

Preresonance Raman Spectrum of the C₁₃H₉ Fluorene-like Radical

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Two important observations were recently reported which add support to the hypothesis that polycyclic aromatic hydrocarbons (PAHs) exist in the interstellar medium (ISM) and are responsible for the unidentified infrared (UIR) emission bands. First, infrared absorption bands observed in the vicinity of the protoplanetary nebula CRL 618 [1] were deduced to arise from the aromatic molecule, benzene, and, second, the first infrared emission spectrum of a polycyclic aromatic cation (pyrene) was seen in a laboratory experiment.[2] The PAH model [3,4], first proposed in 1984-85, suggests that the UIR emission bands, observed from many carbon-rich ISM sources, arise from a number of different PAHs, in either their neutral, ionic, hydrogenated and/or dehydrogenated forms. The model has been much discussed since 1984-5 and many laboratory experiments and astrophysical calculations have been performed which point to the viability of the idea. But the above results are among the first to directly show that PAH ions can emit in the infrared and that PAHs are present in the ISM (although benzene is technically not a PAH, it is in the same family).

We suggest that dehydrogenated PAHs may play a role in interstellar chemistry and could be responsible for some of the diffuse interstellar visible absorption bands (DIBs). It is general knowledge that neutral PAHs when ionized shift their electronic absorption bands to the red. But it is not widely known that removal of a hydrogen from a PAH may also result in a red shift. In general, lower energy photons are required for hydrogen removal than for ionization of neutral PAHs. Thus dehydrogenation could easily compete with ionization processes in ISM regions where penetration of low temperature radiation is important. From recent laboratory experiments, it is now known that the photodehydrogenation of some PAH cations can occur very efficiently. Dehydrogenated neutral and ionic PAHs may therefore play a crucial role in the photochemistry of the ISM.

We present the preresonance Raman spectrum of the C₁₃H₉ fluorene-like radical which was produced from fluorene (C₁₃H₁₀) by removal of one hydrogen (most likely from the sp³ carbon), by either UV photolysis or low energy electron bombardment. The Raman active modes were resonantly excited by 496.5nm laser radiation, which corresponds to the low energy absorption band shoulder of the 2A₂(D₂) ← 2B₂(D₀) (0-0) transition of C₁₃H₉. This electronic transition was recently identified from a combination of experimental observations and vertical excitation energy calculations using time dependent density functional theory.[5] The results of density functional theory (B3LYP/6-31G(d, p)) calculations of the harmonic frequencies of Raman and IR modes are also reported and compared to experimental data.

References:

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