ELSEVIER

Jet-discharge cavity ring-down spectroscopy of ionized polycyclic aromatic hydrocarbons: progress in testing the PAH hypothesis for the diffuse interstellar band problem

D. Romanini [a,*], L. Biennier [a], F. Salama [b], A. Kachanov [a], L.J. Allamandola [b], F. Stoeckel [a]

[a] *Laboratoire de Spectrométrie Physique–CNRS UMR 5588, Université J. Fourier / Grenoble, B.P. 87-38402, Saint Martin d'Hères Cedex, France*
[b] *NASA–Ames Research Center, Space Science Division, MS 245-6, Moffett Field, CA 94035-1000, USA*

Abstract

Naphthalene cations $(C_{10}H_8^+)$ were produced in a slit jet coupled with an electronic discharge, and cavity ring down was used to obtain its absorption spectrum in the region 645–680 nm. Two of the strongest $C_{10}H_8^+$ bands previously characterized by matrix isolation spectroscopy were found, both with a fractional blue shift of about 0.5%. This is the first gas-phase electronic absorption spectrum of an ionized polycyclic aromatic hydrocarbon (PAH). This work opens the way for a direct comparison of laboratory PAH spectra with the diffuse interstellar bands (DIB), the origin of which still constitutes an open problem in astrophysics. © 1999 Elsevier Science B.V. All rights reserved.

Identification of the carriers of the diffuse interstellar bands (DIB), the longest unsolved problem in astrophysical spectroscopy, is fundamental for a correct understanding of the physical and chemical evolution of the interstellar medium (ISM). The DIBs are discrete absorption features superposed on the interstellar extinction curve. These bands, too wide to correspond to atomic transitions, number today more than 200, spanning from the near-ultraviolet (400 nm) to the near-infrared (1.2 μm) [1]. Because of their inferred abundance, the DIB carriers are expected to influence the chemical composition of molecular clouds and many interstellar processes such as the energy balance through the photoelectric effect and the ionization balance through recombination with electrons and ions. The present consensus [1], based on high-resolution astronomical observations, is that the DIBs arise from free, gas-phase, molecular species (neutrals and/or ions) which are ubiquitous in diffuse ISM clouds. Carbon-containing species are considered among the most promising candidates to explain the DIBs due to the large

---

* Corresponding author. Fax: +33 4 76 51 45 44; e-mail: daniel.romanini@ujf-grenoble.fr

abundance of elemental carbon and hydrogen in space.

Among the molecular candidates, a class of large carbonaceous molecules – namely, polycyclic aromatic hydrocarbons (PAH) – have been proposed as the possible carriers of the DIBs [2,3]. These molecules, which are thought to be ubiquitous and abundant in the interstellar medium, are also stable against photodissociation by the strong UV radiation present in this environment. Moreover, a large fraction of the PAHs are expected to be ionized in the ISM and thus absorb lower energy photons (mainly in the visible and near-IR regions of the spectrum) than the neutral precursors [4].

Until recently, the only spectroscopic data available on PAHs came from absorption spectra of neutral and ionized PAHs suspended in strongly perturbing media making all astrophysical comparisons impossible. To address this issue, a large effort has been devoted in the past few years to measure the UV–Visible–NIR (1800–9000 Å range) spectroscopic properties of neutral and ionized PAHs under conditions relevant to astrophysical environments (i.e., isolated species in the least-perturbing solid media possible, inert gas (neon) matrices). These results have been reported and their relevance to astrophysical questions has been discussed [5–10]. Substantial progress has been made using these matrix isolation spectroscopy (MIS) data which are supportive of the idea that PAH ions could be responsible for many of the DIBs [10]. Two major limitations remain, however, with the MIS data. Unknown spectral shifts and band broadening are induced in the matrix by the interaction of the trapped PAH ions with the rare-gas atoms of the lattice. Nonetheless, neon-matrix data remain essential for selecting species which are the most promising interstellar candidates.

The ultimate test can only be made by comparing the astronomical data with spectra measured in the laboratory under conditions which closely mimic those in the interstellar medium, i.e. cold ($\leqslant 100$ K) molecules/ions at very low density in the *gas phase*. This is a technically challenging task in the case of PAHs which have a low vapor pressure. All the more since the most likely DIBs candidates are ionized. Unfortunately, sensitive detection by laser-induced fluorescence cannot be generally applied to this

problem, due to the fast non-radiative processes of internal electronic conversion which are common in large molecules [11].

Alternative high sensitivity spectroscopic techniques are therefore needed. In an attempt to advance in this direction, we applied cavity ring-down spectroscopy (CRDS), which is a high sensitivity direct absorption method. We report here the first direct absorption spectrum of a PAH ion in the gas phase, produced in a continuous supersonic slit jet coupled with an electronic discharge. As this work was in progress, Bréchignac and Pino [12] also obtained spectra from PAH ions (phenanthrene cation) in a supersonic pulsed jet. Their detection scheme is appealing but rather complicated. It involves the use of a multiphoton laser ionization step, of a second delayed laser pulse to excite electronic transitions in the ion, and of a time-of-flight mass spectrometer to probe the populations of the PAH ion complexed with one or two rare-gas atoms. These two approaches are indeed quite complementary. Compared to Bréchignac's scheme, our simple application of a direct absorption method has a more general scope, since it does not rely on specific inter- and intramolecular processes. On the other hand, our measurements are partially affected by inhomogeneous broadening associated with the incomplete cooling of the molecular vibrational and rotational degrees of freedom in the supersonic jet.

CRDS is based on the measure of the exponential decay $I_0 \exp(-\gamma t)$, or 'ring down', of photons trapped inside an optical cavity [13–17]. The ring-down rate γ is proportional to the cavity losses per round trip, which may be written as $\gamma = [A + (1 - R)]/t_0$, where t_0 is the time for one pass through the cavity (at the speed of light), A is the fractional one-pass absorption due to absorption by molecules present inside the cavity, and R is the mirror reflectivity. A pulsed laser is normally used to inject photons into the cavity by transmission through one of the mirrors and the photon ring down is monitored by detecting the light leaking out through the other cavity mirror. Thus, as the laser wavelength is tuned, measuring the ring-down rate allows a direct determination of the sample absorption. This produces variations of the rate above a baseline very slowly dependent on wavelength, due to the broad mirror reflectivity curve. For good mirrors, one can obtain

ring-down rates corresponding to losses per pass on the order of 10^{-4}. If, for example, the ring-down rate is measured with a relative noise of 1%, this means that the smallest absorption by the intracavity sample that can be detected on the ring-down spectrum is as small as $1\% \times 10^{-4} = 10^{-6}$ per pass! An important feature of CRDS is that it is insensitive to the large intensity fluctuations typical of pulsed lasers.

Inside a heated supersonic slit jet assembly, argon gas was passed through naphthalene powder before reaching the slit jet aperture. Electrodes at the same negative potential (~ 500 V) were mounted on both sides of the slit aperture to produce a glow discharge directly in the jet, from the electrodes towards the slit walls. This setup is analogous to that of Davis et al. [18]. The effect of the discharge on the cooling of the molecular degrees of freedom by the supersonic expansion appears to be negligible. From rotationally resolved oxygen spectra taken in similar jet conditions, we observed that the rotational temperature was unaffected by the discharge.

Two high reflectivity mirrors were mounted on the vacuum chamber for CRDS measurements directly in the jet. The ring-down cavity axis was parallel to the slit to maximize the absorption path length. For the injection, a pulsed dye laser was partially mode-matched to the cavity, and a detection

limit of better than 10^{-7} per pass was achieved averaging the ring-down rate over 10–20 laser shots. As the loss per pass was $\sim 5 \times 10^{-5}$, this performance corresponds to a noise level of about 0.2% in the determination of the ring-down rate.

While the jet was run continuously, the discharge was switched on only in coincidence with the laser pulse and for the duration of the ring-down signal. This gave a stable discharge of several hundred milliamperes without overheating the electrodes. For each wavelength step of the laser scan, the ring-down rate was separately averaged with and without discharge, so that two spectra were recorded at the same time. Subtracting one spectrum from the other improved the baseline long-term stability, which is critical when broad spectral features have to be detected, such as in this work.

Ring-down spectra taken at different temperatures of the slit jet assembly are displayed in Fig. 1. As the vapor pressure of naphthalene changes from about 60 mTorr at room temperature to 2 Torr at 60°C, the $C_{10}H_8^+$ concentration in the jet discharge also increases until its absorption spectrum becomes apparent. Although the temperature dependence of the naphthalene vapor pressure is known, its effective partial pressure in the carrier argon flow cannot be easily determined due to the non-equilibrium flow regime.
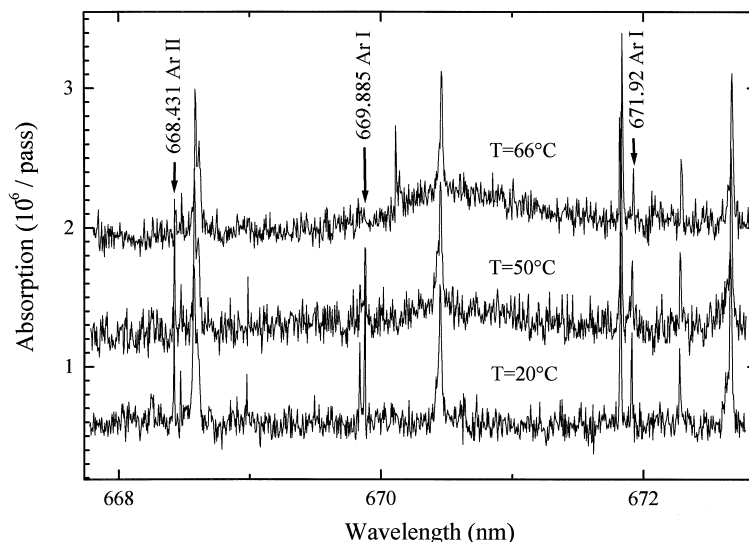

Fig. 1. CRDS absorption spectra of the $C_{10}H_8^+$ band at 6706.5 Å, taken for different temperatures of the slit jet assembly which contain the $C_{10}H_8$ powder. In the spectrum are also marked some metastable (Ar I) and ionized (Ar II) argon lines used for wavelength calibration.

Fig. 2 shows the ring-down spectra in the region where the two strongest absorption bands of $C_{10}H_8^+$ were previously located by MIS measurements. Both bands belong to the $^2B_{3g}(D_2) \leftarrow X\,^2A_u(D_0)$ band system [5]. Given the noise level, a simple Lorentzian model was used as a first guess for fitting the band profile in order to evaluate the position (6706.5 ± 0.5 and 6488.4 ± 1 Å), peak absorption (0.32 and 0.18 × 10^{-6}/pass) and full width (14 and 18 Å) of these bands. The relative intensity and the spacing between the two bands are in perfect agreement with the MIS measurements [5]. We find a fractional blue shift in energy of about 0.5% relative to the MIS spectra, which is well within the predicted limits of the neon-matrix to gas-phase shift [10]. The bandwidths are about 3 times narrower than those in matrix spectra, illustrating the large inhomogeneous broadening induced by the matrix. The residual broadening of the gas-phase spectra is most likely due to one, or a combination, of the following mechanisms. Given the molecular size and our instrumental resolution, an unresolved rotational band structure should be present. At the rotational temperature typical of slit jets (10–20 K), this rotational broadening effect can be estimated to be in the range of a few cm^{-1} for a molecule the size of naphthalene. This is negligibly small compared with the observed broad-

ening. Similarly, a hot band structure should be associated to the several low energy vibrational modes of the naphthalene molecule. This broadening contribution is more difficult to estimate, at this stage. Already, the vibrational temperature in a supersonic slit jet is generally not as low as the rotational temperature ($\sim$ 100 K). In addition, the ionization process could compete with the adiabatic cooling, resulting in an higher effective vibrational temperature for the *ions*. At any rate, hot bands should produce a structured and asymmetric envelope, which should be revealed in future measurements with improved sensitivity. Finally, non-radiative internal conversion of the electronic energy into the dense bath of molecular vibrational levels should be a favorable and common process in larger molecules. A homogeneous broadening characterized by a symmetric Lorentzian profile should then be produced, with a width proportional to the inverse of the time scale for the relaxation process. This being an intrinsic intramolecular process, the associated homogeneous broadening would be present also in the DIBs spectrum, in the case a real match is found with the laboratory PAH spectrum.

Even though the CRDS spectra give the absolute sample absorption per pass (reported in our figures), the PAH cation density is unknown at this stage and
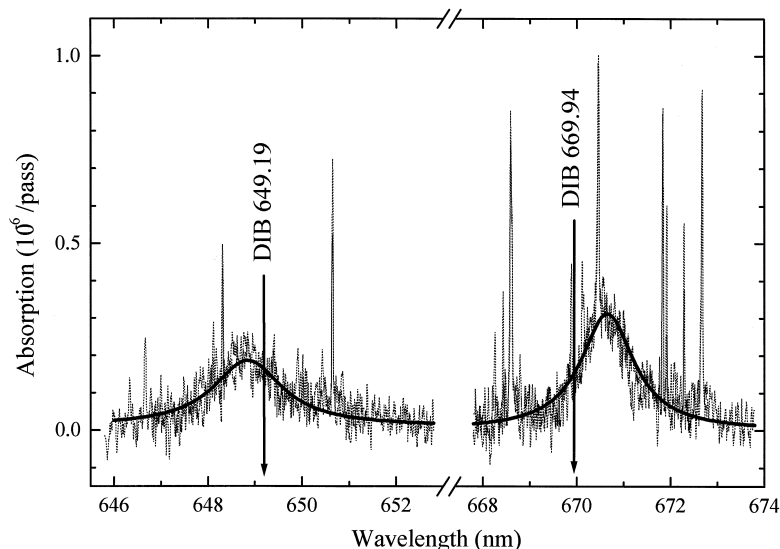

Fig. 2. CRDS spectra of bands at 6706.5 and 6488.4 Å, taken in a supersonic slit jet discharge of argon with $C_{10}H_8$ seeded at about 66°C. The position of two DIBs which fall quite close the the observed transitions is also indicated.

it is thus impossible to estimate the strength of the observed $C_{10}H_8^+$ transitions.

Additional narrow absorption lines are also found in the recorded spectra. These lines are not related to the naphthalene, since they do not vary as its temperature and concentration is substantially increased in the carrier gas (Fig. 1). They display a varying width and several of the narrower lines are easily assigned to metastable or ionized argon transitions, as marked in Fig. 1, which where indeed used for absolute wavelength calibration of the spectra. The origin of the remaining transitions, which include all of the broader ones, is not yet clear.

The comparison of these preliminary laboratory data with the DIBs indicates that the following.

(i) There is *no correspondence* between the 6741.0 and 6520.7 Å DIBs and $C_{10}H_8^+$ stronger absorption bands as previously suggested by MIS [19]. This result is definitive and unambiguous.

(ii) A possible correspondence is found, however, between the 6706.5 and 6488.4 Å $C_{10}H_8^+$ bands and weak DIBs at 6699.4 and 6491.9 Å [20] (Fig. 2). The DIBs wavelengths fall well within the half-width of the $C_{10}H_8^+$ bands, although with opposite shifts. The relative intensity of the two bands is the same (~ 1.8) in the laboratory and in the astronomical observations. The two DIBs also have similar full widths (1.2 and 0.8 Å, respectively) which are about 10 times narrower than those associated with $C_{10}H_8^+$ bands (14 and 18 Å, respectively). Hot bands due to incomplete vibrational cooling, together with a rotational band envelope, could give an asymmetric band profile accounting both for the excess broadening and for the observed shifts in our jet measurements with respect to the DIBs. However, it is difficult to imagine that opposite shifts would result for bands belonging to the same vibrational progression. Further studies should clarify this point. The third possible source of broadening, internal electronic conversion, cannot be invoked at all. This is a intramolecular process independent of the temperature.

(iii) The two stronger $C_{10}H_8^+$ bands measured in the jet at 6706.5 and 6488.4 Å are blue shifted by 34.5 and 31.6 Å, respectively, with respect to the neon-matrix spectra (which are given with a ± 0.3 nm error). This makes about the same fractional shift of 0.5% for both bands. Assuming the same fractional shift for the other strong band in the vibronic progression of the first allowed electronic transition, places the next $C_{10}H_8^+$ band at 6120 Å, surprisingly close to another weak DIBs at 6116.7 Å. This third DIBs has a width of 0.5 Å, comparable with the two DIBs considered above.

In the case of these three weak DIBs, their intensities vary by a factor of 4 from one data set to another. Part of this can be due to the uncertainty in the baseline determination of the astrophysical data. Thus, although this preliminary study seems to support the hypothesis that PAH ions carry some of the DIBs [10], more conclusive evidence awaits the investigation of a number of selected PAH ions which may correlate with stronger DIBs. The existing MIS measurements will provide indispensable reference data to guide these future gas-phase measurements.

In this work, naphthalene was chosen as a test system due to its high vapor pressure and easy handling. The generality of our experimental approach, based on a direct absorption technique, assures that it can be used to obtain the spectra of other PAH ions or radicals as well. We are currently working at our setup since an improvement in the signal-to-noise ratio is definitely possible. Also, a better determination of the vibrational and rotational temperatures in the jet will be needed, so that the estimation of rotational and hot-band broadening effects will be possible. Another important problem is the estimation of the ion density in the slit jet, which would allow deriving the absolute gas-phase transition strengths.

These experimental results represent an important step in the spectroscopy of large aromatic ions or radicals. Considering also the recent results by Bréchignac and Pino [12], who are able to obtain optical cross-sections from their measurements, it is clear that it will soon be possible to assess unambiguously the role of these molecules as carriers for the DIBs.

Acknowledgements

References

[1] A.G.G.M. Tielens, T.P. Snow (Eds.), The Diffuse Interstellar Bands, Kluwer Academic Publ., Dordrecht, Netherlands, 1995.

[2] G.P. Van der Zwet, L.J. Allamandola, Astron. Astrophys. 146 (1985) 76.

[3] A. Léger, L.B. D'Hendecourt, Astron. Astrophys. 146 (1985) 81.

[4] F. Salama, E. Bakes, L.J. Allamandola, A.G.G.M. Tielens, Astrophys. J. 458 (1996) 621.

[5] F. Salama, L.J. Allamandola, J. Chem. Phys. 94 (1991) 6964.

[6] F. Salama, L.J. Allamandola, Nature 358 (1992) 42.

[7] P. Ehrenfreund, L. D'Hendecourt, L. Verstraete, A. Léger, W. Schmidt, D. Défourneau, Astron. Astrophys. 259 (1992) 257.

[8] F. Salama, C. Joblin, L.J. Allamandola, J. Chem. Phys. 101 (1994) 10252.

[9] P. Ehrenfreund, B.H. Foing, L. D'Hendecourt, P. Jenniskens, X. Désert, Astron. Astrophys. 299 (1995) 213.

[10] F. Salama, Low temperature molecular spectroscopy, in: R. Fausto (Ed.), NATO/ASI Series, Series C: Mathematical and Physical Sciences, Vol. 483, Kluwer Academic Press, Dordrecht, Netherlands, 1996, pp. 169–191.

[11] P. Boissel, P.d. Parseval, P. Marty, G. Lefèvre, J. Chem. Phys. 106 (1997) 4973.

[12] P. Bréchignac, T. Pino, to be published in Astron. Astrophys.

[13] A. O'Keefe, D.A.G. Deacon, Rev. Sci. Instrum. 59 (1988) 2544.

[14] D. Romanini, K.K. Lehmann, J. Chem. Phys. 99 (1993) 6287.

[15] G. Meijer, M.G.H. Boogaarts, R.T. Jongma, D.H. Parker, A.M. Wodtke, Chem. Phys. Lett. 217 (1994) 112.

[16] P. Zalicki, R.N. Zare, J. Chem. Phys. 102 (1995) 2708.

[17] D. Romanini, A.A. Kachanov, N. Sadeghi, F. Stoeckel, Chem. Phys. Lett. 264 (1997) 316.

[18] S. Davis, D. Anderson, G. Duxbury, D. Nesbitt, J. Chem. Phys. 107 (1997) 5661.

[19] F. Salama, L.J. Allamandola, Astrophys. J. 395 (1992) 301.

[20] P. Jenniskens, X. Désert, Astron. Astrophys. Suppl. Ser. 106 (1994) 39.