

*Letter to the Editor***Electronic spectra of cold gas phase PAH cations:
Towards the identification of the Diffuse Interstellar Bands carriers**

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Abstract. An original experimental technique capable to produce electronic spectra of cold gas phase cations of large aromatic molecules, previously suggested as a family of potential carriers of Diffuse Interstellar Bands (DIBs), has been developed and put to work. This achievement is demonstrated with the spectrum of the $D_2 \leftarrow D_0$ electronic transition of the phenanthrene cation, $C_{14}H_{10}^+$, in the near infrared. The results are compared with the spectrum of the same species isolated in a neon matrix, showing how the effect of this environment on the spectrum severely limits the capability of the matrix isolation technique for definite DIB assignments.

Key words: molecular data – ISM: molecules**1. Introduction**

The identification of the species responsible for the so-called “Diffuse Interstellar Bands” (DIBs), as absorption features superimposed over the interstellar extinction curve throughout the visible and near infrared spectral range, remains after more than 60 years the most enigmatic mystery of the astrophysical spectroscopy. Many suggestions have been put forward along the years (for a review see Herbig 1995), but none has yet received definite confirmation. Shortly after the so-called PAH hypothesis was introduced to account for the “unidentified infrared” (UIR) emission bands (Léger & Puget 1984, Allamandola et al. 1985, Léger et al. 1987), it was suggested that the ionic derivatives of the polycyclic aromatic hydrocarbons (PAHs) could be among the carriers of the DIBs (Léger & d’Hendecourt 1985, van der Zwet & Allamandola 1985, Crawford et al. 1985). Among the arguments given at that time, and still valid (Léger 1995), is the high abundance of the PAHs, expected to result from their large stability against the UV radiation field in the interstellar field (ISM). Indeed it can be estimated, through the measured flux emitted in the UIR bands, to be of the order of 15% of the total cosmic carbon abundance. This suggestion has motivated systematic investigation of PAH cations spectra using matrix isolation spectroscopy (Salama et al. 1996).

Over the past few years it became clearer, from new observational data consisting of high resolution spectra of selected line-of-sights, that large polyatomic species in the gas phase, most probably carbonaceous, should contribute to some of the DIBs (Herbig 1995, Sarre et al. 1995, Ehrenfreund & Foing 1996, Kerr et al. 1996, Jenniskens et al. 1996, Krelowski & Schmidt 1997, Krelowski et al. 1997, Rouan et al. 1997, Sonnentrucker et al. 1997, Ehrenfreund et al. 1997, Kerr et al. 1998). Among these, two very recent propositions have reached the stage of providing striking coincidences, if not fully convincing. Two new near infrared DIBs at 957.7 and 963.2 nm have been tentatively assigned to the fullerene cation C_{60}^+ (Foing & Ehrenfreund 1994, 1997). However this assignment relies on the laboratory spectrum of C_{60}^+ isolated in a neon matrix (Fulara et al. 1993), and it is well known that the condensed rare gas environment induces unpredictable broadening and shifts of the absorption bands. Then this assignment awaits a laboratory spectrum of C_{60}^+ in the gas phase to be confirmed. On the other hand the gas phase visible spectra of some carbon chain anions have been recently reported (Tulej et al. 1998, Kirkwood et al. 1998). The spectrum of C_7^- exhibits striking coincidences with some DIBs near 600 nm, but such an anion is expected to be very easily photodetached in the ISM. It remains nonetheless to be checked whether possible inconsistencies may exist between the laboratory spectrum and observational data in different spectral regions.

2. Principle of the experimental technique

In order to provide useful comparisons with the astrophysical spectra, pertinent laboratory studies must reproduce properly the physical conditions of low temperatures and absence of collisions which are characteristic of the ISM. We have developed in our laboratory an original technique capable of providing spectra of PAH cations with these conditions fulfilled, i.e. cold and isolated.

Making large quantities of cold cations in the gas phase in order to measure absorption directly is very difficult. The principle of the technique that we use is to induce a fragmentation of the cation consecutive to the resonant absorption of laser

photons, so that the change in the charge-to-mass ratio can be detected with ultimate sensitivity in a time-of-flight (TOF) mass spectrometer. However it is well known that, because of their stability, PAHs (neutrals as well as cations) need a fairly large excitation energy before they begin to fragment on a laboratory accessible timescale (as opposed to astrophysical timescale). This usually requires several laser photons, which means high laser flux, and then a number of experimental difficulties associated to saturation effects, power broadening, non resonant absorption and problems to control the number of photons involved in the process. To avoid these problems we use a special method (Bréchnignac 1998), consisting to study the spectrum of the ionic van der Waals (vdW) complexes $\text{PAH}^+\text{-Ar}$. Attaching an argon atom to the PAH molecule to form a vdW complex is only a weak perturbation, which can be measured experimentally as it will be explained below. Neutral vdW complexes can be easily formed in a supersonic molecular beam. Moreover the supersonic expansion provides efficient cooling of the species (Moutou et al. 1997). The neutral complex PAH-Ar is photoionised by resonant two-photon absorption in the near UV. Then the binding energy of the complex cation $\text{PAH}^+\text{-Ar}$ is so small (about 500 cm^{-1}) that it will fragment readily, for every single photon absorbed, into its constituents PAH^+ and argon. The use of two pulsed lasers of different colours in the ionisation step allows to control exactly the total energy, and thus to produce ionic complexes which are cold both rotationally and vibrationally. The (third) pulsed visible laser inducing the absorption by the cation is delayed with respect to the ionising lasers, so that the PAH^+ fragment produced by ejection of the argon atom is detected in the TOF mass spectrometer separated in time from the rest of the PAH^+ ions, which are produced simultaneously with the complex cations. The recording of this PAH^+ fragment ion signal versus the visible laser wavelength, while scanning it, provides the absorption spectrum of the complex cation. This spectrum differs from the spectrum of PAH^+ by a small vdW red shift. The spectrum of the vdW complex $\text{PAH}^+\text{-Ar}_2$ can be measured similarly. Comparison of the two spectra gives the value of the vdW red shift. Indeed, as it is well known from the study of the spectra of neutral aromatic-rare gas vdW complexes, the binding sites occupied by the two argon atoms are equivalent providing the basis for the shift additivity rule (Hermine et al. 1992, Troxler et al. 1989). Thus the spectrum of the bare PAH^+ cation can be deduced from the spectra of the two vdW complexes (Bréchnignac 1998).

3. The phenanthrene cation spectrum

In their search for potential DIBs carriers among PAH^+ cations, the near infrared and visible absorption spectrum of the phenanthrene ($\text{C}_{14}\text{H}_{10}$) cation, Ph^+ , isolated in neon matrices has been studied by Salama et al. (1994). We have applied the technique described above to obtain the gas phase spectrum of this cation. Phenanthrene vapour is produced in the sample chamber maintained at 90°C , seeded in a mixture of 20% Ar in He with a backing pressure of the order of 3 bars, then expanded through the 0.9 mm orifice of a pulse solenoid valve also heated at 90°C .

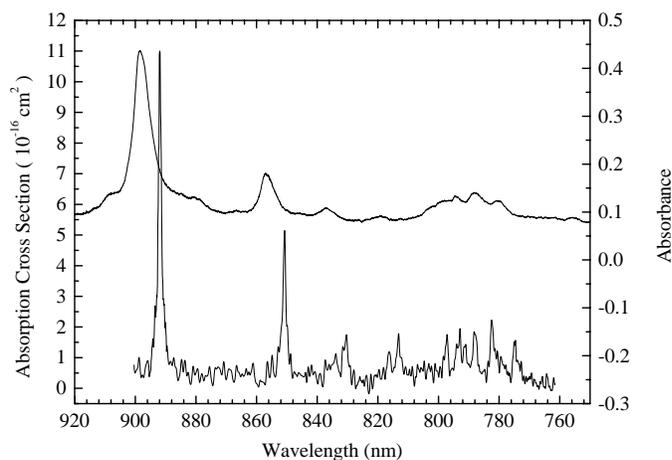


Fig. 1. Absorption spectrum of the $\text{D}_2 \leftarrow \text{D}_0$ transition in the phenanthrene cation $\text{C}_{14}\text{H}_{10}^+$. The top trace, reproduced from Salama et al. (1994), is the absorbance (scale on the right hand side) of a UV-irradiated sample of phenanthrene isolated in a neon matrix. The bottom trace is the gas-phase photofragmentation spectrum (cross section scale on the left hand side) of optically selected phenanthrene⁺-argon van der Waals complex cation in a molecular beam. Note the spectral shift, the similarity of the global pattern, and the difference in the spectral widths.

The molecular species are cooled in the supersonic expansion, and small vdW complexes of Ph-Ar_n are formed. A molecular beam is then extracted thanks to a skimmer placed a few cm downstream from the nozzle. Preparation of the cold $\text{Ph}^+\text{-Ar}$ ions in the molecular beam requires successive absorption by the neutral vdW complex of two UV photons, delivered by two synchronized frequency-doubled pulsed dye lasers pumped by the same Q-switched YAG laser. The energy of the first UV photon is set to 29313 cm^{-1} (the tuning to the resonance of the origin band of the $\text{S}_1 \leftarrow \text{S}_0$ transition in the neutral complex - red shifted by 13 cm^{-1} from the monomer band - provides optical selection of this species) to excite the ground vibrational state in the S_1 electronic state. The energy of the second UV photon is tuned to about 34000 cm^{-1} (slightly above the ionization threshold) to excite the vdW complex from S_1 to the ground electronic cation state D_0 without vibrational excitation. The third near infrared or visible photon, delayed by a few hundred nanoseconds from the UV photons, and whose frequency is scanned through the Ph^+ absorption bands, is delivered by the idler beam generated in an optical parametric oscillator laser system (Spectra-Physics MOPO730, spectral bandwidth 0.2 cm^{-1}). All the ions prepared in the molecular beam by the laser excitation scheme are sent by a static extraction field towards the TOF mass spectrometer. Three mass peaks are of interest to us, the $\text{Ph}^+\text{-Ar}$ parent peak, the Ph^+ fragment peak and the non resonant Ph^+ (background) peak. Thanks to the time delay between the first two laser pulses and the third laser pulse, the fragment peak is completely separated in time from the background peak and the fragment ions are seen on a zero background. This provides the highest sensitivity. The spectrum shown in the bottom trace of Fig. 1 has been obtained by monitoring the intensity of this frag-

Table 1. Absolute and relative positions of the bands in the absorption spectrum of Ph⁺

λ (nm)	σ (cm ⁻¹)	$\delta\sigma$ (cm ⁻¹)	Intensity (a.u.)
891.9	11212	0	100
873.3	11451	239	4
850.8	11754	542	48
834.6	11982	770	9
830.8	12037	825	16
816.6	12246	1034	10
813.4	12294	1082	15
798.1	12529	1317	15
794.0	12595	1383	16
792.0	12625	1413	11
788.8	12678	1466	19
783.3	12766	1554	20
780.6	12811	1599	7
775.7	12891	1679	12
774.3	12914	1702	3

ment peak while the laser wavelength is scanned from 900 nm to 760 nm, the energy of the laser pulse being relatively small (of the order of a few microjoules per pulse). The upper trace is a reproduction of the Ne matrix spectrum obtained by Salama et al. (1994), and assigned to the D₂←D₀ transition in the Ph⁺ cation. The two spectra look strikingly similar. But the comparison emphasizes the effect of the solid phase environment of the cation on the positions of the bands and more importantly on their widths. A red shift of 75 cm⁻¹ (matrix relative to complex) is found. The value of the vdW shift is measured to be 5 cm⁻¹ to the red by comparison with the spectrum of Ph⁺-Ar₂ recorded in the same way. Thus the actual matrix shift (matrix relative to bare Ph⁺) is 80 cm⁻¹ to the red. The matrix broadening is also of the order of 80 cm⁻¹ to be compared with the gas phase widths of about 16 cm⁻¹. Consequently the fine structure of the bands between 770 and 800 nm (the positions and the relative intensities of all the bands are reported in Table I) is well resolved, which was not the case in the matrix spectrum. This raises the question of the origin of the observed width. We know from the rotational contours (only a few cm⁻¹ wide) in the spectra of the neutral species that the rotational temperature is very low (a few Kelvin). As we explained above, the mode of preparation of the cations by threshold ionization ensures that we deal with vibrationally cold cations. The order of magnitude of the laser fluences (a few 10⁻⁴ J/cm²) used to fragment the vdW complexes is not sufficient to produce significant power broadening. Thus we should be in presence of a case of lifetime broadening, as a result of intramolecular dynamics effects. A fast non radiative process, like electronic internal conversion, should take place within the Ph⁺ moiety. Most probably it is due to a coupling between the D₂ and D₁ states, separated by about 8900 cm⁻¹. In comparison the internal conversion from S₂ to S₁ in neutral phenanthrene, separated by 6050 cm⁻¹, exhibit a similar dynamical rate (Amirav et al. 1984).

4. Oscillator strength and astrophysical implications

By analyzing the experimentally obtained dependence of the fragment-to-parent ratio, as measured in the mass spectra, as a function of the laser pulse energy at the peak wavelength (892.3 nm) of the origin band, we have derived (via a simple kinetic model) the absolute value of the absorption cross section at this wavelength. It is interesting to note that this cross section is obtained from a real direct measurement, which does not require any evaluation of the density of cations in the molecular beam. The total cross section, integrated over the whole D₂←D₀ transition spectrum, is calculated and converted into the value of the oscillator strength $f = 0.15 \pm 0.05$. This value is much larger than the one given by Salama et al. (1994) ($f = 6.10 \cdot 10^{-5}$) in their study of the matrix spectra, but on the contrary it is in good agreement with the available theoretical predictions: $f = 0.156$ (Parisel et al. 1992), $f = 0.10$ (Khan 1992). Two remarks can be made concerning the procedure used to derive the oscillator strength from the matrix spectra: it relies on a value for the transition of the neutral species, which may be uncertain¹, and evaluation of the density of cations in the matrix, which is far from being an easy task. Finally the finding that the oscillator strengths of the electronic transitions in PAH cations can take relatively large values is a positive sign for their potentiality as DIBs carriers, since they would not require unrealistic abundances in the ISM.

The accurate knowledge of the positions, widths and strengths of the absorption bands of cold gas phase Ph⁺ cations makes a direct search for it in the DIBs spectrum possible. The main band (origin of the transition) at 891.9 nm turns to be in a spectral region contaminated with heavy water vapor atmospheric absorption, for which no available DIBs data were found. A broad feature on the blue wing of a stellar line can be seen in the spectrum of HD183143 reported in the DIBs survey by Jenniskens and Désert (1994), which could coincide with the first vibronic band of Ph⁺ at 850.8 nm. But the size of the width (about 12 Å) and the blend with the stellar line makes any conclusion hazardous. To complete this comparison, the region of 780 to 800 nm would have to be carefully looked for along various selected line-of-sights, and the visible spectral region from 400 to 480 nm where features appear in the matrix spectra would also have to be investigated in the present gas phase laboratory experiment.

5. Conclusion

In conclusion we have demonstrated the capabilities of our new laser spectroscopy technique to obtain the electronic spectra of cold and isolated PAH⁺s in the gas phase. The spectrum of the D₂←D₀ transition in the Ph⁺ cation in the near infrared region has been obtained, and the corresponding absolute absorption cross sections measured accurately. For the first time the gas phase and rare gas matrix spectra of a polycyclic aromatic cation

¹ the value used by Salama et al. (1994), quoted from Swiderek et al. (1991), is a theoretical value; it is 15 times smaller than our evaluation based on the absorbance measurements in solution reported by Clar (1964)

have been compared. It clearly shows that, although the matrix work is useful to give the overall aspect of such spectra, only the gas phase spectra can valuably be compared to astrophysical spectra, since even the weakly interacting neon matrix is responsible for large broadening of the bands and unpredictable spectral shifts, as shown by the measurements presently in progress in our laboratory. Thus, the electronic spectra of other gas phase PAH cations, which should be reported in the near future, would definitely help to progress in the testing of their suggestion as DIBs carriers.

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