Photodissociation of Gas-Phase Polycylic Aromatic Hydrocarbon Cations

Scott P. Ekern,[†] Alan G. Marshall,*[,†,‡] Jan Szczepanski,[§] and Martin Vala[§]

Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory,
Florida State University, 1800 E. Paul Dirac Circle, Tallahassee, Florida 32310, Department of Chemistry,
Florida State University, Tallahassee, Florida 32306, and Department of Chemistry and Center for Chemical
Physics, University of Florida, Gainesville, Florida 32611

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The photostablities of two dozen polycyclic aromatic hydrocarbon (PAH) cations and a fullerene, C_{60}^+, have been tested. The molecular radical cations have been produced by both electron impact and laser desorption, then trapped and mass-analyzed in a Fourier transform ion cyclotron resonance mass spectrometer. The PAH cations were subjected to visible and UV radiation ($\lambda \geq 185$ nm) from a Xe arc lamp. Fragmentation patterns fall into four groups: photostable, hydrogen loss only, hydrogen and carbon loss, and photodestroyed. The fragmentation patterns are discussed with respect to prior experimental and theoretical models. Implications of these findings for the "PAH hypothesis" and the unidentified interstellar infrared (UIR) emission bands are discussed briefly.

I. Introduction

Since the proposal that polycyclic aromatic hydrocarbons (PAHs) might be the source of the unidentified infrared (UIR) emission bands from various interstellar objects,[1,2] researchers have wrung a remarkable amount of information from a small body of experimental data on the PAHs. Although the experimental PAH band positions are close to the UIR bands, it was noted early on that there were important differences in the frequencies, band profiles, and intensities of the neutral PAHs and the bands seen from space.[3] Modifications to the PAH proposal surfaced soon thereafter and included ionization,[3−5] hydrogenation,[6] and dehydrogenation[7,8] of the PAHs or hydrogenation of amorphous carbon aggregates.[9−11] However, little experimental data on these exotic molecules existed until the work of Szczepanski and Vala and co-workers,[12] Hudgins and Allamandola and co-workers,[13] and d'Hendecourt and Leger.[14] Theoretical work on these species has been reported by Ellinger and co-workers[15−17] and by Langhoff.[18] Those workers primarily addressed the problem of the effect of ionization on PAH band intensities and frequencies, and although the experimental work was performed in low-temperature noble gas matrices, a better match to the UIR relative band intensities was found. Discrepancies persisted, however, and the problem is to date still unresolved.

In 1993 Boissel, Lefevre, and Thiebot (BLT)[19] reported important results on the photostability of PAH cations. In experiments on vapor-phase anthracene and pyrene cations isolated in an ion cyclotron resonance (ICR) ion trap, those workers showed that, when exposed to broad-band visible radiation, pyrene lost two hydrogens whereas anthracene lost acetylene and two hydrogens. The mechanism proposed to explain these findings involved a multiple sequential photon absorption process. The cation internal energy thus increases stepwise until a dissociation limit is reached and the cation fragmented. The important inference drawn from these experiments was that PAH cations are unstable in the vapor phase under even mild photolysis conditions. Dunbar and co-workers have also studied this problem on a variety of organic molecular cations but generally used IR laser excitation.[20] If the multiple-photon absorption mechanism is generally true for all (or even most) PAH cations under visible and/or ultraviolet radiation, the contribution of dehydrogenated or fragmented species to the UIR emission may be more important than originally believed. Thus, further investigation of this possibility is certainly warranted.

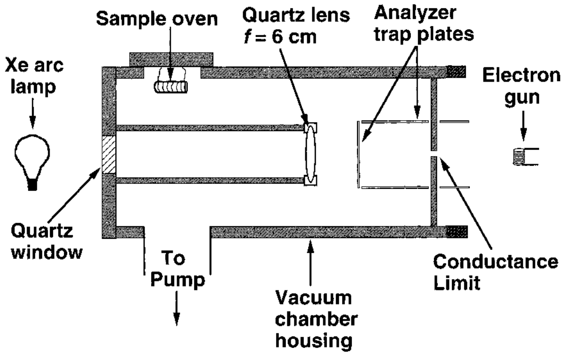

Figure 1. Schematic diagram of experimental apparatus for electron ionization, photolysis, and Fourier transform ion cyclotron resonance mass analysis of polycyclic aromatic hydrocarbons.

Although a number of photoionization and photodissociation studies have been conducted on neutral PAH species,[20−23] very few have directly tested the photostability of cationic PAHs. In this paper, we report the general photostability of a series of PAH cations. Vapor-phase PAH cations have been trapped in an ICR cell and subjected to broad-band visible and ultraviolet radiation. Four classes of photodissociation have been found, ranging from photostable to complete photodestruction.

II. Experimental Section

The experimental setup is shown in Figure 1. All ICR mass spectra were obtained with an FTMS-2000 Fourier transform

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[*] To whom correspondence may be addressed.
[†] National High Magnetic Field Laboratory, Florida State University.
[‡] Department of Chemistry, Florida State University.
[§] University of Florida.

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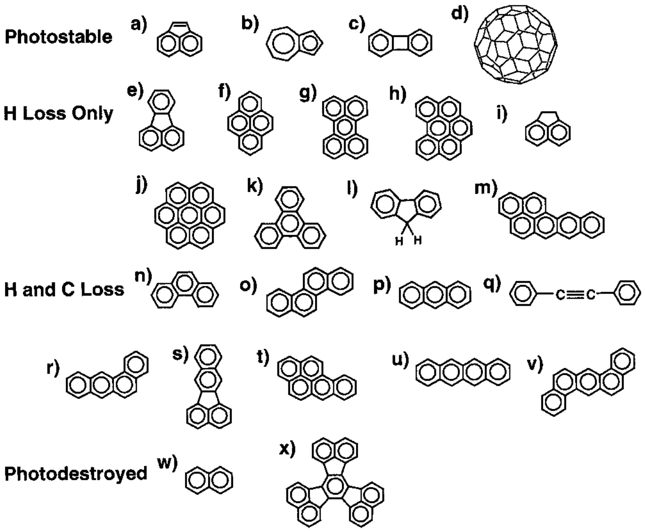

Figure 2. Structures of the fullerene, C_{60} (**d**), and the various PAHs in the present and previous (**j** and **m** in Figure 2) electron ionization/photolysis/FT-ICR MS experiments:[25] acenaphthylene (**a**), azulene (**b**), biphenylene (**c**), fluoranthene (**e**), pyrene (**f**), perylene (**g**), benzo[*ghi*]perylene (**h**), acenaphthene (**i**), coronene (**j**), triphenylene (**k**), fluorene (**l**), naphtho[2,3-*a*]pyrene (**m**), phenanthrene (**n**), chrysene (**o**), anthracene (**p**), biphenylacetylene (**q**), benz[*a*]anthracene (**r**), (**s**) benzo[*k*]fluoranthene, benzo[*a*]pyrene (**t**), tetracene (**u**), dibenzanthracene (**v**), naphthalene (**w**), and decacyclene (**x**).

ion cyclotron resonance (FT-ICR) mass spectrometer (Finnigan Corp., Madison, WI), comprising dual 1.875 in. cubic source and analyzer ion traps centered in the bore of a 3.0 T superconducting magnet, automatic solids insertion probe, and an Odyssey data station. The usual analyzer and source diffusion pumps were replaced with cryopumps (CTI Helix Cryotorr 8). PAH neutrals were introduced into the ICR chamber from a resistively heated oven (Nichrome wire-wrapped quartz tube). Pressure in the vacuum chamber was typically 1 × 10^{-9} Torr. An electron gun located behind the source ion trap effected ionization of the PAHs. Its energy was set just above each PAH's appearance potential to minimize fragmentation.

For C_{60}, laser desorption/ionization was performed with a Q-switched Nd:YAG laser (532 and 1064 nm, Continuum Surelite I). The laser beam was focused by a 1 m focal length lens through a quartz window into the analyzer. The target was a 1 cm diameter stainless steel disk, coated with C_{60}, located adjacent to the analyzer trap.

Ions were photolyzed by use of a 300 W Xe arc lamp (ILC Technology/Varian, Palo Alto, CA) placed 1 m from the center of the analyzer ion trap. The radiation passed through a shutter and was focused with a 6 cm fused silica lens. The spectral profile of the arc lamp is smooth down to the near-IR and resembles a 6200 K blackbody. The transmission characteristics of the lens and quartz window allow wavelengths longer than 185 nm (6.70 eV) to enter the vacuum chamber. The radiation flux entering the chamber was estimated at 10^{17} photons s^{-1} cm^{-2} nm^{-1} and was found to be insufficient to photoionize any of the neutral PAHs studied. Unless otherwise noted, all mass spectra were taken both before photolysis and after a 0.5 s exposure to the full spectral output of the lamp.

The structures of the PAH radical cations studied are shown in Figure 2 and include a number of pericondensed, catacondensed, and nontraditional PAHs, as well as C_{60}^+. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further modification. The C_{60} laser desorption target was made by dissolving the fullerene in toluene and allowing the solvent to evaporate, leaving a film on a stainless steel plate. No toluene adducts or fragments were detected.

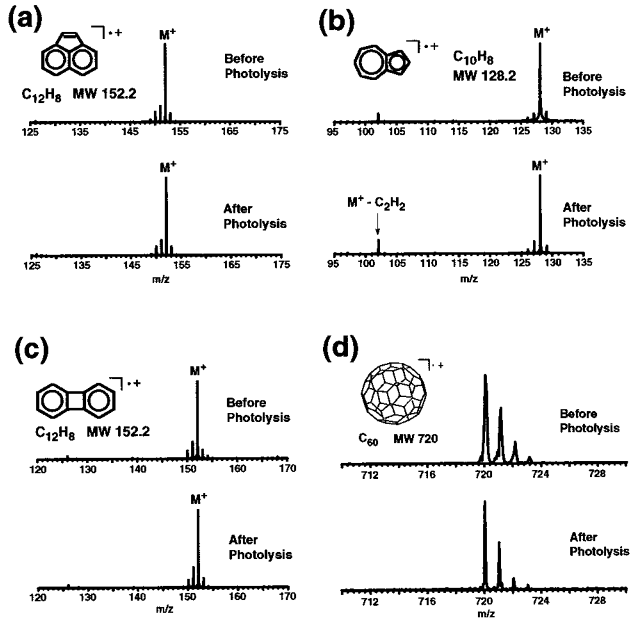

Figure 3. FT-ICR mass spectra acquired before and after photolysis (0.5 s, 1.0 mW/nm) of four photostable PAH cations: acenaphthylene (**a**), azulene (**b**), biphenylene (**c**), and C_{60} (**d**). The parent molecular ion is denoted as M^+.

III. Results

The PAH molecular radical cations studied here may be classified (see Figure 2) according to their photolysis behavior into four groups: (A) photostable, (B) loss of hydrogen only, (C) loss of hydrogen and carbon, and (D) photodestroyed. Each type of behavior will be discussed individually.

A. Photostable Cations. The four cations that exhibited photostability were acenaphthylene (**a**), azulene (**b**), biphenylene (**c**), and the fullerene, C_{60} (**d**) (cf. Figure 2 for structures and Figure 3 for mass spectra). With the exception of C_{60}^+, these species were among the smallest studied here. Interestingly, all four species contain one (or more) four- or five-membered ring. Their stability is somewhat surprising, since these smaller species have fewer degrees of freedom over which to distribute the absorbed photon energy. Except for C_{60}^+, all cations of molecular weight greater than 152 u dissociated in some manner (see below).

Unlike acenaphthylene (**a**) and biphenylene (**c**), azulene (**b**) is more difficult to classify. Figure 3b shows the presence of a fragment ion at 102 u, resulting from loss of acetylene from the parent ion, both before and after photolysis. The abundance of this fragment ion increases only slightly on photolysis (from 12% of the parent ion abundance before photolysis to 16% of parent ion abundance after photolysis). Compared with other photodissociation patterns observed, that increase is small. Therefore, under the present conditions, azulene is essentially photostable.

In a recent ab initio study,[24] it was concluded that both acenaphthylene and biphenylene were the stable photoproducts of acetylene loss from phenanthrene (**n**) and anthracene (**p**). The present results validate the photostability of the former two radical cations and, in addition, show the photoinstability of the latter two cations. However, the present results shed no light on the identity of the fragment ions of mass 152 u seen upon photolysis of phenanthrene and anthracene. Whether they are closed ring compounds (such as acenaphthylene and biphenylene) or chainlike or monocyclic compounds will have to await future experiments.

B. Loss of Hydrogen Only. Of the 24 cation species studied, nine lost only hydrogen upon photolysis. The nine compounds were fluoranthene (**e**), pyrene (**f**), perylene (**g**), benzo[*ghi*]perylene (**h**), acenaphthene (**i**), coronene (**j**), triphenylene (**k**), fluorene (**l**), and naphtho[2,3-*a*]pyrene (**m**) (cf. Figure 2 for structures and Figure 4 for mass spectra). We have previously reported[25] that coronene (**j**) and naphtho[2,3-*a*]pyrene (**m**) cations are completely dehydrogenated to C_{24}^+ during photolysis. As for coronene and naphtho[2,3-*a*]pyrene, the dehydrogenation of the other cations in this group also showed a dependence on lamp power. All figures presented in this paper show the effects of maximum lamp output. Figure 4 shows that, with the exception of acenaphthene (**i**), the maximum photon flux (~1 mW/nm) was sufficient to strip off at least one-third of the hydrogens from the parent ion. On the other hand, at minimum lamp power (~500 mW/nm), the loss of only two or four hydrogens is usually seen.

C. Loss of Hydrogen and Carbon. Nine species lost both hydrogen and carbon to some extent (Figure 5). These included the PAHs phenanthrene (**n**), chrysene (**o**), anthracene (**p**), benz[*a*]anthracene (**r**), benzo[*k*]fluoranthene (**s**), benzo[*a*]pyrene (**t**), tetracene (**u**), dibenzanthracene (**v**) (cf. Figure 6), and the non-PAH biphenylacetylene (**q**). A similar PAH, pentacene ($C_{22}H_{14}$), was also attempted but showed evidence of facile thermal decomposition. The product ion mass spectra of the above nine species fall into two general groups: a series corresponding to loss of *n* hydrogens from the parent ion, and a similar series derived from the parent ion minus C_2H_2 (26 u). These species could arise either from loss of *n*H followed by loss of C_2 or from loss of acetylene from the parent followed by dehydrogenation of both parent and daughter ions. The results of Jochims et al.[21,22] indicate that acetylene is photolyzed intact from the molecular ion. Their single-photon experiments find the appearance potentials of the acetylene loss fragments to be generally less than 1 eV higher than the H loss potential. Considering such a small difference in appearance potential, it seems reasonable that the hydrogen atom and acetylene loss mechanisms operate concurrently.

Two of the cations, dibenzanthracene (**v**) and tetracene (**u**), show evidence of sequential loss of four carbons as well as loss of hydrogens within each group, further complicating an understanding of the order of fragmentation. The losses could involve acetylene molecules, CH fragments, and hydrogen followed by carbon elimination or a combination. Moreover, in contrast to the acetylene appearance potential mentioned above, no appearance potential is known for the ejection of neutral CH from PAHs with which to make a comparison. The long, extended structures of these PAHs distinguish them from other PAHs and may account for their observed fragmentation behavior.

D. Photodestruction. Two PAH cations naphthalene (**w**) (cf. Figure 7) and decacyclene (**x**) were found to be completely destroyed upon photolysis. The mass spectrum of photolyzed naphthalene cation shows regularly spaced losses of up to four acetylenes (26 u each). The remaining C_2 cation is presumed to be photostable, since no C^+ species was detected.

The second species destroyed was decacyclene. This PAH is, however, thermally unstable and falls apart on heating. Although pyrolysis is not unusual behavior for such a large PAH, the thermal product in this case is interesting. After sublimation from the oven and subsequent ionization, only a single species at 152 u was detected. Although several PAHs have masses of 152 u, the acenaphthylene structure (**a** in Figure 2) seems likely here, since decacyclene is built of three acenaphthylene-like units.

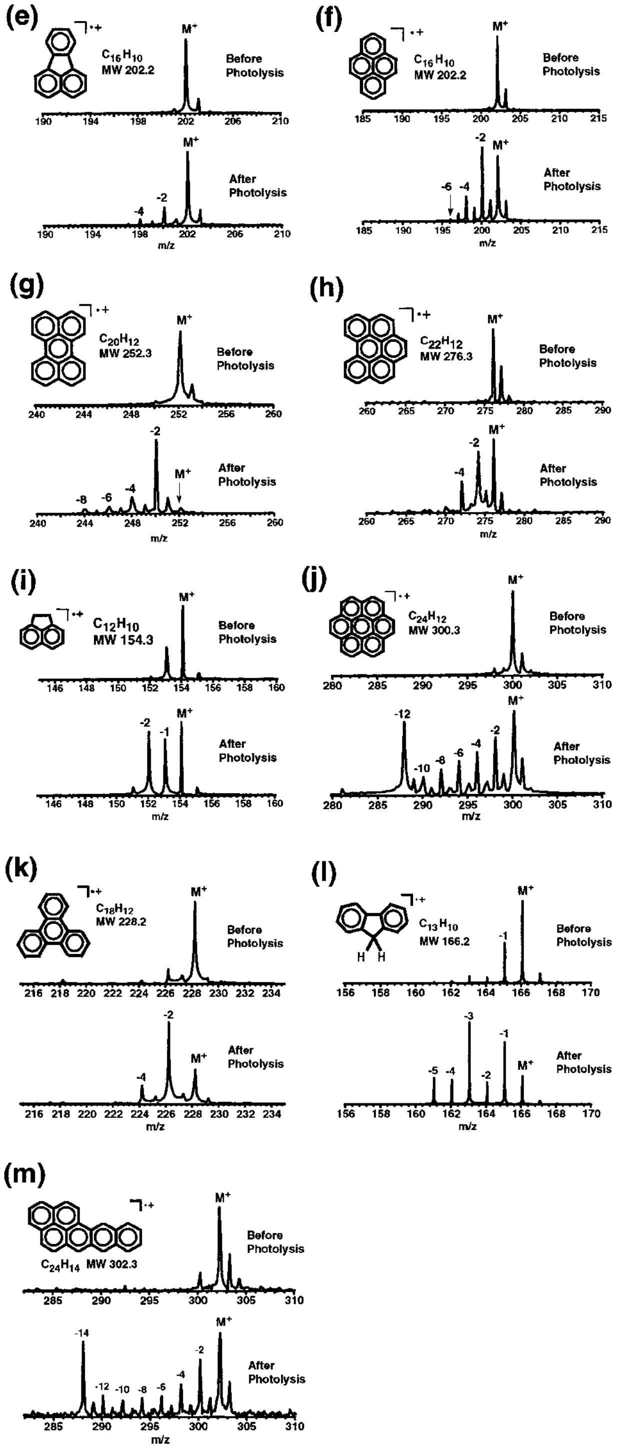

Figure 4. FT-ICR mass spectra acquired before and after photolysis (0.5 s, 1.0 mW/nm) of the nine PAH cations that lost hydrogen only: fluoranthene (**e**), pyrene (**f**), perylene (**g**), benzo[*ghi*]perylene (**h**), acenaphthene (**i**), coronene (**j**), triphenylene (**k**), fluorene (**l**), and naphtho[2,3-*a*]pyrene (**m**). The $-n$ numbers correspond to the number of hydrogens lost, and the parent molecular ion is denoted by M^+.

IV. Discussion

The above results prompt four questions that are addressed below. (1) Why are some of the small PAH (≤152 u) parent

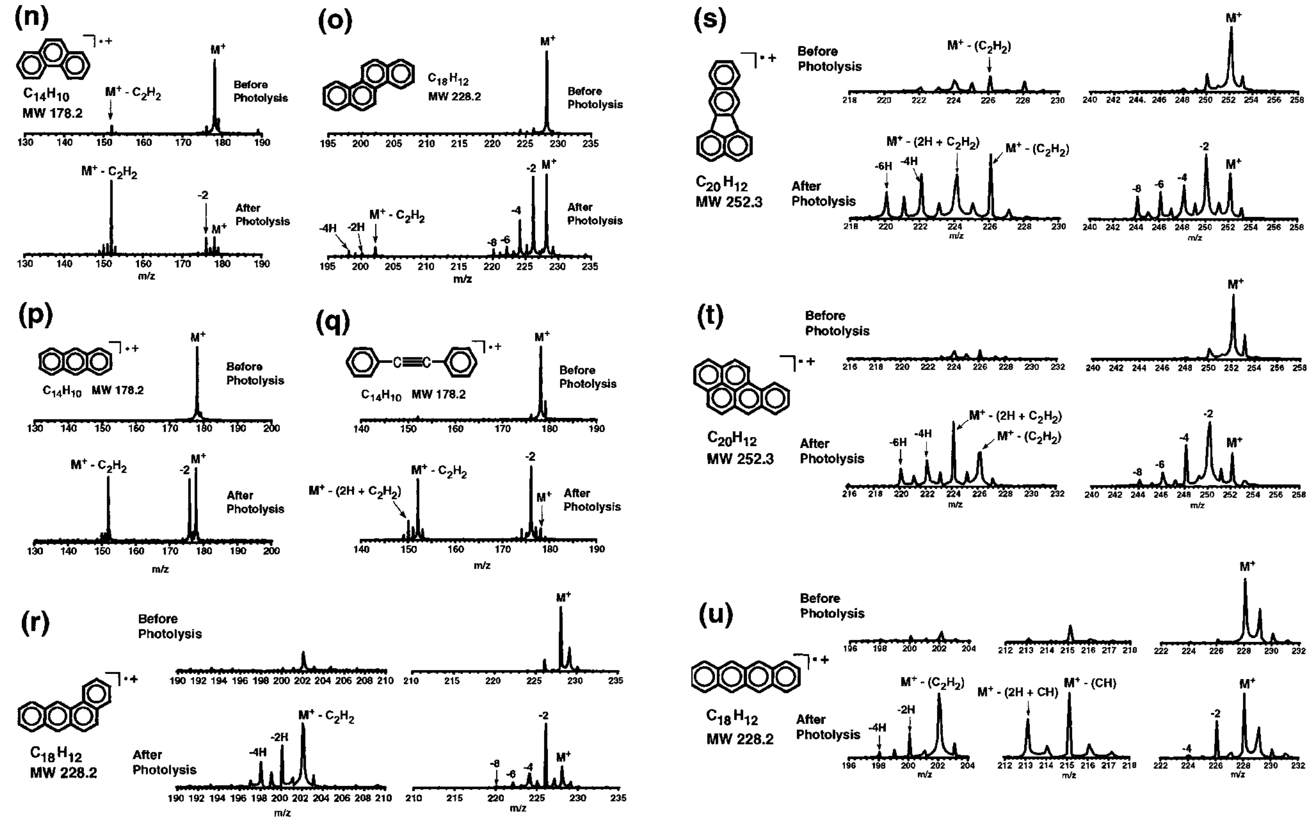

Figure 5. FT-ICR mass spectra acquired before and after photolysis (0.5 s, 1.0 mW/nm) of PAH cations that lost both hydrogen and carbon: phenanthrene (**n**), chrysene (**o**), anthracene (**p**), biphenylacetylene (**q**), benz[*a*]anthracene (**r**), benzo[*k*]fluoranthene (**s**), benzo[*a*]pyrene (**t**), and tetracene (**u**). The $-n$ numbers correspond to the number of hydrogens lost from the parent molecular ion, and the $-n$H numbers correspond to the number of hydrogens lost from the main carbon loss fragment (M^+-CH or $M^+-C_2H_2$). The parent molecular ion is denoted by M^+.

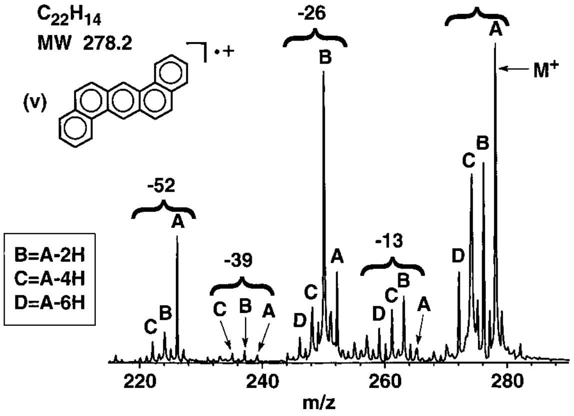

Figure 6. FT-ICR mass spectrum after photolysis (0.5 s, 1.0 mW/nm) of dibenzanthracene (**v**). The five groups of dissociation fragments are separated by brackets along with their mass shift from the parent molecular ion group. Note that each sucessive group is separated by the mass of a CH molecule (13 u).

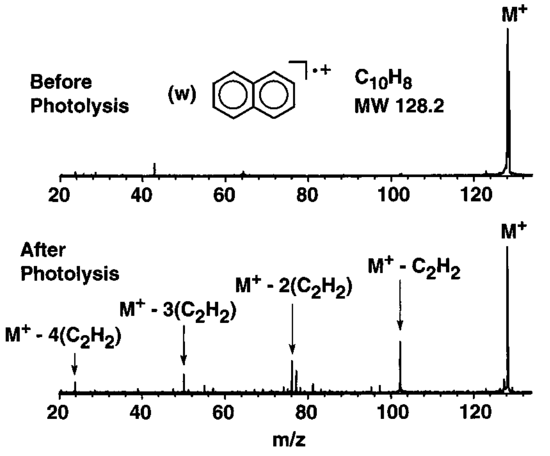

Figure 7. FT-ICR mass spectra acquired before and after photolysis (0.5 s, 1.0 mW/nm), showing the complete dissociation of the naphthalene (**w**) cation. The parent molecular ion is denoted as M^+, and each subsequent acetylene loss fragment by $M^+ - n(C_2H_2)$.

cations stable? (2) Is there a pattern to the PAH photofragmentation? (3) What are the structures of the various fragments, and what makes them resistant to further photolysis? (4) How do these results apply to the hypothesized presence of PAH cations in stellar and interstellar regions?

Polycyclic aromatic hydrocarbons have long been considered resistant to dissociation because of their high CH and CC bond energies.^{26} In view of their plentiful degrees of vibrational freedom, the PAHs were thought to be capable of readily redistributing the absorbed photon energy into intramolecular vibrational modes. However, as the present and previous results show, the cations of many of the PAHs are susceptible to photodissociation at input photon energies less than CH or CC bond energies. The photodissociation of the PAH cations depends on (1) excited-state energies attainable by the incident radiation, (2) excited-state lifetimes sufficiently long to ensure multiphoton absorption, and (3) sufficient density of excited-state levels to enable the multiphoton absorption to occur. A sufficiently long excited-state lifetime requires that the radiative decay rate be slow compared with the flux of absorbed incident radiation. At first glance, the four PAHs found here to be photostable appear to meet these criteria (although further experimental evidence is needed), so why then do they not photodissociate? The common characteristic of all four is the presence of at least one four- or five-membered ring in the parent

TABLE 1: Various Parameters for Possible Correlation with Observed PAH Cation Fragmentation Patterns[a]

PAH	observed fragments	molecular weight	formula (C, H)	symmetry[b]	C/H ratio	IP[c]	ΔH_f(ion)[c]	ΔH_f(neut)[c]
photostable								
a		152	12, 8	C_{2v}	1.5	8.22	(252)	62
b		128	10, 8	C_{2v}	1.25	7.41	240	69
c		152	12, 8	D_{2h}	1.5	7.56	279	104
d		720	60, 0	I_h				
H loss only								
e	−4H	202	16, 10	C_{2v}	1.6	(7.95)	253	69
f	−6H	202	16, 10	D_{2h}	1.6	7.41	222	52
g	−8H	252	20, 12	D_{2h}	1.6	6.90	233	74
h	−4H	276	22, 12	C_{2v}	1.83	7.15	237	72
i	−2H	154	12, 10	C_{2v}	1.6	(7.68)	(214)	37
j	−12H	300	24, 12	D_{6h}	2.0	7.29	245	77
k	−4H	228	18, 12	D_{3h}	1.5	7.84	245	64
l	−5H	166	13, 10	C_{2v}	1.3	7.89	227	45
m	−14H	302	24, 14	C_s	1.7			
H and C loss								
n	−2H; (2C, 2H)	178	14, 10	C_{2v}	1.4	7.86	230	49
o	−8H; (2C, 2H)	228	18, 12	C_{2h}	1.5			
p	−2H; (2C, 2H)	178	14, 10	D_{2h}	1.4	7.45	227	55
q	−2H; (2C, 2H)	178	14, 10	D_{2h}	1.4	7.90	278	96
r	−8H; (2C, 2H)	228	18, 12	C_s	1.5	7.43	239	68
s	−8H; (2C, 2H)	252	20, 12	C_{2v}	1.6			
t	−8H; (2C, 2H)	252	20, 12	C_s	1.6	7.12	233	69
u	−4H; (2C, 2H)	228	18, 12	D_{2h}	1.5	6.97	229	68
v	−6H; (2C, 2H)	278	22, 14	C_{2h}	1.57	7.38	250	80
photodestroyed								
w	−8C, 8H	128	10, 8	D_{2h}	1.25	8.14	223	36

[a] The PAH designations are taken from Figure 2. [b] Symmetry of the neutral PAH (assuming that the point group of the ion is the same as that of the neutral precursor). [c] From Lias, S. G.; Bartmess, J. E.; Lieberman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas-Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1).

ion structure. The presence of the smaller ring(s) may lead to enhanced photostability by either (1) raising the dissociation barrier sufficiently high that it cannot be reached within the radiative lifetime or (2) decreasing the radiative lifetime. In support of the first interpretation, Ling, Martin, and Lifshitz have recently reported[24] that both acenaphthylene and biphenylene cations are more stable than other $C_{12}H_8^+$ isomers; acenaphthylene is particularly stable. It is also possible that the photon flux absorbed by the smaller species may be less than that for the larger PAHs because of less favorable absorption profiles. It is generally true that the larger PAHs absorb at longer wavelengths in the visible than do the smaller PAHs. However, before more concrete conclusions can be drawn, more work is needed on the UV and visible absorption spectra of these ionic species.

The photolysis behavior of the various PAH cations studied here does not show any simple property−structure correlation from which the observed pattern can be understood. As is evident from Table 1, no simple relationship exists between the observed fragmentation patterns and molecular weight, symmetry, number of carbons, heat of formation of the ion, hydrogen atom arrangement, ionization energy of the neutral parent, or carbon/hydrogen ratio. One relationship does hold but with several exceptions. *A PAH may lose one or more C_2H_2 (acetylene) groups if it contains four adjacent hydrogens on a ring not fused to a four- or five-membered ring.* Stated another way, a PAH must contain at least one "exposed" aromatic ring; if not, the parent loses only hydrogens. The exceptions are triphenylene (**k**), fluorene (**l**), and coronene (**j**). This relationship is similar to a prior suggestion by Boissel that only noncompact PAHs may lose one or more C_2H_2 groups, whereas compact PAHs only lose two hydrogens.[19]

Coronene (**j**) cation ($C_{24}H_{12}^+$), which does not conform to this relationship, and naphtho[2,3-*a*]pyrene (**m**) cation ($C_{24}H_{12}^+$), which does conform, may lose all of their hydrogens upon photolysis. The common end product, C_{24}^+, from both species may point to a common intermediate, perhaps formed by ring opening and isomerization. There is evidence[27] that the preference to dissociate via certain pathways (e.g., hydrogen elimination) may arise from common reaction mechanisms that produce the same fragment product ions. Monocyclic or linear intermediates have been invoked previously[27] to explain the pattern observed in the chemically activated dissociation (CAD) product ion mass spectra. Further experimentation will be necessary to decide this issue for these cations.

In our experiments, filters were not used to limit excitation to the lowest-lying electronic transition of the parent ion, as in the BLT experiments. Our broad-band excitation may span an energy range wide enough to open several dissociation channels. Thus, the photolysis products we observe may not be limited to the lowest energy process, perhaps complicating interpretation. Interestingly, our observed fragmentation patterns for pyrene (**f**) and anthracene (**p**), following excitation at all wavelengths longer than 185 nm, are *identical* to those observed by BLT, who excited only the first electronic transition.[19] That similarity is not unexpected according to the BLT model, which states that multiple-photon absorption by an ion will cease only when the internal energy has increased to a point sufficient to access the lowest-lying dissociation channel. An increase in flux is expected to increase the yield of fragment ions but not increase the parent internal energy such that new dissociation channels become available. On the basis of the single-photon results of Jochims et al.,[21,22] the lowest energy fragmentation pathways from PAHs are loss of hydrogen atom(s) and loss of acetylene. Higher energy channels involving the loss of C_3H_3 or C_2H are thus not expected and are not seen in multiple-photon experiments.

Acenaphthene (**i**) ion loses one or two hydrogens, presumably reverting to the stable acenaphthylene (**a**) cation, and does not isomerize during that process. On the other hand, the other four PAHs that lose hydrogens may undergo ring openings to linear or monocyclic forms. Further work on the appearance potentials of those product fragment ions will be necessary to decide this issue. Natalis and Franklin have, however, shown[28] that the appearance potentials of the $(M-H)^+$ ions increases with increasing parent ion resonance energy. Those authors found that result difficult to understand unless the loss of hydrogen is accompanied by one or more ring openings. The fragment ions resulting from hydrogen loss show a preferential loss of an even number of hydrogens. Recent work has addressed the question of whether hydrogens are lost sequentially from the cation or as an H_2 molecule, deciding in favor of the former.[22,29] Hydrogen loss from a ring-opened (possibly linear) species would then not depend greatly on the individual PAH properties but rather on the precursor chain species formed prior to the stable product polyacetylenic chains.

Jochims et al.[21] have proposed a scheme to account for the photofragmentation of the isomers azulene (**b**) and naphthalene (**w**). They conclude that the isomers are linked by a common intermediate form from which hydrogen and acetylene loss occurs. However, our results, which show that azulene is photostable and naphthalene is completely photodissociated, do not support such a common intermediate structure. This radical difference in photolysis behavior suggests that mechanisms of ionization and energy deposition in these two species are not similar.

An important question is why the nine PAHs that lose both hydrogens and carbons form fragment ions that are resistant to further photodissociation. For example, anthracene (**p**) or phenanthrene (**n**) cations photodissociate into product fragments of mass 152 u. Acetylene loss comes from either the 1,2-positions or the 2,3-positions, leaving a naphthyl fragment with a CHCH chain or two CH groups attached, respectively. Why should that fragment ion be resistant to further photodissociation? The only difference between those fragment ions and the naphthalene cation itself (which is completely photodestroyed) is the presence on the former of the CH or CHCH groups. Their roles may be inferred from previous work by Smalley and co-workers[30] on the vibrational relaxation in electronically excited *n*-alkylbenzenes. They found excitation into various ring distortion modes (so-called system modes) but is soon followed by very rapid intramolecular vibrational redistribution (IVR) processes that redistribute the energy into so-called bath modes. The bath modes are dominated by torsional motion about the phenyl−alkane chain bond. The longer the alkane chain, the more complete is the vibrational relaxation. Thus, in the present instance, it is likely that the CHCH chain on the naphthyl group in the product fragment facilitates the IVR process by providing a higher density of low-energy torsional states into which the excess energy can flow. Such an energy bath ("sink") may then preclude further destruction of the main ring system.

If such an IVR process is central to the preservation of certain fragment structures, then why does naphthalene completely photodestruct? Two possible schemes for the sequential loss of acetylenes in naphthalene are shown in Figure 8. The total destruction of the naphthalene cation may result from an insufficient density of states in the increasingly smaller fragments so that the rapid IVR process is not possible and further dissociation may proceed. Various other fragmentation pathways of the naphthalene cation have been studied both theoretically[23,31] and experimentally.[21,22,26,32] Those authors mainly considered the loss of hydrogen, and/or just one acetylene, with identification of the resulting fragment ion. Jochims et al.[22] put the energy requirement for the loss of acetylene from naphthalene cation at 7.49 eV, which would require a multiple-photon absorption process to attain the requisite internal energy in their experiment. However, sequential loss of acetylene leading to the complete dissociation of the naphthalene cation has not been observed previously. Indeed, that behavior is unique among the PAH cations studied here. The products of all other PAH cations that lose one or two acetylene molecules are resistant to further photolysis.

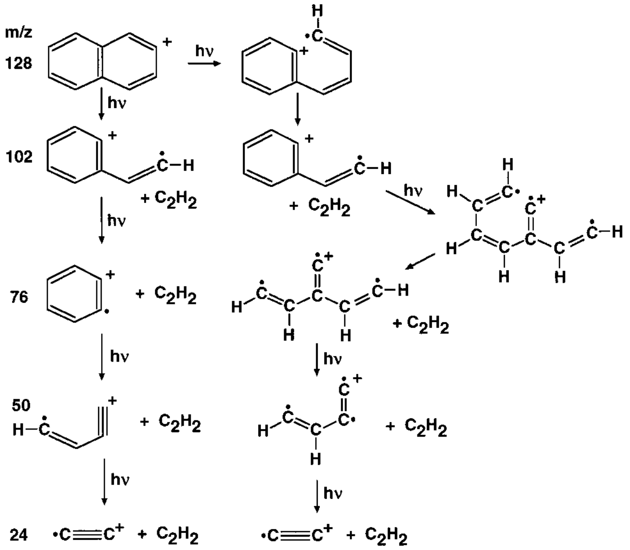

Figure 8. Possible routes for naphthalene photodestruction.

The present results, together with the previous results of Boissel and co-workers,[19,29] show that most PAH cations are inherently unstable to multiphoton photolysis. From the present results, it is clear that the manner and extent to which a PAH cation is multiphoton-photodissociated depends not only on its molecular structure but also on the incident photon flux. That conclusion has important implications for the possible involvement of the PAHs in the unidentified interstellar infrared emission bands. It is necessary to discuss the two extremes of photon flux. In the limit of very low photon flux, such as found in reflection nebulae, multiphoton processes are not expected to be important. Dehydrogenation and photodestruction by means of a multiphoton mechanism will not be competitive with radiative vibrational decay. However, the stable species giving rise to the UIR emission bands are probably not the PAHs to which so much attention has been paid to date. Instead, other stable species such as the stable product fragments observed here may play an important role. At the other extreme of high photon flux, in stellar regions such as at the inside interface with HII regions and in the central regions of planetary nebulae, both the radiation flux and the degree of dehydrogenation/dissociation will be high. It is highly likely that the flux in those regions is sufficiently high that reverse reactions such as rehydrogenation will not be able to compete.

Allain, Leach, and Sedlmayr have recently presented[33,34] model calculations on the photodestruction of PAHs in the interstellar medium and conclude that ionized and partially dehydrogenated PAHs are less stable than their neutral parents to photodestruction. They also conclude that only PAHs with more than 50 carbon atoms may survive the UV radiation field in the regions of the interstellar medium in which the UIR bands are observed. They find that the smaller PAHs will be destroyed within several years in that environment. Allamandola, Tielens, and Barker[3] state that in stellar regions, dehydrogenation will outpace rehydrogenation. They further show that PAHs with fewer than 20−30 carbon atoms should be stripped of their hydrogens, whereas the larger PAHs should remain hydrogenated. However, under the conditions of our present experiments, exactly the opposite is observed. The smallest PAHs (<20 carbons) are photostable, whereas some of the largest (coronene (**j**) and naphtho[2,3-*a*]pyrene (**m**)) are completely dehydrogenated. Although our mass-resolving power is more than sufficient to determine the chemical formulas of the various PAH photofragment ions, the present experiments do not establish their molecular structures. Since their structures govern their IR emission properties to a large degree,[18,35] further work on the structures as well as absorption and emission characteristics of the stable photoproduct ions remains a high priority.

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