Infrared Spectroscopy of Matrix-Isolated Polycyclic Aromatic Hydrocarbon Cations. 4. The Tetracyclic PAH Isomers Chrysene and 1,2-Benzanthracene

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The mid-infrared spectra of the polycyclic aromatic hydrocarbon (PAH) cations of the tetracyclic isomers chrysene ($C_{18}H_{12}{}^+$) and 1,2-benzanthracene ($C_{18}H_{12}{}^+$) are presented. As with previous PAH cations studied to date, the CC stretching and CH in-plane bending mode absorptions are about an order of magnitude stronger than the aromatic CH out-of-plane bending absorptions and nearly 2 orders of magnitude more intense than the corresponding bands in the neutral molecule. The CH bands arising from the out-of-plane bends in the cation are slightly weaker than the corresponding bands in the neutral species. The strongest cation bands of these species fall between 1300 and 1330 cm^{-1}, close to the peak of the most intense interstellar emission feature in HII regions and reflection nebulae. A strong PAH cation band at slightly higher frequency than 1300 cm^{-1} may be associated with an asymmetric CC stretching vibration involving rings adjacent to the kink in the chain of aromatic rings.

I. Introduction

Over the past several years, evidence has been mounting that polycyclic aromatic hydrocarbons (PAHs) are the carriers of a very common family of interstellar infrared fluorescence bands. These bands originate in many galactic and extragalactic objects, suggesting that the carriers are common throughout interstellar space[1]. Their intensity indicates that they are as abundant as the most abundant interstellar polyatomic molecules known. Nevertheless, proper testing of this assignment and the possible exploitation of PAHs as probes of the interstellar medium has been limited by the lack of spectroscopic data on PAHs under interstellar conditions. Specifically, most interstellar PAHs are expected to be isolated (i.e., gaseous) and ionized in the emission regions.[2] In light of this deficiency, we have undertaken a study of the infrared spectroscopic properties of matrix-isolated PAHs and their ions. Although the primary motivation for this research is to investigate the role of PAHs in the interstellar medium, the results are of general interest as ionized PAHs are considered to be important intermediates in combustion,[3] and many PAH intermediates and primary reaction products are carcinogenic.[4]

Previous papers of this series have focused on the infrared spectral properties of the cations of naphthalene,[5] the thermodynamically most favored PAHs through coronene[6] (phenanthrene, pyrene, benzo[*e*]pyrene, benzo[*ghi*]perylene, and coronene), and the polyacenes[7] (anthracene, tetracene, and pentacene). In this paper we continue to investigate the frequency and intensity trends associated with structure, focusing on those PAH isomers having the empirical formula $C_{18}H_{12}$, each of which is composed of four six-membered aromatic moieties. Such small PAHs are relevant from the astrophysical point of view. Molecules containing about 20−30 carbon atoms are thought to dominate the interstellar infrared fluorescence at the shortest wavelengths.[1a,2] In subsequent papers in this series further aspects of PAH cation structure will be explored. The neutral spectra of these PAHs will be presented in detail elsewhere.[8,9]

Theoretical and experimental efforts in this area are also underway at several other institutions. Defrees and Miller carried out the earliest theoretical calculations on the expected infrared spectral properties of the naphthalene and anthracene cations and predicted surprising relative band strength differences between the neutral and ionized forms of these PAHs.[10a] Subsequently, Defrees et al.[10b] and Pauzat et al.[11] have greatly expanded this work. Most recently Langhoff has calculated the spectra of many PAHs at the density functional theory (DFT) level and compared them with theoretical and experimental data.[12] In addition, Professor Vala and co-workers at the University of Florida have published the infrared spectroscopic properties for a variety of PAH cations[13] and d'Hendecourt et al. have reported the spectrum of the coronene cation.[14]

This paper is laid out as follows. The experimental technique is briefly summarized in section II. In section III the criteria used to identify the cation bands are reviewed, and the mid-infrared spectra of the chrysene and 1,2-benzanthracene cations are presented and discussed. The spectra are also compared to that of the tetracene cation, another $C_{18}H_{12}$ isomer whose spectrum has been presented previously.[7] The band frequencies and relative intensities of the chrysene and 1,2-benzanthracene cations are also compared to theoretical values.

II. Experimental Section

The experimental technique will be described only briefly since a detailed description of our procedure is available elsewhere.[5,6] Samples were prepared by co-deposition of the PAH of interest in the gaseous state with an overabundance of argon onto a 10 K CsI window suspended in a high vacuum chamber ($p \sim 10^{-8}$ mTorr). The optimum temperatures for vaporization of the PAHs in this study were 110 °C for chrysene and 95 °C for 1,2-benzanthracene. The IR spectrum of the sample was recorded immediately after deposition. Comparison of this spectrum with that obtained after in situ vacuum

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ultraviolet irradiation permitted identification of the ion features which appeared upon photolysis.

An estimation of an upper limit to the percent ionization of the PAH sample was obtained by measuring the percentage decrease in the integrated areas of the neutral bands upon photolysis. If all of the neutral PAHs that disappeared were converted to the cation, this number would directly reflect the ionization efficiency. Ion yield upper limits ranging from 2 to 10% are typically realized with this technique. The ion yields for the data presented here were 2.5% for chrysene and 2.3% for 1,2-benzanthracene.

The chrysene (98% purity) and 1,2-benzanthracene (99% purity) used in this study were obtained from the Aldrich Chemical Co. and were used without further purification. The argon (Matheson prepurified, 99.998% minimum) passes through a length of liquid nitrogen cooled copper tubing just prior to deposition.

III. Results

A detailed discussion of the means by which PAH cation bands can be distinguished from those of other photoproducts has been presented previously.[5,6] Briefly, identifications are based on three criteria. First, the bands must appear only upon photolysis when the associated neutral PAH is present in the matrix. Second, the bands attributed to the cation must be enhanced by the presence of an electron acceptor (CCl_4) in the matrix ($Ar/CCl_4 \approx 1000/1$). This behavior establishes that the bands arise from a positive ion. Third, all the bands attributed to the cation must evolve together and in a manner distinct from other photolysis features. These band correlation plots are presented below along with the appropriate spectroscopic data. As was the case in previous studies[5−7], the intensities of the bands corresponding to the PAH cation peak after 4−8 minutes of photolysis and then remain essentially constant or fall off slightly upon further photolysis. Conversely, the bands of other photoproducts tend to increase steadily with time. Non-PAH related photoproduct bands are not common, typically numbering 2−4 in each case. Most common were bands at 904 cm^{-1} (HAr_2^+) and 1589 cm^{-1}. These appeared moderately strong in a number of experiments. Less frequently, other weak photoproduct bands were encountered at 1388 and 1104 cm^{-1} (HO_2^+) and at 1039 cm^{-1} (O_3), as well as bands attributable to CO_2 and CO.

The mid-infrared spectra of the chrysene and 1,2-benzanthracene cations (both $C_{18}H_{12}^+$ isomers) are presented below. Only those regions of the spectrum where cation bands appear are shown. The frequencies and relative intensities of the bands for these compounds are compared with those of tetracene (a third $C_{18}H_{12}^+$ isomer) in Table 1. The individual integrated band peak areas ($\int\tau\, d\nu$) were determined using a program provided by Nicolet. The detailed spectral properties of the tetracene cation have been discussed elsewhere.[7] The behavior of the remaining tetracyclic $C_{18}H_{12}$ PAH isomer, triphenylene, was anomalous, appearing to dissociate rather than ionize under our experimental conditions. It is thus excluded from the discussion. Furthermore, since the PAH pyrene ($C_{16}H_{10}$) *is* tetracyclic but *is not* isomeric with the other members of the family, it is also excluded from the discussion. It is discussed in reference 6.

A. Mid-infrared Spectroscopy. *The Aromatic CH Stretching Region, 3200−2900 cm^{-1}.* No features were found in the aromatic CH stretching region that could be attributed to the chrysene or 1,2-benzanthracene cation. On the basis of several experiments in which the ion yield was maximized by incorporating an efficient electron acceptor in the matrix, we estimate that the upper limit to the CH stretch intensity of the chrysene cation is less than 0.03 of the intensity of the strongest cation band, that at 1316 cm^{-1}. This is consistent with the results of previous studies[5−7] and with current theoretical calculations which indicate that these modes are inherently weak in the cations.[10−12] The experimental difficulty in the detection of new bands in this region arises because the spectrum of the more abundant neutral molecule is rich in features arising from the CH stretches and overtone and combination bands. Thus, it is not surprising that the weaker bands of the cation are screened by the much stronger absorptions of the neutral parent present in the matrix.

TABLE 1: Infrared Frequencies and Relative Intensities for the Cations of the Tetracyclic PAHs

chrysene		1,2-benzanthracene		tetracene	
ν (cm^{-1})	I_{rel}	ν (cm^{-1})	I_{rel}	ν (cm^{-1})	I_{rel}
676.0	0.019	911.2	0.060	929.4	0.046
834.0	0.075	1102.3	0.069	1155.8	0.012
879.8	0.062	1182.2	0.026	1178.5	0.44
1047.2	0.098	1209.3	0.011	1302.9	0.009
1096.3	0.045	1225.7	0.31	1331.8	0.058
1137.2	0.62	1231.0	0.033	1349.1	0.33
1146.5	0.005	1332.5	1.00	1358.4	1.00
1216.6	0.13	1350.5	0.067	1371.2	0.013
1229.6	0.93	1375.9	0.084	1402.1	0.038
1272.4	0.078	1391.7	0.41	1406.4	0.069
1279.8	0.071	1405.8	0.078	1409.6	0.18
1287.0	0.033	1477.0	0.068	1414.4	0.089
1304.1/1306.9	0.20	1528.0	0.077	1422.5	0.027
1315.7	1.00	1540.1	0.19	1478.3	0.53
1327.3	0.088	1577.5	0.13	1488.0	0.13
1332.9/1335.9	0.94			1543.3	0.23
1367.7	0.019			1604.7	0.017
1418.9	0.044				
1433.1	0.50				
1437.4	0.049				
1447.6	0.43				
1456.0	0.012				
1481.4	0.031				
1499.1	0.49				
1509.0	0.062				
1515.9	0.16				
1533.1	0.014				
1560.3	0.61				
1579.1/1583.6	0.27				
1593.2	0.012				

The Chrysene Cation, $C_{18}H_{12}^+$. The mid-infrared spectrum of the chrysene cation is shown in Figure 1. The band frequencies and relative intensities of the chrysene cation are listed in Table 1. In Table 2 these experimental data are compared with theoretically predicted values. The evolution of the bands assigned to the cation with Ly-α photolysis is shown in Figure 2. There are undoubtedly other cation bands which are screened by neutral features.

The chrysene cation has a rich spectrum, with numerous bands attributable to CC stretching and CH in-plane bending modes distributed evenly between 1600 and 1100 cm^{-1}. While many of the bands in this region are moderately strong, the spectrum shows three prominent bands at 1332.9/1335.9, 1315.7, and 1229.6 cm^{-1}. The frequencies suggest that the the modes producing these bands are likely to possess some CC stretching and CH in-plane bending character. However, the strongest of these bands, that at 1315.7 cm^{-1}, arises from a nearly pure CC stretch. Vector analysis shows it to be an asymmetric CC stretching vibration mainly involving the rings adjacent to the kink in the chain of aromatic rings as shown in Figure 3 (Langhoff and Bauschlicher, private communication).

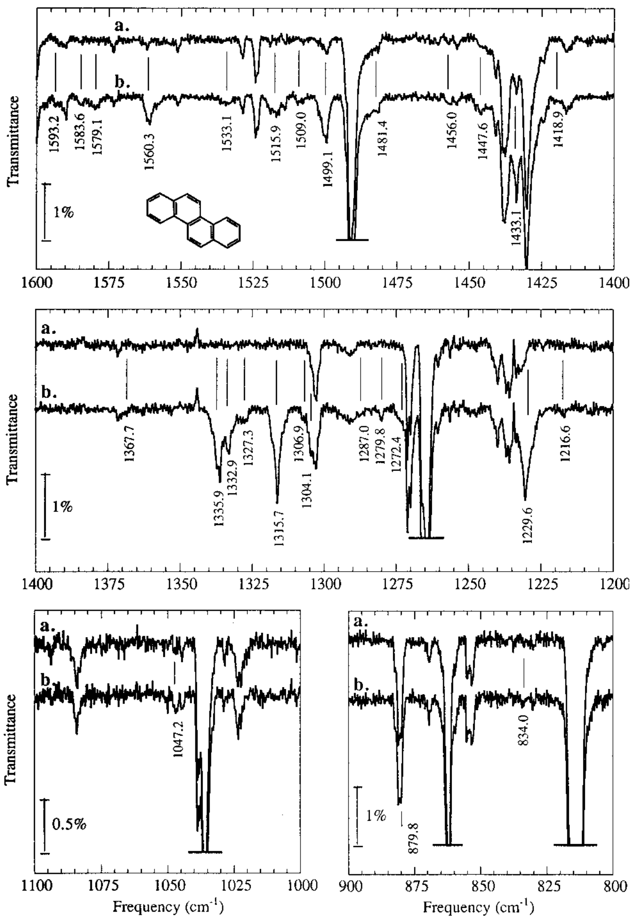

Figure 1. Mid-infrared spectrum of the chrysene cation isolated in an argon matrix at 10 K: (a) before photolysis; (b) after 8 min in situ photolysis. The cation bands are labeled with their positions. The cation bands at 676, 1137.2, and 1146.5 cm^{-1} are not shown.

Two new bands were found in the CH out-of-plane bending region. Chrysene has two rings which contain two adjacent hydrogen atoms per ring and two with four adjacent H atoms. In the neutral molecule, the bands corresponding to these modes fall at 812.6 cm^{-1} (doubly adjacent CH) and 761.0 cm^{-1} (quadruply adjacent CH). In the cation, the corresponding bands are shifted to higher frequency, falling at 879.8 and 834.0 cm^{-1}, respectively. The 879.8 cm^{-1} cation band falls slightly above the high end (860 cm^{-1}) of the range normally attributed to doubly adjacent H atoms. The 834.0 cm^{-1} position, on the other hand, is well above the frequencies normally associated with four adjacent H's (770 cm^{-1}). While the blue-shifting of the CH out-of-plane modes is consistent with the behavior of other PAH cations, the magnitude of this blue-shift ($\sim$70 cm^{-1}) is significantly greater than that observed for other PAH cations ($\sim$30 cm^{-1}). Nevertheless, the excellent agreement between the measured cation band positions and those predicted theoretically (877 and 836.2 cm^{-1}, Table 2), supports these assignments. On the basis of on the measured upper limit of 2.5% ionization and using the argument previously employed for other PAHs,[6,7] we estimate that the 834.0 cm^{-1} cation band is $\sim$3 times weaker than the corresponding mode in the neutral (761.0 cm^{-1}). The 879.8 cm^{-1} band, however, appears to have a strength which is comparable to that for its neutral counterpart (812.6 cm^{-1}). Furthermore, in neutral chrysene the strongest CH out-of-plane bending absorption is a factor of six times more intense than the strongest CC stretching feature.[8] In the chrysene cation, on the other hand, the situation is reversed with the strongest CC stretching feature (1315.7 cm^{-1}) more intense than the strongest CH out-of-plane bend (834.0 cm^{-1}) by a factor of 13. Together, these observations indicate that the intensities of the CC stretching absorptions in the cation are enhanced by nearly 2 orders of magnitude over the analogous absorptions in the neutral molecule. This is consistant with the factor of 50 enhancement predicted theoretically.[12]

TABLE 2: Comparison of the Experimental Frequencies and Relative Intensities of the Chrysene and 1,2-Benzanthracene Cations with Theoretical Predictions

chrysene				1,2-benzanthracene			
experimental[a]		theoretical[b]		experimental[a]		theoretical[b]	
ν (cm^{-1})	I_{rel}	ν (cm^{-1})	I_{rel}	ν (cm^{-1})	I_{rel}	ν (cm^{-1})	I_{rel}
		564.5	0.04			522.2	0.05
						756.2	0.10
						769.4	0.04
						827.3	0.04
676.0	0.02			911.2	0.06	909.2	0.07
		760.7	0.20				
834.0	0.08	836.2	0.13	1102.3	0.07	1098.4	0.03
		848.5	0.03			1153.8	0.07
879.8	0.06	877	0.03	1182.2	0.03	1188.2	0.03
1047.2	0.1	1039.1	0.06	1209.3	0.01		
1096.3	0.04	1086.3	0.03	1225.7	0.31	1233.3	0.29
1137.2	0.62	1146.5	0.15	1231.0	0.03	1242.7	0.11
						1287.1	0.08
						1300.9	0.08
1146.5	0.005			1332.5	1.00	1334.8	1.00
1216.6	0.13			1350.5	0.07		
1229.6	0.93	1224.9	0.76	1375.9	0.08		
1272.4	0.08	1254.2	0.05	1391.7	0.41	1373.0	0.23
1279.8	0.07	1265.6	0.06	1405.8	0.08		
						1471.6	0.20
1287.0	0.03	1302.0	0.04	1477.0	0.07	1499.0	0.05
1304.1/1306.9	0.20			1528.0	0.08		
						1523.1	0.23
1315.7	1.00	1331.7	1.00	1540.1	0.20	1535.0	0.07
						1557.2	0.12
1327.3	0.09			1577.5	0.13	1587.8	0.11
1332.9/1335.9	0.94						
1367.7	0.02						
1418.9	0.04						
1433.1	0.50	1426.7	0.15				
1437.4	0.05	1443.8	0.10				
1447.6	0.43	1493.2	0.33				
1456.0	0.01						
1481.4	0.04						
1499.1	0.50	1507.3	0.45				
1509.0	0.06						
1515.9	0.16						
1533.1	0.01						
1560.3	0.61	1536.7	0.86				
1579.1/1583.6	0.27	1559.5	0.27				
1593.2	0.01						
		3104.2	0.05				

[a] This work. [b] Langhoff. Only bands with theoretical relative intensities greater than 0.02 are listed.

Last, we attribute the 676.0 cm^{-1} band to a CCC out-of-plane bend due to its position slightly below the low end of the frequency range associated with the CH out-of-plane bending mode in aromatics containing five-adjacent hydrogen atoms.

Again referring to Table 2, we see that although peak positions and relative band strengths for most of the weak and moderately strong bands compare quite favorably to the theoretical values predicted for this cation by Langhoff using density functional theory (DFT),[12] some discrepancies exist. For example, theory predicts the strongest band in the spectrum should fall at 1331.7 cm^{-1}. While the strong 1332.9 and 1335.9 cm^{-1} bands do fall close to this position, neither represents the most intense feature in the spectrum. Instead, the most intense experimental band is observed to lie at a frequency of 1315.7 cm^{-1} (Figure 1).

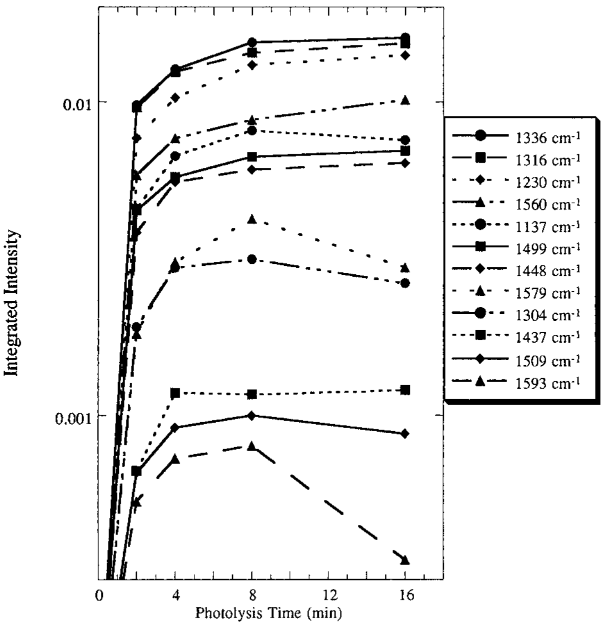

Figure 2. Growth of some of the chrysene cation integrated band areas (cm^{-1}) as a function of photolysis time.

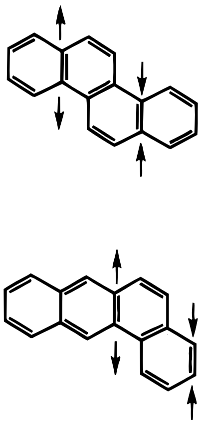

Figure 3. Vibrational mode of the chrysene and 1,2-benzanthracene cations responsible for the strongest band. Atom dispacements kindly calculated by Bauschlicher and Langhoff.

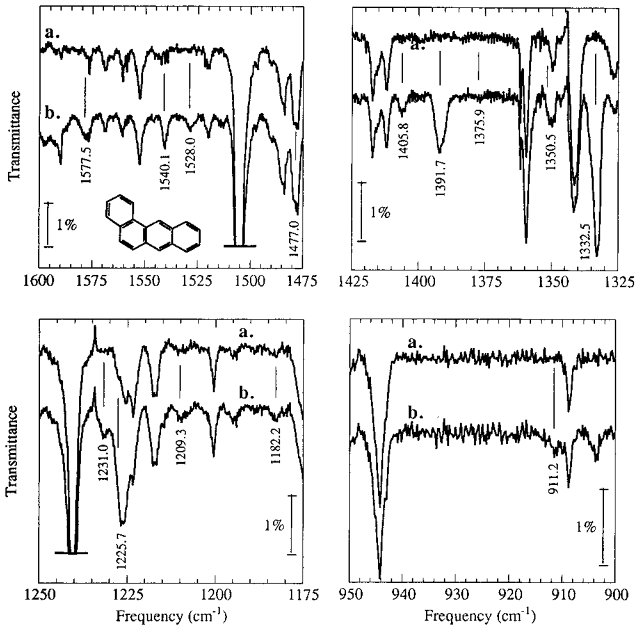

Figure 4. Mid-infrared spectrum of the 1,2-benzanthracene cation isolated in an argon matrix at 10 K: (a) before photolysis; (b) after 8 min in situ photolysis. The cation bands are labeled with their positions. The band at 1102.3 cm^{-1} is not shown.

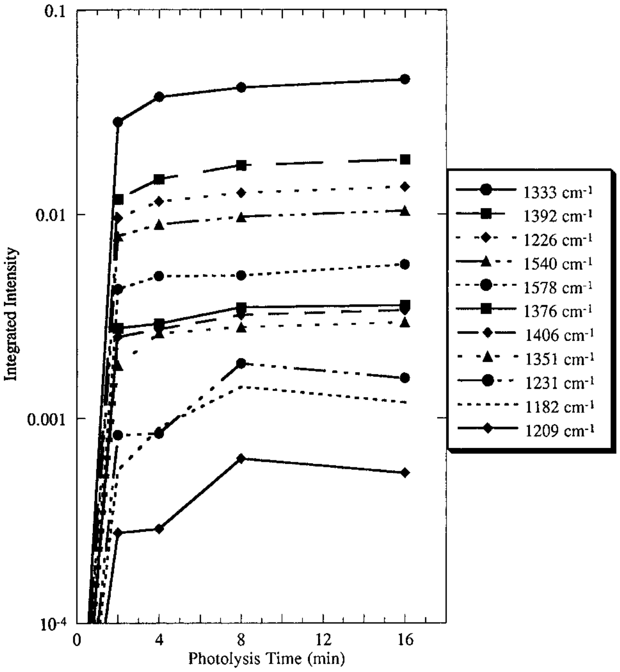

Figure 5. Growth of some of the 1,2-benzanthracene cation integrated band areas (cm^{-1}) as a function of photolysis time.

Furthermore, theory predicts two moderately strong bands at frequencies near 1500 cm^{-1} (1507 and 1493 cm^{-1}) while experimentally only a single moderately strong band is observed (1499 cm^{-1}).

Finally, theory predicts a very strong band at a frequency of 1536.7 cm^{-1}. However, experimentally, there is no sign of an important feature in this vicinity where screening by the neutral species is not a problem (Figure 1). In view of the availability of theoretical predictions with which to compare our data, numerous experiments were repeated on this molecule to ensure that the frequencies and relative intensities listed in Table 1 contain no artifacts. Since the overall agreement between experiment and theory is quite good, the few discrepancies may simply be due to the fact that the theoretical spectrum does not include contributions from overtone and combination bands. Although it is known that relative band intensities can be altered in matrix-isolated species, the absence in our data of the strong theoretically predicted 1536.7 cm^{-1} is puzzling, as it is very unlikely that matrix effects would completely suppress a strong band. A possible explanation might involve a Fermi resonance within the cation. If an appropriate combination mode of the cation happened to fall near the predicted 1536.7 cm^{-1} band, the feature would split into two equidistant components, one higher in frequency, the other lower. Interestingly, two moderately strong bands are indeed observed at 1515.9 and 1560.7 cm^{-1}, approximately 20 cm^{-1} above and below the predicted position.

The 1,2-Benzanthracene Cation. The mid-infrared spectrum of the 1,2-benzanthracene cation is shown in Figure 4. The band frequencies and relative intensities are listed in Table 1 and compared to theoretically calculated values in Table 2. The evolution of the bands assigned to the cation with Ly-α photolysis is plotted in Figure 5.

The bands associated with the 1,2-benzanthracene cation lie in three distinct groups. Those between 1600 and 1500 cm^{-1} are directly attributed to CC stretching vibrations, those between about 1500 and 1300 cm^{-1} with vibrations involving differing amounts of CC stretches and CH in-plane bends, and those between 1300 and 1100 cm^{-1} are generally associated with CH in-plane bends. The region is dominated by one strong band at 1332.2 cm^{-1}. As with chrysene, we attribute this to a nearly pure CC stretch based on the vector analysis of Langhoff and Bauschlicher described in the previous section (see Figure 3).

Only one band has been detected which may be associated with a CH out-of-plane bending mode of the 1,2-benzanthracene cation. That band falls at 911.2 cm^{-1}. Since this molecule has two rings with quadruply adjacent H atoms, one with doubly adjacent hydrogens, and one with two non-adjacent hydrogen atoms, three bands would be expected. Presumably, the other CH out-of-plane bending modes for the cation are screened by the strong CH out-of-plane features of the neutral molecule (non-adjacent CH, 882.7 cm^{-1}; doubly adjacent CH, 805.2 cm^{-1}; and quadruply adjacent CH, 746.9 cm^{-1}) or by one of the other numerous neutral bands that fall in this region. Indeed, there is a moderate neutral feature near 758 cm^{-1}, only 2 cm^{-1} from the theoretically predicted position of the quadruply adjacent CH out-of-plane bend of the cation.

Given the theoretical data and the positions of the nonadjacent CH out-of-plane bending modes in other PAH cations,[7] it is reasonable to attribute the 911.2 cm^{-1} band to this mode. This lies slightly above the high end of the frequency range normally associated with the out-of-plane bending vibrations of non-adjacent H atoms in aromatic hydrocarbons, again suggesting that the force field in the cation is somewhat altered from that in the neutral species. On the basis of the measured upper limit of 2.3% ionization, we estimate that the intensity of the non-adjacent CH out-of-plane bending mode of the 1,2-benzanthracene cation is suppressed by a factor of ∼5 from the corresponding mode in the neutral molecule. In neutral 1,2-benzanthracene the non-adjacent CH out-of-plane bending absorption is a factor of 4 more intense than the strongest CC stretching feature.[8] Again, in the cation the situation is reversed with the strongest CC stretching band (1332.5 cm^{-1}) a factor of 16 more intense than the non-adjacent CH out-of-plane bend (911.2 cm^{-1}), and consistant with a 2 orders-of-magnitude enhancement in the CC stetching modes in the cation.

As shown in Table 2, peak positions and relative band strengths for most of the weak and moderately strong bands compare quite favorably to the theoretical values predicted for this cation. Most theoretical peak frequencies are within 10 cm^{-1} of the experimental values, and all fall within 22 cm^{-1}. Furthermore, the strongest band falls at 1332.2 cm^{-1}, only 2.3 cm^{-1} from the strongest predicted value. The good agreement between theory and experiment in this case as well as for a number of the other PAHs underscores the significance of the discrepancies discussed above in the case for chrysene.

It is interesting that the strongest bands in both chrysene (1315.7 cm^{-1}) and 1,2-benzanthracene (1331 cm^{-1}) are quite close to the peak frequency of the 7.6 μm (1320 cm^{-1}) component of the most intense broad interstellar emission feature in HII regions and reflection nebulae.[15] Furthermore, these frequencies are slightly lower than the strongest band in tetracene (1358 cm^{-1}). Comparing these bands with those of the other PAHs studied to date suggests that a strong band slightly higher in frequency than 1300 cm^{-1} may be associated with an asymmetric CC stretching vibration involving the rings adjacent to the kink in the chain of aromatic rings such as that shown in Figure 3.

VI. Conclusions

The mid-infrared spectra of the chrysene and 1,2-benzanthracene cations isolated in argon matrices are presented. As has been the case with previous PAH cations studied, no new features were found in the CH stretch region between 3200 and 2900 cm^{-1}, implying that the CH stretching modes of the cation are comparable to or weaker than those of the neutral species. Theory predicts them to be weaker.[12]

The strongest mid-infrared absorption bands of these PAH cations fall between 1600 and about 1200 cm^{-1}, corresponding to the CC stretching and CH in-plane modes. The most intense of these tend to fall near 1330 cm^{-1}. These modes are 2−5 times stronger than the bands due to the CH out-of-plane bending modes. This relationship is just the opposite of that observed for neutral PAHs in which the CH out-of-plane modes are the more intense by a factor of 2−10. This striking variation in the intensities of the vibrational modes accompanying ionization reflects a dramatic alteration in the charge distribution within the molecule from one in which π electrons are delocalized to one in which charge density varies across the molecule. While such an exaggerated effect is perhaps surprising, this behavior has been predicted theoretically and observed experimentally for all other PAH cations studied to date (over 20).

This pronounced intensity shift is important for the interpretation of the astronomical emission spectra which are dominated by very intense features in the 1660−1200 cm^{-1} region. Since most PAHs in the emission zones would be ionized, this spectral characteristic of PAH cations gives strong support to the interstellar PAH hypothesis. Interestingly, the strongest absorptions of the chrysene and 1,2-benzanthracene cations fall between 1300 and 1330 cm^{-1}, close to the peak of the most intense interstellar emission feature in HII regions and reflection nebulae. Comparing these bands with those of the other PAHs studied to date suggests that a strong band slightly higher in frequency than 1300 cm^{-1} may be associated with an asymmetric CC stretching vibration involving rings adjacent to the kink in the chain of aromatic rings such as that shown in Figure 3. It is precisely this sort of data which is needed to analyze the interstellar spectra, which in turn provide insight into the chemical processes and evolution of these widespread interstellar species.

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