# INFERENCE OF A 7.75 eV LOWER LIMIT IN THE ULTRAVIOLET PUMPING OF INTERSTELLAR POLYCYCLIC AROMATIC HYDROCARBON CATIONS WITH RESULTING UNIDENTIFIED INFRARED EMISSIONS

MICHAEL S. ROBINSON, LUTHER W. BEEGLE, AND THOMAS J. WDOWIAK Astro and Solar Systems Physics Program, Department of Physics, The University of Alabama at Birmingham, Birmingham, AL 35294-1170 Received 1996 May 14; accepted 1996 July 19

## ABSTRACT

The discrete infrared features known as the unidentified infrared (UIR) bands originating in starburst regions of other galaxies, and in H II regions and planetary nebulae within the Milky Way, are widely thought to be the result of ultraviolet pumped infrared fluorescence of polycyclic aromatic hydrocarbon (PAH) molecules and ions. These UIR emissions are estimated to account for 10%-30% of the total energy emitted by galaxies. Laboratory absorption spectra including the vacuum ultraviolet region, as described in this paper, show a weakening of the intensity of absorption features as the population of cations increases, suggesting that strong  $\pi^* \leftarrow \pi$  transitions are absent in the spectra of PAH cations. This implies a lower energy bound for ultraviolet photons that pump infrared emissions from such ions at 7.75 eV, an amount greater than previously thought. The implications include size and structure limitations on the PAH molecules and ions which are apparent constituents of the interstellar medium. Also, this might affect estimations of the population of early-type stars in regions of rapid star formation. *Subject headings:* dust, extinction — infrared: ISM: lines and bands — ISM: molecules —

molecular data — ultraviolet: ISM

### 1. INTRODUCTION

A significant fraction of the energy radiated by a galaxy is by infrared fluorescence (Allamandola, Tielens, & Barker 1989), a mechanism producing emission in a number of discrete infrared wavelength bands. These emissions originate in starburst regions of galaxies and in the H II regions and planetary nebulae of the Milky Way. With respect to other galaxies, it has been estimated that the radiated energy in these bands, which have become known as the unidentified infrared (UIR) emission bands, constitutes 10%–30% of the total galactic emission (Pajot et al. 1986; Puget 1987; Ghosh & Drapatz 1987). The polycyclic aromatic hydrocarbon (PAH) molecular family is considered by many Léger & Puget 1984; Allamandola et al. 1985; and Blanco, Bussoletti, & Colangeli 1988) to be the quantum converters of ultraviolet stellar radiation to the UIR bands. This includes both the neutral and ionized forms of the PAH species, which come in a multitude of sizes ranging from something as small as naphthalene (10 carbon atoms) to very large molecules similar to the constituents of hydrocarbon soot. Also, PAH species in the interstellar medium will in general be dehydrogenated to some extent, and again very importantly, ionized. PAH cations of any size, or possibly large ( $> \sim 30$  carbon atoms) neutral PAH molecules, are likely to be responsible for a significantly larger fraction of the UIR emission than is due to smaller, neutral PAH molecules. While there is a fairly good match in the 3.3  $\mu$ m region between laser-induced emission spectra of small, neutral PAH molecules and the UIR bands in that spectral region (Williams & Leone 1995), the match between the vibrational modes of small, neutral PAH molecules and the longer wavelength UIR features is not exhibited in a recent experiment (Cook et al. 1996). The UIR should be considered significant not only for the intrinsic interest in identifying the specific carriers of these bands, which has been the focus of most study on these bands since their discovery by Gillet, Forrest, & Merrill (1973), but also for what it can reveal about stellar objects obscured within clouds of gas and dust.

Five well-studied objects that are representative in exhibiting the UIR emission features have been discussed by Allamandola, Tielens, & Barker (1989): the nucleus of the starburst galaxy M82, the ionization bar in the Orion H II region, planetary nebula NGC 7027, the reflection nebula NGC 7023, and the reflection nebula surrounding HD 44179 (the Red Rectangle). The spectra of the stars illuminating NGC 7023 (a B3 V star) and the Red Rectangle (two A0 V stars) peak in the ultraviolet between 1600 and 3000 Å (7.75 and 4.13 eV). Hotter stars power the other objects so that in principle very energetic ionizing photons (hv > 13.6 eV) are available to pump their infrared emission. However, spatial studies of the Orion Bar and NGC 7027 indicate that most of the UIR emission comes from less energetic regions of these objects. In general, UIR emission is less intense from the vicinity of hotter sources. In all of these UIR emitting objects, therefore, the 3.3, 3.4, and 11.2  $\mu$ m features are thought to be pumped by nonhydrogenionizing radiation (hv < 13.6 eV) (Allamandola et al. 1989).

Because the ionization potentials of PAH molecules are in the region 7-8.5 eV (Leach 1995), PAH cations can be created by radiation less than the Lyman limit, including by Ly $\alpha$  radiation. This suggests that PAH cations can be expected to exist in these less energetic regions that are not conducive to the production of hydrogen ions. Since PAH species are likely to be ionized by the interstellar ultraviolet field, a systematic study of PAH molecules and cations in the spectral region 1.22–5.00  $\mu$ m<sup>-1</sup> (1.52–6.2 eV) was undertaken in this laboratory. Those experiments (Lee & Wdowiak 1993; Lee 1993) demonstrated that the strong ultraviolet absorption features in that wavelength range of neutral PAH species seem to disappear upon ionization. These features would, therefore, probably not be observed in the interstellar medium, providing an answer to an objection to the original PAH hypothesis raised by Leach (1987,

1995) and Donn, Allen, & Kharma (1989) that strong ultraviolet absorption features well known to be exhibited by neutral PAH species are not observed in the ultraviolet extinction curve. Vibrational transitions are much less affected by ionization, therefore PAH cations will still be observable in the infrared, while not in the ultraviolet.

## 2. EXPERIMENTAL TECHNIQUE

Since the equipment available for previous experiments limited measurements to  $1/\lambda < 5 \ \mu m^{-1}$  a vacuum ultraviolet spectrometer system was constructed that allows us to obtain spectra at  $1/\lambda > 5 \ \mu m^{-1}$ . With this equipment we have undertaken an investigation of the absorption characteristics of PAH cations to 7.75 eV (6.25  $\mu$ m<sup>-1</sup>). We have extended the spectral range of measurements in the ultraviolet from  $2.5 < 1/\lambda < 5 \ \mu m^{-1}$  to  $2.5 < 1/\lambda < 6.25$  $\mu m^{-1}$ , an increase of 50% in terms of energy over previous laboratory measurements of PAH cations. The method used for matrix isolation of PAH samples in a boron oxide glass (B<sub>2</sub>O<sub>3</sub> $\frac{2}{3}$ H<sub>2</sub>O) matrix, and the production of PAH cations by gamma irradiation, has been described in general previously (Lee & Wdowiak 1993). With this technique it is possible to obtain a column density of  $\geq 10^{16}$  cations cm<sup>-2</sup>, allowing useful absorption spectra to be obtained. While the matrix does perturb the spectrum to some extent, the spectra show characteristic absorption features that should also occur in the gas phase. The matrix does shift the wavelengths of absorption bands, usually redward, from what is observed or expected in the gas phase as well as broadening a feature. What is expected to be the same in the matrix as in the gas phase is that transitions correspond to similar spectral features.

To extend the energy range of spectroscopic investigation up to 6.25  $\mu$ m<sup>-1</sup>, we substituted sapphire disks (9.5 mm diameter) which are also transparent at wavenumbers up to and greater than 6.25  $\mu$ m<sup>-1</sup>, in place of quartz, which is transparent only to 5.00  $\mu$ m<sup>-1</sup>. The boron oxide glass used as a matrix is transparent up to  $1/\lambda < 6.25 \ \mu m^{-1}$ . A recent description of new nonlinear optical crystals which are transparent over a wide region in the ultraviolet (Chen et al. 1995) provides a theoretical formation for understanding this transparency of B<sub>2</sub>O<sub>3</sub> glass at wavelengths greater than 5  $\mu$ m<sup>-1</sup> ( $\lambda$  < 200 nm). In layered borate materials, such as  $KBe_2BO_3F_2$  (KBBF), the active group responsible for the nonlinear optical properties is the  $(BO_3)^{-3}$  anion group. The electronic structure of the  $(BO_3)^{-3}$  anion has an energy gap, limited by three dangling oxygen bonds, of 173 nm. By interlinking the three dangling oxygen bonds with cations such as beryllium, Chen et al. (1995) could shift the absorption band to 150-160 nm. We surmise that in the boron oxide glass used as a matrix in our experiments the dangling oxygen bonds are interlinked by the second boron atom, also shifting the energy gap to around 150–160 nm.

A stock mixture of PAH and boric acid was prepared which, when melted between two sapphire disks, would yield an areal density of  $\sim 1 \times 10^{17}$  PAH molecules cm<sup>-2</sup> and a molar ratio of boron oxide glass to PAH of  $\sim 1150:1$ . The samples were prepared by placing 15 mg of stock mixture between two sapphire disks on a hot plate and heating the mixture to 240°C, creating a boron oxide glass melt into which the PAH dissolves. When the melt was cooled and solidified the samples were examined under a filtered mercury lamp emitting radiation in the 3000–4000 Å range. After removal of the lamp the persistent luminescence of the triplet state indicated that most of the PAH was well dispersed as isolated molecules in the glass. This longlived phosphorescence of the  $T_1 \rightarrow S_0$  transition in PAH molecules is not observed in neutral material taken directly from the bottle. To produce the PAH ions we exposed the samples to a 105 rad minute<sup>-1</sup>, <sup>137</sup>Cs source located at the University of Alabama at Birmingham Gamma Ray Facility.

Measurements of the spectra of the PAH/glass-sapphire sandwich in the range 1.22–5.00  $\mu m^{-1}$  were made at room temperature before and after irradiation using the HP 8452 UV/visible diode array spectrometer equipped with a deuterium source and interfaced with a computer. This is the same instrument used for this laboratory's earlier investigation of PAH cations (Lee & Wdowiak 1993). The integration time for all samples was 1 s. Following these measurements, the same samples were then measured in the range 4.00-6.25  $\mu m^{-1}$  at room temperature using the computer-controlled Acton Research model VM-502 0.2 m vacuum monochromator equipped with a deuterium source, 1200 lines  $mm^{-1}$  grating, and the model DA-781 photomultiplier detector. The measurements were taken with the monochromator evacuated to a pressure of approximately  $1 \times 10^{-5}$  torr. Both the entrance and exit slits of the monochromator were set at 200  $\mu$ m. All spectra were taken at a resolution of 5 Å and an integration time of 2.5 s.

The data from the two instruments overlapped well in the region 4.00–5.00  $\mu m^{-1}$  except that all spectra from the HP 8452 spectrometer, including the spectra from earlier experiments (Lee & Wdowiak 1993), showed an absorption peak at 5.00  $\mu$ m<sup>-1</sup>, a peak which was not seen in the spectra of benzo[e]pyrene of benzo[ghi]perylene taken with a Vacuum Ultraviolet Spectroscopy system. Because 5.00  $\mu m^{-1}$  is at the extreme end of the effective range of the HP 8452 spectrometer and within the effective range of the Vacuum Ultraviolet Spectroscopy system, we concluded that this particular absorption observed only with the HP 8452 was an instrumental artifact occurring at that instrument's extreme range. All figures show the data from the two instruments combined such that from 1.22 to 4.00  $\mu$ m<sup>-1</sup> the data are from the HP UV/visible diode array spectrometer and from 4.00 to 6.25  $\mu$ m<sup>-1</sup> the data are from the Acton Research vacuum ultraviolet monochromator.

### 3. DISCUSSION OF SPECTRA

Absorption spectra in the region from  $1/\lambda = 1.22 \ \mu m^{-1}$ to 6.25  $\mu$ m<sup>-1</sup> have been obtained on four PAH molecules: pyrene, benzo[e]pyrene, benzo[ghi]perylene, and coronene. The spectrum of each molecule was determined at three progressively greater levels of exposure to gamma radiation: unirradiated, 30 hr exposure (approximately 188 krad), and 60 hr exposure (approximately 377 krad). For each spectrum, the continuum was determined by fitting a sixth-order regression to points of minimum absorbance along the spectrum. This continuum was then subtracted from the original data to yield the spectra shown. This step was taken because during the course of an experiment the continuum tended to increase and partially obscure the reduction in intensity of the absorption features. Because the change does not correlate with amount of exposure to radiation, we concluded that the shift in the continuum

absorbance is a consequence of aging, a matrix effect, and is not related to exposure to radiation or the presence or absence of PAH ions. In Figure 1 the spectra of each molecule at each level of irradiation are shown with the interstellar extinction curve (Seaton 1973) included as the top graph. For each molecule, except coronene, an absorption peak was observed above 5  $\mu$ m<sup>-1</sup>. These higher energy absorption features, like the absorption features below 5  $\mu$ m<sup>-1</sup>, show reduction in intensity as radiation dose increases. Thus, strong cationic ultraviolet absorption features are absent at energies less than 7.75 eV (6.25  $\mu$ m<sup>-1</sup>). As had been demonstrated previously (Lee & Wdowiak 1993; Lee 1993) the observed reduction in absorption upon irradiation is reversible upon mild heating, indicating that recovery of the neutral molecule takes place when electrons diffuse back to the cation with subsequent recombination.

The experiments described here clearly indicate that PAH cations do not have strong absorption features in the ultraviolet over a wavelength range of 160–300 nm. It is important to explain, in terms of the changes in the elec-



FIG. 1.—Absorption spectra of the neutral (*thick solid line*), 30 hr irradiated (approx. 188 krad, *thin solid line*), and 60 hr irradiated (approx. 377 krad, *dotted line*), sapphire-boron oxide glass PAH samples vs. the sapphire-boron oxide glass references under the same conditions. As an increasing number of the PAH molecules become cations the  $\pi^* \leftarrow \pi$  features diminish. The interstellar extinction curve (Seaton 1979) is shown in the topmost graph.

477

tronic structure of these molecules upon ionization, why spectral features from these transitions apparently weaken as the sample population is increasingly ionized. In the case of the neutral molecule, in the ground state all orbitals are filled with paired electrons so the  $\pi^* \leftarrow \pi$  transitions are from filled to empty orbitals. Removal of an electron to form the cation will result in different transition probabilities, as one of the ground-state orbitals will contain a single, unpaired electron. The reduction by one in the number of  $\pi$ electrons could also affect the shape of the molecule, perhaps even dramatically. A recent report (Lindner et al. 1996) provides the first definitive experimental determination of the shape of the benzene cation. As a result of ionization the molecule is distorted in shape into two distortion isomers each possessing  $D_{2h}$  symmetry (a distorted hexagon); however, the energy difference between these distortion isomers is quite small. This small energy difference allows for quantum tunnneling between these states and a degree of pseudorotation which gives little reason to view the cation in terms of  $D_{2h}$  structures with locally nondegenerate electronic configurations. The cation is therefore fluctional, dynamically coupled, and must be viewed in  $D_{6h}$ (regular hexagon) symmetry. While those results give some idea as to how the electronic states of the aromatic structure of benzene are affected by ionization, they do not yet provide a sufficient basis for describing the changes in electronic structure in the larger PAH molecules upon ionization.

#### 4. ASTROPHYSICAL IMPLICATIONS

The investigation reported here has shown at higher energies (5.00–6.25  $\mu$ m<sup>-1</sup>) the same weakening of absorption features seen earlier at lower energies ( $<5 \ \mu m^{-1}$ ). This indicates that significant ultraviolet absorption by PAH cations occurs only at energies greater than 6.25  $\mu$ m<sup>-1</sup> (7.75 eV). Therefore, ultraviolet pumping at the PAH cation vibrational modes corresponding in frequencies to the UIR is inferred to occur only at energies greater than 7.75 eV. The absorbance of pericondensed PAH molecules at energies above about 6  $\mu$ m<sup>-1</sup> (7.4 eV) is known to increase smoothly to a maximum at about 14  $\mu$ m<sup>-1</sup> (17.4 eV) in a single broad absorption peak composed of  $\sigma^* \leftarrow \sigma$ ,  $\sigma^* \leftarrow \pi$ ,  $\pi^* \leftarrow \sigma$  and Rydberg spectral transitions (Leach 1995). Joblin (1992) has presented an absorption spectrum of the 10-ring ovalene molecule which shows this characteristic absorption of PAH molecules. It is expected that there would be a similar spectral feature of PAH cations because the  $\sigma^* \leftarrow \sigma$  transition would still take place. Using the neutral PAH molecule spectrum from Joblin (1992) we have estimated the cross section of the PAH cations at wavelengths shorter than our measurements by eliminating that portion obviously due to  $\pi^* \leftarrow \pi$  transitions (Fig. 2). Our experiments indicate that  $\pi^* \leftarrow \pi$  transitions probably do not contribute significantly to the absorption spectra of PAH ions; only the higher energy transitions involving the structural sigma, bonding and antibonding, orbitals may be consequential. It is possible that some weak absorption features similar to those occurring at longer wavelengths, or a continuum, may continue to lurk in the residual absorption of these spectra due to those neutrals that remain in our experiments.

This inferred lower limit on photon energy for ultraviolet absorption raises an important question for the PAH



FIG. 2.—To estimate the absorption cross section per carbon atom of the ovalene cation in the gas phase, the neutral molecule spectrum (*dotted line*) obtained by Joblin (1992) was fitted with Lorentzians. The dashed line spectrum (*a*) is that obtained when Lorentzian components contributing at less than  $6.25 \ \mu m^{-1}$  and presumably due to  $\pi^* \leftarrow \pi$  transitions are removed, and the solid line spectrum (*b*) shows the situation when component removal is extended to  $10 \ \mu m^{-1}$ .

hypothesis in that the UIR emission attributed to cationic PAHs is presumably pumped by ultraviolet absorption. If PAH ions only absorb ultraviolet radiation with photon energy greater than 7.75 eV, then the condition that UIR emission be favored over photodissociation upon absorption of a ultraviolet photon could set important size and structure limitations on which PAH molecules and ions could play a role in the interstellar medium. Gas-phase measurements on PAH ions in the vacuum ultraviolet region would be extremely valuable for answering questions of astrophysical interest. However, the production of a population of gas phase PAH ions in a column density of  $10^{16}$  cm<sup>-2</sup> is extremely difficult.

Previously it had been suggested (Lee & Wdowiak 1994) that the increase of the continuum absorbance as the population of ions in the matrix increased might, if a property of the ions and not an effect of the matrix, represent an ultraviolet absorption continuum which could be a mechanism for pumping the UIR emissions. Our experience during this investigation was, however, that the change in the continuum absorption did not correlate well with radiation dose, while the reduction in the intensity of absorption features did. This strongly indicates that the apparent continuum observed when PAHs isolated in a glass matrix are irradiated is most likely a matrix effect, hence probably not a phenomenon of the PAH molecules or ions. We therefore conclude that this continuum is probably not a mechanism for pumping the UIR.

Given that a significant proportion of all energy radiated by galaxies is in the UIR bands and the evidence which indicates that PAH cations can be the primary quantum converters of ultraviolet radiation to UIR emissions, our inferred 7.75 eV lower limit on photon energy for this conversion might impact estimates of the number of massive, early-type stars within regions of rapid star formation.

This work was supported under NASA grants NAGW-749, NAGW-3902, NAGW 4079, and NAGW-4158. We also thank Wei Lee for many useful discussions and David Agresti for his valuable assistance.

### REFERENCES

- Allamandola, L. J., Tielens, A. G. G. M., & Barker, J. R. 1985, ApJ, 290, L25
- . 1989, ApJS, 71, 733
- Blanco, A., Bussoletti, E., & Colangeli, L. 1988, ApJ, 334, 875 Chen, C., Wang, Y., Wu, B., Wu, K., Zeng, W., & Yu, L. 1995, Nature, 373, 322
- Cook, D. J., Schlemmer, S., Balucani, N., Wagner, D. R., Steiner, B., & Saykally, R. J. 1996, Nature, 380, 277
  Donn, B. D., Allen, J. E., & Khanna, R. K. 1989, in Interstellar Dust, ed. L. J. Allamandola & A. G. G. M. Tielens (Dordrecht: Kluwer), 181
- Ghosh, S. K., & Drapatz, S. 1987, in Polycyclic Aromatic Hydrocarbons Gilosh, S. K., & Diapatz, S. 1957, in Polycyclic Aromatic Hydrocarbons and Astrophysics, ed. A. Léger, L. d'Hendecourt, & N. Boccara (Dordrecht: Reidel), 317
   Gillett, F. C., Forrest, W. J., & Merrill, K. M. 1973, ApJ, 183, 87
   Joblin, C. 1992, Ph.D. thesis, Univ. Paris
   Leach, S. 1987, in Polycyclic Aromatic Hydrocarbons and Astrophysics, and A formatic Hydrocarbons and Astrophysics, and M. Karry, Cherodoxic Distribution (Dordrecht: Beidel) 000

- ed. A. Léger, L. d'Hendecourt, & N. Boccara (Dordrecht: Reidel), 99

- Leach, S. 1995, Planet. Space Sci., 43, 1153 Lee, W. 1993, Ph.D. thesis, Univ. Alabama at Birmingham Lee, W., & Wdowiak, T. J. 1993, ApJ, 410, L127
- 1994, in Molecules and Grains in Space, ed. I. Nenner (New York: AIP), 675
- Léger, A., & Puget, J. L. 1984, A&A, 137, L5
- Lindner, R., Müller-Dethlefs, K., Wedum, E., Haber, K., & Grant, E. R.
- 1996, Science, 271, 1698 Pajot, F., Boisse, P., Gispert, R., Lamarre, J. M., Puget, J. L., & Serra, G. 1986, A&A, 157, 393
- Puget, J. L. 1987, in Polycyclic Aromatic Hydrocarbons and Astrophysics, ed. A. Léger, L. d'Hendecourt, & N. Boccara (Dordrecht: Reidel), 303 Seaton, M. J. 1979, MNRAS, 187
- Williams, R. M., & Leone, S. R. 1995, ApJ, 443, 675