was used to continuously tune the laser, while the total fluorescence was filtered and detected with a photomultiplier tube.

Dimethyl-*s*-tetrazine and I₂ were expanded through a 50 μ pinhole with a back pressure of 50 psi helium into the molecular beam chamber. It was important to maintain the pressure in the vacuum chamber below 10⁻⁴ Torr in order to minimize the absorption contribution from the background gas.

Figure 2 shows the ICA absorption spectra of I₂ and DMT. For I₂, the band of the B³Π_{0_u⁺} ← X¹Σ_{g⁺} transition at 5586.5 Å is shown. The ICA spectrum demonstrates the well documented line shape distortions characteristic of the intracavity absorption of gases.⁴ The excitation

spectrum (not shown) was similar to that reported for I₂ by Smalley *et al.*⁹ The portion of the excitation spectrum of DMT in Fig. 2(b) shows the well-known (0-0) transition at 5714 Å and the 520 cm⁻¹ vibration.^{7,8} The ICA and the fluorescence excitation spectrum of the 520 cm⁻¹ vibration are compared in Fig. 2(c). The broadening observed in the excitation spectrum is due to the resolution of our laser, while that of the intracavity absorption is limited by the resolution of the spectrometer. The energy and overall line shape of the transition in the ICA spectrum correlate very well with the excitation spectrum.

The density of DMT in the beam is calculated to be 4 × 10¹¹ molecules/cm³. The laser interacts with ~ 4 × 10⁹ molecules, which results in an 80% reduction in the laser power at the absorption maximum. The absorption cross section calculated for intracavity absorption, when compared with the value obtained by extracavity absorption experiments,¹⁰ leads to an enhancement factor of 580 at (P/P_{th})/(P - P_{th}) = 3.8, where P is the pump power (2.5 W) and P_{th} is the threshold power (0.3 W).¹¹ Using the results of Harris' paper,⁶ we conclude that an enhancement factor of about 10⁶ is characteristic for our experiments at powers near the laser threshold. With knowledge of the enhancement factor in the linear regime for a particular molecular transition, one can determine absorption cross sections for other transitions of that

molecule in the supersonic beam without the need to know the various branching ratios which are necessary for obtaining the same information from excitation spectra. We are currently carrying out these measurements on DMT.

In conclusion, the efficacy of applying intracavity absorption spectroscopy to vibrationally and rotationally cold large molecules in supersonic beams has been demonstrated. Despite the low molecular density and small optical path length encountered in the jet, the absorption properties can be determined. Moreover, we feel that because of the large enhancement factor, this technique can also be used to probe forbidden transitions in a molecular beam. Further technical development, particularly with regard to increasing the resolution and extending the tuning range of the dye laser, will improve the versatility of this technique.

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¹D. H. Levy, L. Wharton, and R. E. Smalley, *Chemical and*

Biological Applications of Lasers VII, edited by C. B. Moore (Academic, San Francisco, 1977).

²A. Amirav, V. Even, and J. Jortner, *Chem. Phys.* 51, 31 (1980).

³V. Vaida and G. M. McClelland, *Chem. Phys. Lett.* 71, 436 (1980).

⁴(a) P. Kumar, G. O. Brink, S. Spence, and H. S. Lakkaraju, *Opt. Commun.* 32, 129 (1980); (b) T. W. Hänsch, A. L. Schawlow, and P. E. Toschek, *IEEE J. Quantum. Electron.* 8, 802 (1972); (c) W. T. Hill III, R. A. Abreu, T. W. Hänsch, and A. L. Schawlow, *Opt. Commun.* 32, 96 (1980); (d) R. G. Bray, W. Henke, S. K. Liu, K. F. Reddy, and M. J. Berry, *Chem. Phys. Lett.* 47, 213 (1977); (e) V. M. Baev, T. P. Belikova, E. A. Sviridenkov, and A. F. Suchkov, *Sov. Phys. JETP* 47, 21 (1978); (f) G. H. Atkinson, T. N. Heimlich, and M. W. Schuyler, *J. Chem. Phys.* 66, 5005 (1977); (g) H. Schröder, H. J. Neusser, and E. W. Schlag, *Opt. Commun.* 14, 395 (1975).

⁵J. S. Shirk, T. D. Harris, and J. W. Mitchell, *Anal. Chem.* 52, 1701 (1980).

⁶S. J. Harris, *J. Chem. Phys.* 71, 4001 (1979).

⁷G. G. Asmuth, K. K. Innes, and V. A. Job (to be published).

⁸R. M. Hochstrasser, D. S. King, and A. B. Smith III, *J. Am. Chem. Soc.* 99, 3923 (1977).

⁹R. E. Smalley, D. H. Levy, and L. Wharton, *J. Chem. Phys.* 64, 3266 (1976).

¹⁰M. Paczkowski, R. Pierce, A. B. Smith III, and R. M. Hochstrasser, *Chem. Phys. Lett.* 72, 5 (1980).

¹¹The enhancement factor is linear in the function $(P/P_{th})/(P-P_{th})$, as discussed in Ref. 6.

Optical detrapping in solids

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Trapping and detrapping processes are of prime importance in energy transport phenomena in crystals. Guest emission after host excitation,¹ even at very low guest (impurity) concentration, is the most striking feature of excitation trapping. This trapping process, which occurs through exciton motion and radiationless relaxation at the trap site, is still a subject of current interest.² When the trap depth (Δ) far exceeds the Debye frequency (ω_D), we speak of a deep trap, and the reverse process of detrapping is not observed. In the opposite case, where $\Delta \ll \omega_D$, we have a shallow trap and here we can easily observe the phenomenon of phonon-assisted detrapping. Harris and co-workers³⁻⁵ have recently studied this effect in some detail in molecular solids and proposed a stochastic model for phonon-assisted detrapping.

In this communication we are concerned with *optical* (photon-assisted) detrapping. Here the excitation from a deep trap is transferred by a laser to the host exciton band.

So far, laser-induced energy transfer processes have

only been observed in gases.^{6,7} Jortner and Ben-Reuven,⁸ however, theoretically examined laser-induced transfer in solids and suggested the possibility of observing trap-host energy transfer in molecular crystals.

In this letter we demonstrate the feasibility of such an experiment and show that the effect can be used to explore the band structure of the host-acceptor state. The system we have chosen is pentacene (PTC) in naphthalene (NT), whereby the pentacene is a deep trap ($\Delta = 14887 \text{ cm}^{-1}$). The relevant energy diagram is shown in Fig. 1. The transfer we discuss in this report is between the lowest excited singlet state of PTC and the lowest singlet exciton band of NT.

The experiment was performed by exciting, collinearly, a PTC in NT mixed crystal by two nitrogen-pumped dye lasers. One dye laser operates at the PTC transition ($16588 \text{ vac cm}^{-1}$), while the other is tuned to a frequency which corresponds with the PTC trap depth Δ . Both lasers are focused in the crystal to a spot of $\sim 100 \mu$ diameter. Under these conditions the peak power at the sample of both lasers is $\sim 2 \text{ MW cm}^{-2}$.