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Intramolecular vibrational energy redistribution (IVR) manifests itself in energy resolved emission in forming splitted and congested groups of emission lines due to the mixed character of the excited vibration.[1-3] Felker and Zewail have beautifully demonstrated quantum beats in the energy resolved emission spectra of anthracene.[4-6] The existence of these quantum beats as well as the weak rotational effect of their dephasing was invoked[6] as a strong argument for the dominating role of anharmonic coupling on IVR in anthracene. Recently intrastate IVR was shown to induce interstate intersystem crossing in 9-cyanoanthracene[7] and this IVR was found to be triggered by rotational dependent Coriolis coupling.[8] Rotational induced IVR was also shown in benzene[9,10] and invoked in pyrazine.[11] Here we report on our study of rotational effect on the energy resolved emission of anthracene.

Pulsed planar jets of anthracene were generated by expansion of seeded argon through a 33 m $\times$ 0.22 mm slit nozzle.[12,13] The nozzle temperature was 140–150 °C and the argon backing pressure was chosen at $\sim$90 Torr to minimize both sequence congestion and van der Waals complexes. The resulting rotational temperature was 20–25 K.[14] An excimer pumped dye laser (0.2 cm^{-1} resolution) crossed the planar jet 10 mm from the nozzle with its light attenuated to avoid saturation. The fluorescence was focused and analyzed by an 0.3 m McPherson monochromator.

In Fig. 1, we show on the upper trace the energy resolved emission of anthracene after exciting its 1380 cm^{-1} vibrational band. The emission spectrum is practically identical with that previously observed.[5] At the high energy side, we see sharp isolated emission lines that are due to the doorway "pure" 1380 cm^{-1} vibration state while near 3625 Å (and longer) we observe a highly congested bunch of several lines manifesting the dilution (IVR) of the doorway state that carries the oscillator state, among several optical inactive "dark" background states. In order to study rotational effects on the relative doorway state character, we show in the lower spectrum (trace B) the excitation spectrum of this vibration while light is collected through an energy window marked in asterisks on the upper spectrum. Thus, only emission to the 390 cm^{-1} ground state vibration is detected.[15]

From comparison with the excitation spectrum A, it is clearly observed that the doorway state character strongly depends on the rotational state and it is much smaller on the two sides of the band. In addition, although it is a mixed vibrational state, spectrum B is even slightly narrower than the 0–0 transition under these conditions.

In Fig. 2, we show the excitation spectrum of anthracene near its 1380 cm^{-1} vibration (upper trace) together with its energy resolved emission spectra when it was excited on different positions and rotational states of its rotational contour. The emission spectra are assigned A, B, C according to their excitation wavelength indicated on the upper excitation trace. We show here for clarity only the portion of the emission to states near 1380 cm^{-1} ground state energy.

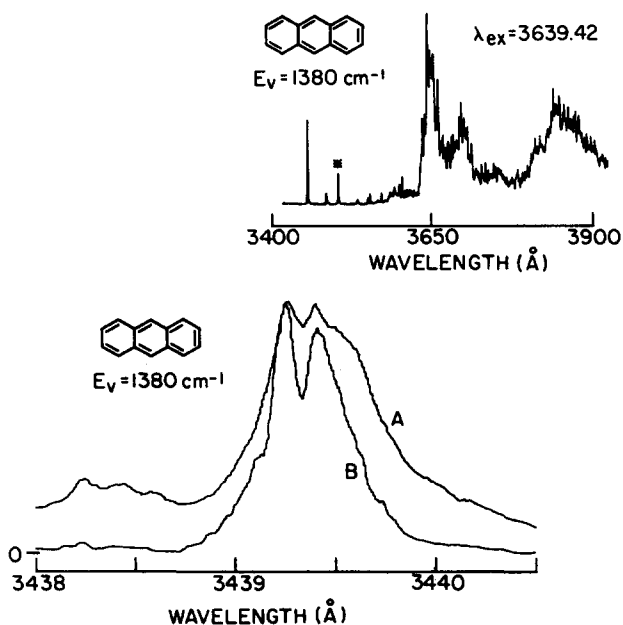A remarkable difference is observed between traces A, B, and C which differ in excitation energy only by 1.6 and 3.2

FIG. 1. Excitation and energy resolved emission of anthracene 1380 cm^{-1} vibration. The upper trace shows the energy resolved emission after excitation at the center of the rotational contour (1 Å resolution). Nozzler temperature is 150 °C, and argon backing pressure is 90 Torr. The lower trace A is the energy unresolved excitation (LIF) spectrum, while trace B was taken by collecting the emission to the 390 cm^{-1} ground state vibration (marked in *) alone. The base line marked in 0– and the other experimental conditions are the same. Note the reduced height of B at higher rotational states.
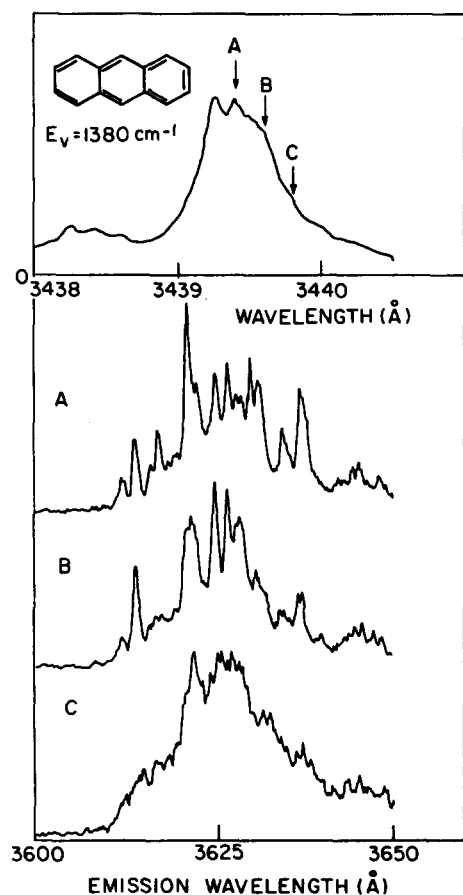
FIG. 2. Excitation (upper curve) and energy resolved emission of anthracene on the spectral range of 3600–3650 Å. The excitation wavelengths for traces A, B, and C are marked in arrows on the upper excitation spectrum. The monochromator resolution was 0.7 Å. Other conditions are as in Fig. 1. Note the dramatic rotational dependence of the energy resolved emission.

cm^{-1}. An increased rotational energy completely changes the emission trace A, which is very similar to that previously observed.[5] Trace B has fewer pronounced lines and trace C is so highly congested that it shows no resemblance to trace A, demonstrating largely increased number of coupled background states.

From Figs. 1 and 2, we conclude that in addition to anharmonic coupling, Coriolis coupling is very important dominating IVR at high enough rotational states. Similar behavior was recently demonstrated in 9-cyanoanthracene.[8]

The emerging picture is that anharmonic coupling has a greater strength and it can couple states far apart to form Fermi resonances,[15] but it is highly restricted in terms of selection rules and can induce coupling only to a small subset of the total vibrational density of states. On the other hand, Coriolis coupling has much less stringent selection rules and its strength, although weaker than anharmonic, is strongly increased with the rotational states. Thus, even in supersonic jets, it is the dominant mechanism leading into IVR.[8–11]

Comparing our demonstrated role of Coriolis coupling with the results and interpretations of Felker and Zewail,[6] we note the following: their observed beats were most pronounced in doorway state emission which we showed to have a much smaller contribution of high rotational states. Emission near 3625 Å was studied only on peaks, thus selecting only a subset of the low rotational states as is evident from Fig. 2. The emission from high rotational states is spread as the unresolved background observed in trace C. This background is responsible for the large unmodulated portion in the beats observed. Unlike in two level systems, we have here several states coupled and an increased coupling strength is expected to cause a smaller energy shift and can rationalize the "weak" quantum beats dephasing observed.[6]

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