

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2004 issue.

NOTES

Helium nanodroplet isolation spectroscopy of perylene and its complexes with oxygen

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(Received 29 October 2003; accepted 16 January 2004)

[DOI: 10.1063/1.1667462]

Helium nanodroplet isolation (HENDI) is an established and unique way to carry out spectroscopic investigations of a broad range of molecular species.¹ The very low temperature of and the very weak interaction with the helium matrix allow for the observation of significantly simplified spectra. As the superfluid environment is similar to the gas phase, frequently rotational structure can be observed.

In the present work, we have taken advantage of the fact that bolometric detection allows for the observation of species that do not fluoresce or do so too weakly to be observed by conventional optical spectroscopic detection systems. By using a beam depletion bolometric detection method, we have been able to observe the $S_1 \leftarrow S_0$ excitation spectra of complexes of perylene with one or more molecules of oxygen. Because of the quenching properties of molecular oxygen, this experiment would not have been possible using fluorescence detection. To our knowledge, no gas phase measurements of the perylene-oxygen complex $S_1 \leftarrow S_0$ excitation spectra have been reported to date in the literature. Since the work we report here is a preliminary study, as we present the results, we will explain why we believe that HENDI spectroscopy can provide new insights into the very important process of fluorescence quenching.

The HENDI spectrometer used in these experiments has already been described in detail elsewhere² and we will only briefly describe the features that are particular to the experiments reported here.

Perylene is evaporated in an oven at a temperature of 135 °C which corresponds to a vapor pressure of about 0.1 mbar. The droplets cross a 2 cm long heated (190 °C) pick-up cell connected to the oven in order to be doped by the molecules of interest.

The laser source is a frequency-doubled Ti:Al₂O₃ laser pulsed at a repetition rate of 2.7 kHz with a bandwidth of the order of 0.5 cm⁻¹. In order to increase the interaction time between the droplet beam and the laser, we use a multipass arrangement which makes the laser interact with the droplets beam at least 50 times.

Upon electronic excitation of the embedded molecules

due to the absorption of a photon, some of the absorbed energy will be released by the dopant towards the droplet. This energy will be dissipated by evaporation of helium atoms out of the droplet until thermal equilibrium at 0.38 K is reestablished. Since the evaporated atoms leave the droplet with random velocity directions, a loss of helium flux in the direction of propagation of the droplet beam will result from this process. This depletion of the beam is measured by a bolometer that acts, in this case, as a thermal flux detector. Detection at the repetition rate of the laser could not be used due to the long time constant of the bolometer and the laser is chopped at 270 Hz, allowing the amplification of the bolometer signal with a lock-in amplifier.

While it is possible to detect in this way the spectra of fluorescing molecules if enough vibronic energy is released into the droplet, it is clear that this detection scheme is ideal to observe spectra of weakly or nonfluorescent species.

To begin with, we have used our beam depletion detection setup to measure excitation spectra of the perylene monomer. The spectrum of the 4_0^1 vibronic band, shown in Fig. 1, exhibits a typical structure for a polyaromatic hydrocarbon molecule embedded in a helium droplet³ composed of a sharp zero phonon line (ZPL) followed at higher energies by a broad phonon wing (PW), on top of which additional structure is observed. This structure has been seen for other vibronic bands of the transition, and the beam depletion spectra of the monomer compare well with the laser-induced fluorescence spectra that have been recorded earlier in the laboratory⁴ and remeasured recently by Slenczka and collaborators.⁵ We have to point out that perylene is a bad candidate for bolometric detection because of its large fluorescence quantum yield. However, if perylene is complexed with oxygen, which is known to be an efficient fluorescence quencher, we can expect an increase of the detection efficiency.

Figure 2 shows the beam depletion spectra observed when a pick-up cell filled with molecular oxygen was crossed by the droplet beam before the perylene pick-up cell. Several new absorption bands appear to the red of the 0_0^0

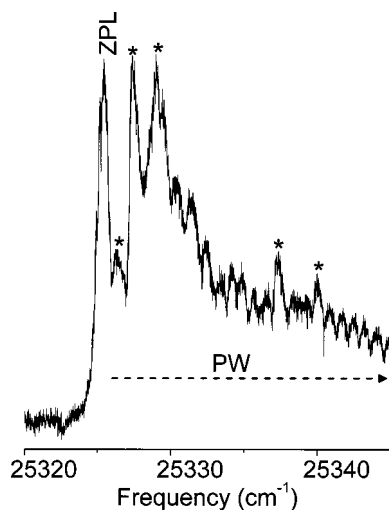


FIG. 1. The 4_0^1 transition of perylene inside helium droplets obtained by beam depletion bolometric detection. The sharp absorptions that emerge from the phonon wing are marked with a star. The oscillation superimposed to the signal is due to an etaloning effect that occurs while the laser is being tuned.

transition of the monomer located at $24\,030\text{ cm}^{-1}$ (band "M" on Fig. 2). By increasing the pressure of oxygen in the pick-up cell, we can observe the evolution of the relative intensities of the different bands and propose an assignment. At $23\,984\text{ cm}^{-1}$ the band labeled "D" in Fig. 2 is assigned to the perylene-oxygen dimer (complex 1:1) and the band labeled "T" at $23\,910\text{ cm}^{-1}$, which appears at a higher pressure of oxygen in the pick-up cell, is assigned to the perylene-(oxygen)₂ trimer (complex 1:2). Other peaks, marked by asterisks in Fig. 2, are due to the presence of impurities in the spectrometer and we suspect them to be due to complexes formed with the systems of interest (monomer and/or complexes) and molecular nitrogen.

It is interesting to point out that the intensities of the complex spectra appear to be approximately the same as the intensity of the monomer 0_0^0 transition. This is an indication that the quenching efficiency of molecular oxygen plays an important role in this case. On one hand, most of the excited perylene molecules will fluoresce and we can assume that only a small fraction of the excitation energy will contribute to the signal observed by beam depletion. On the other hand, when the fluorescence is quenched by the presence of oxygen, most of the excitation energy will contribute to the beam depletion signal. Observing the same relative intensities for the monomer and for the complexes indicates that the fraction of perylene molecules that are complexed with oxygen is also small. We must, however, be careful when comparing the relative intensities out of our data. We would not only need to know the fluorescence quantum yields, which are not known, but the amount of vibrational energy deposited is also important in the ratio of the two signal strengths. We know that the monomer peak shown in Fig. 2 is the origin of the transition but vibrational assignment of the complexes spectra has not been made, and we do not know how much vibrational energy is readily transferable to the droplet. As a matter of fact, the increase of the base line seen

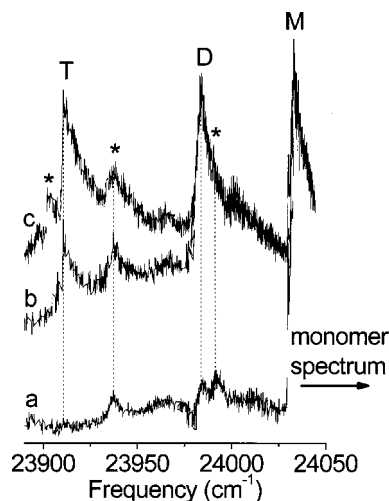


FIG. 2. Excitation spectra of the complexes of perylene with oxygen in helium droplets taken with (a) traces of oxygen and nitrogen, (b) 7.5 mbar of oxygen, and (c) 15 mbar of oxygen in the first pick-up cell.

in Fig. 2 when the pressure is increased in the oxygen pick-up cell may indicate that the observed bands sit on top of phonon wings of lower vibronic transitions of the complexes and that "D" and "T" are spectra of complexes vibrationally excited in S_1 .

The fact that we can observe spectra of the 1:2 complex is very encouraging. It is known that it is possible to control the structure of heterogeneous van der Waals complexes in helium droplets by using different pick-up sequences.^{6,7} This is due to the very low temperature of the helium droplets which makes it difficult for a system trapped in a local minimum of its potential energy surface to isomerize. Hence, if we first form the dimer of oxygen in the droplet and then add the perylene, we will not have the same resulting complex as if we first form the complex perylene-oxygen in the droplet then add another oxygen molecule. In the first case, we should form the complex perylene:(oxygen:oxygen), where perylene sits next to the oxygen dimer, whereas in the second case, we can also form the sandwich complex oxygen:perylene:oxygen where the oxygen molecules are located on each side of the perylene. By comparison of the spectra obtained with different pick-up sequences, we think that it will be possible to study the fluorescence quenching processes from an unprecedented structural point of view.

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