INFRARED FLUORESCENCE FROM PAHs IN THE LABORATORY

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1 - Introduction

Several celestial objects, including UV rich regions of planetary and reflection nebulae, stars, HII regions and extragalactic sources, are characterized by the unidentified infrared emission bands (UIR bands). This family consists of features at 3050 cm^{-1} (3.3μm), 2950 cm^{-1}(3.4μm), 1615 cm^{-1}(6.2μm), 1310 cm^{-1} (7.7μm), 1150 cm^{-1} (8.6μm) and 85 cm^{-1} (11.8μm), with weaker signatures at 1785 cm^{-1} and 1430 cm^{-1}, and was first detected in the planetary nebula NGC 7027 (Gillet et al., 1973; Merrill et al., 1975; Russel et al., 1977). The features have typical widths of 3% to 10% of their wavelength (Allamandola, 1984; Willner, 1984).

A few years ago, it was proposed that polycyclic aromatic hydrocarbon species (PAHs) are responsible for most of the UIR bands (Duley and Williams, 1981; Lèger and Puget, 1984; Allamandola, Tielens and Barker, 1985). This hypothesis is based on a spectroscopic analysis of the observed features. The 3050 cm^{-1} band for example is known to be characteristic of the aromatic stretching vibration in PAHs (Bellamy, 1968), as is the 6.2 μm signature.

Comparisons of observed infrared spectra with laboratory absorption spectra of PAHs support the PAH hypothesis. (Lèger and d' Hendecourt, 1987; Allamandola, Tielens and Barker, 1987). An example spectrum is represented in Fig 1, where the Orion Bar 3.3 micron spectrum is compared with the absorption frequencies of the PAHs Chrysene ($C_{18}H_{12}$), Pyrene ($C_{16}H_{10}$) and Coronene ($C_{24}H_{12}$).

This paper presents the laser-excited 3.3 μm emission spectrum from a gas phase PAH (azulene, $C_{10}H_8$). The infrared fluorescence theory (IRF) is briefly explained, followed by a description of the experimental apparatus, a report of the results and discussion.
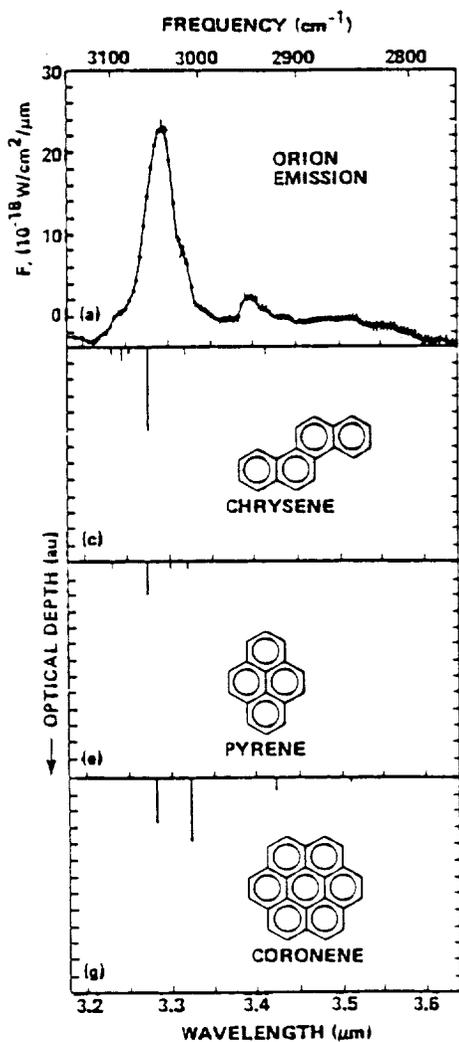
Fig 1 : The 3 micron emission spectrum from the Orion Bar compared with the absorption spectra of chrysene, pyrene and coronene.

2 - Infrared Fluorescence Theory

The IRF emission due to a $\Delta v = 1$ vibrational transition in a polyatomic molecule of total vibrational energy E can be calculated from the basic expression for a single oscillator (Herzberg, 1968; Durana and MacDonald, 1976; Rossi et al., 1983)

$$I(E,i,v) = N_v(E) \; h\nu_i \; A_i^{v,v-1}$$

where ν_i is the frequency of the emitting mode, $A_i^{v,v-1}$ is the Einstein coefficient for the $v \rightarrow v-1$ transition (equal to $v \; A_i^{1,0}$ in the harmonic oscillator approximation), and $N_v(E)$ is the number of molecules with total energy E and v quanta in the ith vibrational mode.

152

Under the ergodic assumption, the energy is distributed statistically among the accessible vibrational states of the molecule, and

$$N_v(E) = N(E) \, \frac{\rho_{s-1}(E - vhv_i)}{\rho_s(E)}$$

where $N(E)$ is the total number of excited molecules, s is the number of oscillators, $\rho_s(E)$ is the total density of states with vibrational energy E, and $\rho_{s-1}(E-hv_i)$ is the density of states, omitting the emitting mode i and its vibrational energy content. Hence the theoretical IRF intensity for a particular $\Delta v=1$ transition and for the emitting mode i

$$(1) \qquad I(E,i,v) = N(E) \; hv_i \; v \; A_i^{1,0} \; \frac{\rho_{s-1}(E - vhv_i)}{\rho_s(E)}$$

The reliability of the IRF theory recently has been tested by experimental data that showed excellent agreement with theoretical predictions (Shi, Bernfeld and Barker, 1988).

Emission spectra from PAHs can be predicted using equation 1 and an assumed Lorentzian profile (30 cm⁻¹ width) as shown in Fig 2 where the calculated emission spectrum is for a C-H stretch mode (3050 cm⁻¹) of chrysene as a function of the vibrational energy content of the molecule (Barker, Allamandola, and Tielens, 1987). The main peak corresponds to the transition between the vibrational states v=1 and v=0. The second peak represents the transition v=2→ 1; the shift is due to the anharmonicity of the vibrational potential of the molecule. A more realistic simulation would include the other C-H stretch modes, which may have slightly different frequencies. All PAH species would exhibit a similar spectrum, but the peak locations are peculiar to each molecule and will be somewhat shifted.
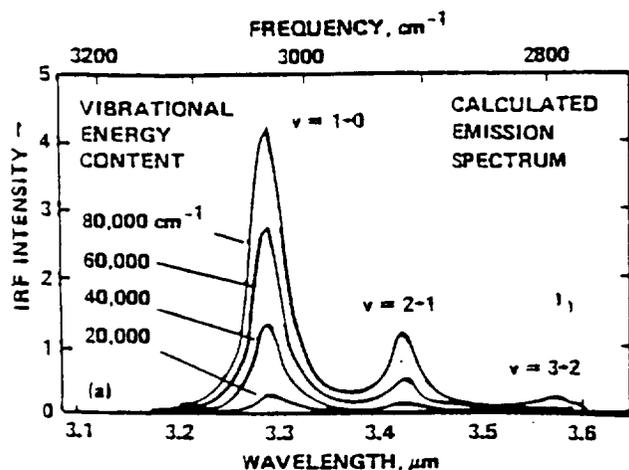
Fig 2 : .The calculated emission spectrum for chrysene in the C-H stretching region as a function of vibrational energy content.

3 - Experimental

Azulene ($C_{10}H_8$) is a very convenient laboratory subject because its rapid interconversion (IC) processes can be exploited in order to prepare vibrationally excited molecules in the electronic ground state. In this experiment, a 308 nm (32000 cm^{-1}) UV laser is used to excite azulene to its S_2 excited electronic state and subsequent IC to high vibrational levels of the electronic ground state takes place in ~1.4 ns, a lifetime much shorter than the interval between collisions. This method thus provides an ensemble of vibrationally excited molecules which emit infrared light via fluorescence.

The present experiment employs both IRF and optoacoustic techniques (Shi, Bernfeld and Barker, 1988). The first method measures the IRF emission intensity while the second one determines the number of vibrationally excited molecules. The IRF emission per azulene molecule can be deduced from the ratio of these two measurements.

The experimental apparatus is presented schematically in Fig 3. The fluorescence cell is fitted with Suprasil fused silica windows for the laser beam. The fluorescence is viewed through a sapphire window by a 77 K InSb photovoltaic detector (5 μs time-response) and matched preamplifier. A spherical gold mirror with a 5 cm focal length is placed inside the cell so that the detector matches the mirror center of curvature. The detector image is then located on the detector itself, which views a 77 K background. This method improves the fluorescence signal by collecting more light and by reducing the background noise. The azulene vapor pressure in both cells is regulated by maintaining the azulene reservoirs at fixed temperature with a temperature-regulated bath

The fluorescence emisson is isolated by a 2.5-5 μm bandpass filter (BPF) and wavelength resolved by a CVF filter maintained at 77 K. The resolution of the system is defined by an ajustable slit placed between the BPF and the CVF. A 40 cm^{-1} resolution was chosen in this experiment. The sensitivity of the instrument is essentially constant over the wavelength range of interest. Both the IRF emission and the optoacoustic signal are simultaneously acquired and averaged using a digital oscilloscope. The data are transfered to a computer and analysed using non-linear least squares.
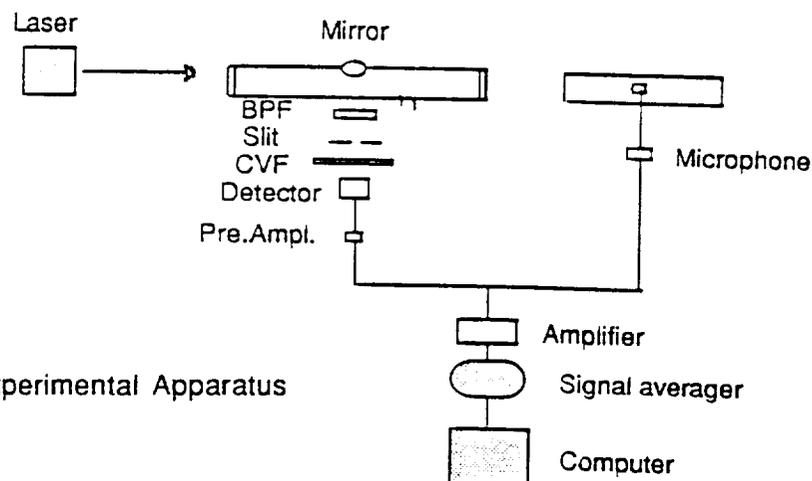

Fig 3 : Experimental Apparatus

154

4 - Results and discussion

A typical fluorescence decay signal is shown in Fig 4. The decay is due to collisional deactivation and is fitted by an exponential function. The IRF intensity at t=0 is then extrapolated from the intensity at t= 5µs, the time response of the system.

A preliminary IRF emission spectrum is presented in Fig 5. This spectrum resembles the observed IR spectrum, although azulene, used in this experiment for its photophysical properties, is probably not responsible for the IR emission in the interstellar medium, where a typical PAH size would range between 20 and 50 carbon atoms (Allamandola, Tielens and Barker, 1987). The peak position in Fig 5 is 3075 ± 20 cm^{-1}, which corresponds to the v=1→0 C-H stretching transition frequency. The measured spectrum is for all azulene C-H stretch modes, which have frequencies between 3020 cm^{-1} and 3080 cm^{-1}(Chao and Khanna, 1977). The asymmetry in the spectrum may result from the convolution of the Δv=1-0 and Δv=2-1 with the bandpass of the system, which is about 40 cm^{-1}. Thus the v=2→1 transition can not be resolved under these conditions. Nevertheless, the preliminary results presented in this paper are consitent with the hypothesis that PAHs are responsible for the UIR bands emission.

Experiments now underway are using a higher resolution (28 cm^{-1}) and should provide a better-resolved IR fluorescence spectrum from azulene. Future work will investigate other PAHs, both in cells and in cold molecular beam expansions, which mimic temperatures found in the interstellar medium.
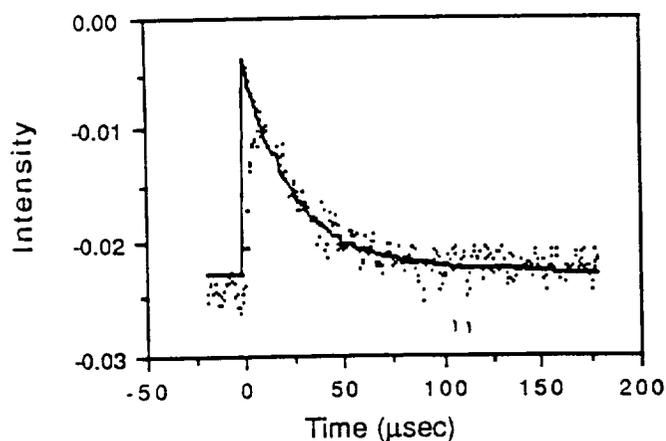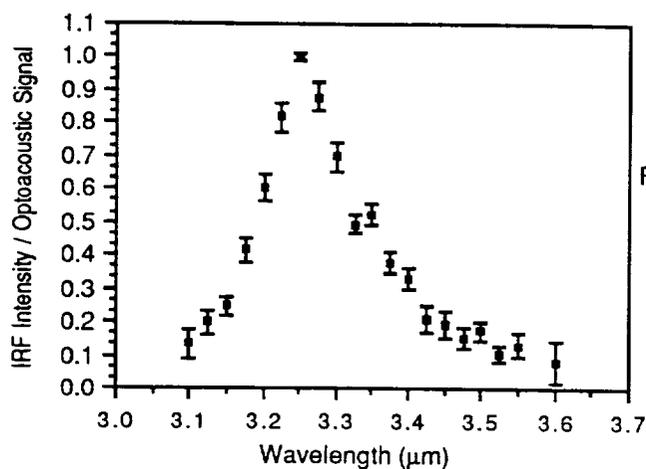

Fig 4 : IRF decay curve for azulene.

Fig 5 : IRF emission spectrum for azulene

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156