VISIBLE SPECTROSCOPY OF JET-COOLED PHENYLACETYLENE CATION

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In our laboratory, we have initiated a program on the visible spectroscopy of Polycyclic Aromatic Hydrocarbons (PAHs) cations, in the context of their possible contribution to the Diffuse Interstellar Bands mystery. Despite Phenylacetylene (PA) is not polycyclic, it is a reactant in the formation of PAHs and among the products of Naphthalene$^+$ dissociation. We have used our molecular beam mass spectrometric photodepletion technique [a] to study the $D_3 \leftarrow D_0$ transition of this cation. Ions of PA$^+$–Ar (van der Waals complexes, formed by the association of a PA molecule and an argon atom) are formed by resonant two-photon ionization with two tunable lasers, and the absorption of a third laser beam is detected by a time-of-flight mass spectrometer. Indeed due to the smallness of the binding energy the third photon absorption causes argon departure. The visible spectrum of the complex cation is recorded while monitoring the fragmentation ratio as a function of the energy of this photon. The method is selective and very sensitive. Since rare gas atom adsorption is a very small perturbation for the electronic transitions, the main pattern in these absorption signatures originates from the bare cation states. The $D_3 \leftarrow D_0$ transition was recorded from 17 000 to 21 000 cm^{-1}. A progression built on the intramolecular mode 13 can be seen, as well as a few other vibronic bands. Under some ion preparation conditions, the $13^0{}_1$ hot band is present, whose intensity is affected by vibrational predissociation. The van der Waals shifts can be measured as well so that rather detailed information on binding energies can be derived. The spectra also reveal the existence of intrinsic spectral broadening, which can be rationalized in terms of intramolecular non radiative transitions taking place in such a large molecular species, in particular by fast internal conversion.

[a] T. Pino, N. Boudin and Ph. Brechignac, J. Chem. Phys. 111, 7337 (1999); Ph. Brechignac, T. Pino, N. Boudin, Spectrochim. Acta Part A 57, 745 (2001).