INFRARED STUDY OF UV/EUV IRRADIATION OF NAPHTHALENE IN H_2O+NH_3 ICE

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We have carried out photon irradiation study of naphthalene ($C_{10}H_8$), the smallest polycyclic aromatic hydrocarbon (PAH) in water and ammonia ice mixtures. Photons provided by a synchrotron radiation light source in two broad-band energy ranges in the ultraviolet/near extreme ultraviolet (4–20 eV) and the extreme ultraviolet (13–45 eV) ranges were used for the irradiation of H_2O+NH_3+$C_{10}H_8$ = 1:1:1 ice mixtures at 15 K. We could identify several photo-products, namely CH_4, C_2H_6, C_3H_8, CO, CO_2, HNCO, OCN^-, and probably quinoline (C_9H_7N) and phenanthridine ($C_{13}H_9N$). We found that the light hydrocarbons are preferably produced for the ice mixture subjected to 4–20 eV photons. However, the production yields of CO, CO_2, and OCN^- species seem to be higher for the mixture subjected to EUV photons (13–45 eV). Therefore, naphthalene and its photo-products appear to be more efficiently destroyed when high energy photons ($E > 20$ eV) are used. This has important consequences on the photochemical evolution of PAHs in astrophysical environments.

1. Introduction

In the early twentieth century, a series of diffuse interstellar bands (DIBs) were recorded on photographic plates. More than 100 of such bands are observed nowadays in the ultraviolet (UV), visible and near infrared (IR) regions of the electromagnetic spectrum[1−4]. The identification of

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the carriers responsible for these DIBs has become one of the most active challenges in astrophysical spectroscopy.[5,6] Polycyclic aromatic hydrocarbons (PAHs) are now thought to be the best candidates to account for the DIBs in the interstellar medium (ISM), or most likely their cations.[7,8] It has been suggested that PAHs could represent ∼17% of the cosmic carbon, and consequently be the most abundant free organic molecules in the Universe [7 and references therein].

PAHs constitute a group of very stable organic molecules made up from carbon and hydrogen only, assembled into aromatic cycles of 6 sp^2-carbon atoms like benzene (C_6H_6) bound together. Such cycles are flat, so that PAHs are in most cases also flat, like graphite layers. It is believed that these molecules are formed in the outflows of dying carbon-rich stars from which they are ejected into the ISM[7].

The presence of PAHs in the ISM has been confirmed by the astronomical observations of their C–H stretching and out-of-plane bending modes, both in emission[9−11] and in absorption[12−15] in embedded protostars. PAHs may condense onto refractory dust grains with other volatile species (ices), among which H_2O is the most abundant, and are abundant and ubiquitous in many different astrophysical environments.[7,16,17] Bernstein *et al.*[18,19] and Sandford *et al.*[20] have been investigating the ultraviolet (UV) processing of PAHs in H_2O ices, emphasizing the possible connections between interstellar and meteoritic PAHs, and have shown that PAHs undergo both oxidation and reduction photo-reactions in ices, resulting in the production of aromatic hydrocarbon species similar to some of those identified in carbonaceous chondrites and interplanetary dust particles (IDPs).

In this paper, we report results obtained from an experimental study of photon irradiations of naphthalene ($C_{10}H_8$), the smallest PAH (only two aromatic cycles), in H_2O+NH_3 ice mixtures at low temperature. Photons in the 4–20 and 13–45 eV ranges, i.e., from the ultraviolet to the extreme ultraviolet (EUV) ranges, were used to irradiate H_2O+NH_3+$C_{10}H_8$ = 1:1:1 ice mixtures at 15 K in two separate experiments. EUV photons can excite molecules beyond their ionization continua and produce various neutral and ionic fragments. It has been shown that certain molecular species can be synthesized after irradiation with EUV photons, but not necessarily after vacuum ultraviolet (VUV) irradiation[21] and vice versa. Finally, the use of two different energy ranges allows us to study the dependence of the production yields of several photo-products with the photon energy.

2. Experimental Protocol

The experimental apparatus and techniques have previously been described elsewhere.[21] In the present work, the UV/EUV irradiations of the icy samples containing naphthalene were performed in a stainless steel vacuum chamber ($P < 5 \times 10^{-10}$ torr). The reagents used in this work and their purities are as follows: H_2O (liquid, triply distilled), NH_3 (gas, Sigma-Aldrich, 99.5% purity), and $C_{10}H_8$ (powder, Sigma-Aldrich, 99% purity). The $H_2O+C_{10}H_8+NH_3$ samples were vapor-deposited onto a KBr substrate at 15 K, by injecting a gas mixture of H_2O+NH_3 and the $C_{10}H_8$ vapor simultaneously through two separated stainless steel thin tubes (2-mm inner diameter). The relative proportions of the final $H_2O+NH_3+C_{10}H_8 =$ 1:1:1 mixtures were controlled from the partial pressures inside the stainless steel bottles where they were mixed. The typical thickness of the ice films was 1–3 μm, measured by monitoring the variation of interference fringes of a He-Ne laser light reflected by the KBr substrate.

A Fourier-transform infrared spectrometer (FTIR) (Perkin-Elmer FTIR-1600) was used to record infrared (IR) spectra between 4000 and 500 cm^{-1} with a 4 cm^{-1} resolution. The IR and EUV beams form an angle of 90° on the substrate, so that IR spectra could be recorded *in situ* during the whole experiment, i.e., before, during and after irradiation. Once the gas deposition was completed, the vacuum chamber was left idling for a few hours so that all gases could condense on the KBr substrate. The irradiation experiments were performed after the pressure in the chamber reaches $\sim 5 \times 10^{-10}$ torr. The IR spectrum of one of the $H_2O+NH_3+C_{10}H_8 =$ 1:1:1 mixtures before irradiation is shown in Fig. 1.

The broad-band UV/EUV beams were provided by the high-flux beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The incident photon energy used was the 0th order of the white light in the 4–20 and 13–45 eV ranges using 450 and 1600 lines mm^{-1} gratings, respectively.[22] The incident photon flux was constantly monitored by an in-line gold mesh. The irradiations were performed until a total integrated incident photon dose of about 1.5×10^{20} photons was reached for each irradiation experiment. We could therefore identify the compounds photo- produced after irradiation with 4–20 and 13–45 eV photons, and compare the results for both photon energy ranges.
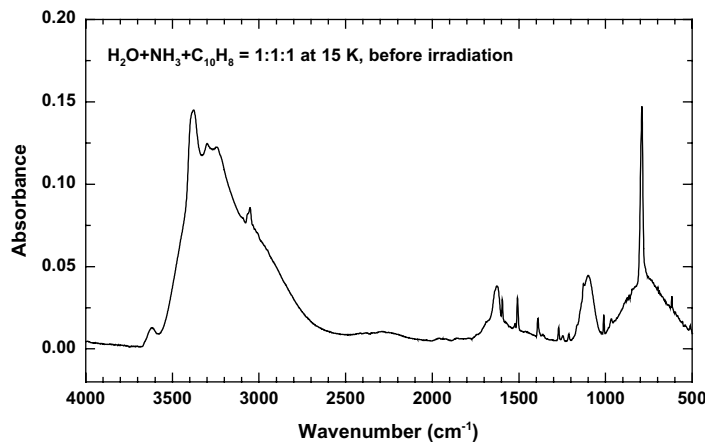
Fig. 1. Infrared absorbance spectrum of one of the $H_2O+NH_3+C_{10}H_8$ = 1:1:1 ice mixtures at 15 K in the 4000–500 cm^{-1} range before irradiation.

3. Results and Discussion

3.1. *Photo-dissociation of naphthalene*

Figure 2 shows the IR spectra (difference of absorbances) of the $H_2O+NH_3+C_{10}H_8$ = 1:1:1 ice mixtures at 15 K irradiated with UV/EUV photons. The measured spectral positions of the absorption features and the identified species are summarized in Table 1. As can be seen from Fig. 2 most of the major features in both spectra look alike although their peak absorbances are different. The signatures of some photo-products however only appear on the spectrum obtained after 4–20 eV irradiation (upper trace), but not on the spectrum obtained after 13–45 eV irradiation (lower trace). These compounds are the aliphatic hydrocarbons ethane (C_2H_6), proprane (C_3H_8), and the aromatic benzyl radical ($C_6H_5CH_2$), the later being only tentatively identified. It is likely that these compounds are easily destroyed by high energy ($E > 20$ eV) photons or that they readily react with other chemical species. Two other compounds (CH_2N and C_2O), whose features are marked with an asterisk, were only tentatively identified. In the following, we will discuss the possible photo-induced chemical reaction mechanisms of these compounds, and their link with the irradiation photon energy.

The photo-products formed after irradiation with 4–20 eV photons include CH_3OH (1030 cm^{-1}), CH_4 (1305 cm^{-1}), C_2H_6 (2873 and 2931 cm^{-1}), C_3H_8 (2959 cm^{-1}), CO (2134 cm^{-1}), CO_2 (2338 cm^{-1}), HNCO (2255 cm^{-1}), OCN$^-$ (2159 cm^{-1}) and NH_4^+ (1453 cm^{-1}). Three other
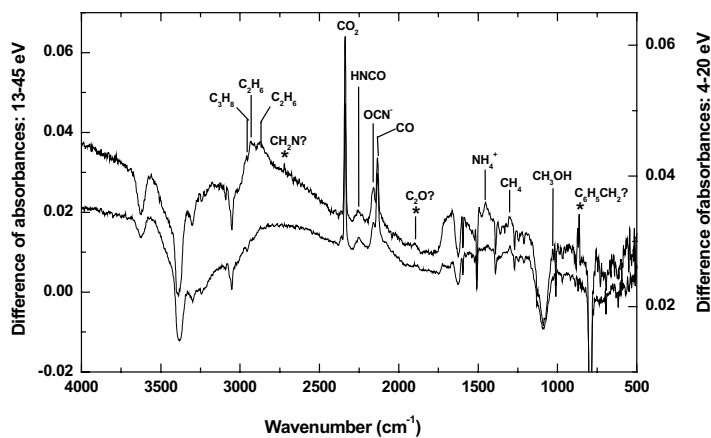
Fig. 2.   IR spectra (difference of absorbances) of the $H_2O+C_{10}H_8+NH_3 = 1{:}1{:}1$ ice mixtures at 15 K after irradiation with 4–20 eV (upper trace) and 13–45 eV (lower trace) photons. The features marked with* correspond to the tentatively identified compounds listed in Table 1.

Table 1.   Photo-products identified in the IR spectra of the $H_2O+C_{10}H_8+NH_3 = 1{:}1{:}1$ ice mixtures at 15 K after UV/EUV irradiation. The species marked with * were tentatively identified. The abbreviation n.d. stands for "not detected".

Species	Peak position (cm^{-1})	
	after 4–20 eV irradiation	after 13–45 eV irradiation
C_3H_8	2959	n.d.
C_3H_8	2931	n.d.
C_2H_6	2873	n.d.
CH_2N*	2722	n.d.
CO_2	2338	2338
HNCO	2255	2253
OCN^-	2159	2160
CO	2134	2135
C_2O*	1898	1902
NH_4^+	1453	1450
CH_4	1300	1299
CH_3OH	1030	1030
$C_6H_5CH_2*$	863	n.d.

absorption features, marked with an asterisk in Fig. 2, were only tentatively identified. They could be assigned to CH_2N (methylene amidogen) (2722 cm^{-1}), C_2O (1898 cm^{-1}) and the benzyl radical $C_6H_5CH_2$ (863 cm^{-1}).[23,24] They are also listed in Table 1.

In the $H_2O+NH_3+C_{10}H_8$ ice samples, naphthalene is the only molecule containing carbon atoms. Thus, all photo-products containing carbon can only be formed from the UV/EUV photolysis of $C_{10}H_8$. This means that the aromatic cycles have to be dissociated into smaller fragments to produce aliphatic hydrocarbon chains (containing only C and H atoms). It is known that breaking aromatic cycles of PAHs is not an efficient process when using photons in the 5–10 eV range. Indeed, using a microwave discharge H_2 flow lamp as the light source, Bernstein *et al.*[18] showed that only substitution reactions of H atoms and/or addition of heteroatoms are efficient process in the 5–10 eV energy range.

As listed in Table 1, CH_4 has been produced after the photon irradiation of the $H_2O+NH_3+C_{10}H_8$ ice mixtures with both energy ranges. However, C_2H_6 and C_3H_8 were only identified in the IR spectrum of the mixture subjected to 4–20 eV photons. Separate experiments, where pure $C_{10}H_8$ and a $H_2O+C_{10}H_8$ mixture were irradiated with 4–20 eV photons at low temperature, were carried out in our laboratory. In the obtained IR spectra, we identified the features of CH_4, C_2H_6 and C_3H_8, indicating that alkanes C_nH_{2n+2} ($n \geq 1$) can be directly produced from the photolysis of naphthalene and/or via secondary chemical reactions involving radicals such as CH_3 and C_2H_5. For instance, C_2H_6 could be a secondary product of the photo-dissociation of CH_4:

$$CH_4 + h\nu \rightarrow CH_3\bullet + H\bullet$$

$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$
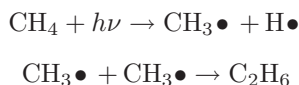
where the species followed by dots are radicals.

If the CH_3 radical is efficiently produced, then it may also react with the HO radical (produced from the photo-dissociation of H_2O) to form methanol (CH_3OH). Pure methanol ice displays two strong absorption features at 1030 and 1128 cm^{-1}.[25] Unfortunately, in our IR spectra the feature around 1128 cm^{-1} overlaps with one of the depletion features of naphthalene (see Fig. 2), and thus it can not be observed. However, a discernible feature around 1030 cm^{-1} can be assigned to methanol, and indirectly support the photochemical pathway leading to the production of CH_3 radicals and therefore aliphatic molecules such as C_2H_6 and C_3H_8.

Furthermore, the feature at 863 cm^{-1}, probably due to the benzyl radical $(C_6H_5CH_2)$[24], can clearly be identified in the IR spectrum of the 4–20 eV irradiated sample (upper trace of Fig. 2) but not in the spectrum of the 13–45 eV irradiated sample (lower trace of Fig. 2). This result

indicates that naphthalene is progressively photo-dissociated into fragments becoming smaller and smaller as the photon energy increases from the UV to the EUV ranges. In other words, high energy ($E > 20\,\text{eV}$) photons appear to dissociate naphthalene with a higher efficiency than less energetic UV photons. Therefore, we can conclude that although both 4–20 and 13–45 eV photons can dissociate naphthalene, only 13–45 eV photons can totally break the aromatic structure of the naphthalene molecule.

In addition to the production of small aliphatic hydrocarbons, we have also identified the IR features of O- and N-containing compounds, namely CO (2134 and 2135 cm^{-1} in the 4–20 and 13–45 eV experiments, respectively), CO_2 (2338 cm^{-1}), OCN$^-$ (2159 and 2160 cm^{-1}) and HNCO (2255 and 2253 cm^{-1}). These molecules are probably formed by recombination of small aliphatic compounds (or their radicals) with HO and NH$_2$, produced from the photo-dissociation of water and ammonia, respectively. The possible mechanisms of formation of such compounds will be discussed in Sec. 3.2.

Finally, some weak absorption features in the 1600–1300 and the 820–720 cm^{-1} ranges can be assigned to nitrogen-bearing PAHs (see Fig. 3 and Table 2), called polycyclic aromatic nitrogen heterocycles (PANHs).
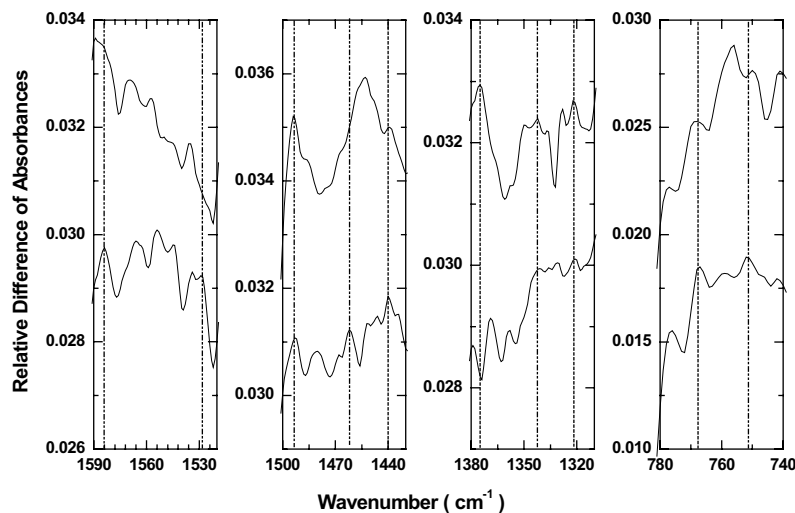

Fig. 3.   IR spectra (difference of absorbances) of the $H_2O+C_{10}H_8+NH_3$ = 1:1:1 ice mixtures at 15 K after irradiation with 4–20 (upper trace) and 13–45 eV (lower trace) photons in 4 chosen small wavenumber ranges. The dashed lines correspond to the weak absorption features of quinoline and phenanthridine (see Table 2).

Table 2. Weak absorption features have tentatively been assigned to quinoline (C_9H_7N) and phenanthridine ($C_{13}H_9N$) in the 1600–1300 and 820–720 cm^{-1} ranges[26] observed for the $H_2O+C_{10}H_8+NH_3 = 1:1:1$ ice mixtures at 15 K after UV/EUV irradiation (see Fig. 3).

Species	Peak position (cm^{-1})	
	after 4–20 eV irradiation	after 13–45 eV irradiation
C_9H_7N	1439	1440
	1375	n.d.
	1322	1321
	767	767
$C_{13}H_9N$	n.d.	1584
	n.d.	1529
	1494	1493
	n.d.	1462
	1342	1341
	756	752

The positions of these features appear to be in good agreement with the absorption features of quinoline (C_9H_7N) and phenanthridine ($C_{13}H_9N$) in water ice at 15 K.[26] Quinoline is a molecule of naphthalene where one of the carbon atoms has been substituted by a nitrogen atom. We plan to carry out further investigations using a higher resolution FTIR spectrometer ($0.1\,cm^{-1}$) and a brighter photon source in order to better resolve the observed features.

These important results indicate that naphthalene and possibly other PAHs can be photo-dissociated in cold astrophysical environments by EUV photons and contribute to the reservoir of carbon whose photochemical evolution can lead to the production of complex organic molecules in the ISM.

3.2. *Production yields of CO, CO_2 and OCN^-*

We have determined the production yields of CO, CO_2 and OCN^-, photo-produced during the irradiation of the $H_2O+NH_3+C_{10}H_8 = 1:1:1$ ice mixtures at 15 K with 4–20 and 13–45 eV photons, using data analysis procedures which have been previously described elsewhere.[21] The column densities of CO, CO_2 and OCN^- are plotted as a function of the photon dose in Figs. 4, 5 and 6, respectively. Absorption strengths of $A(CO,\ 2134\,cm^{-1}) = 1.1 \times 10^{-17}\,cm\ molec^{-1}$, $A(CO_2,\ 2340\,cm^{-1}) =$
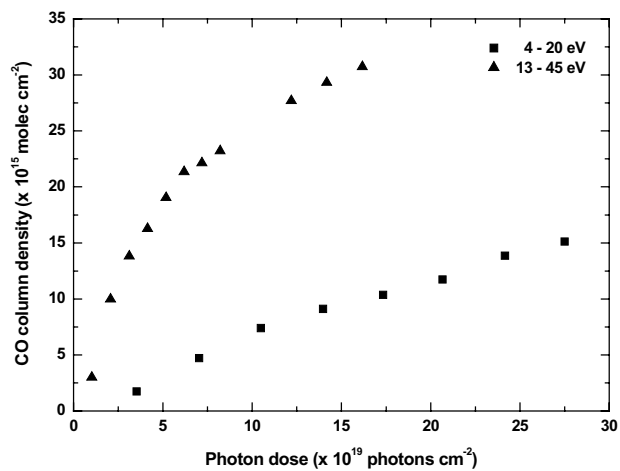
Fig. 4. Plot of the column density of CO as a function of the 4–20 eV (squares) and 13–45 eV (triangles) photon doses.
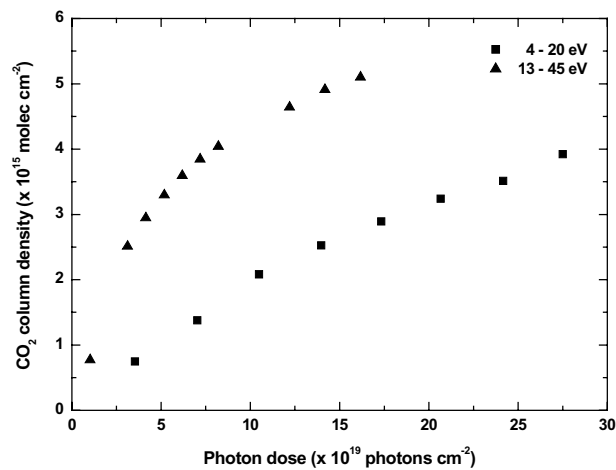

Fig. 5. Plot of the column density of CO_2 as a function of the 4–20 eV (squares) and 13–45 eV (triangles) photon doses.

7.6×10^{-17} cm molec^{-1} and $A(\mathrm{OCN}^-, 2160\,\mathrm{cm}^{-1}) = 4 \times 10^{-17}$ cm molec^{-1}, respectively[27,28], were used for these calculations.

Figures 4–6 show that the column densities for CO, CO_2 and OCN$^-$, photo-produced during the 13–45 eV experiment (triangles) are respectively
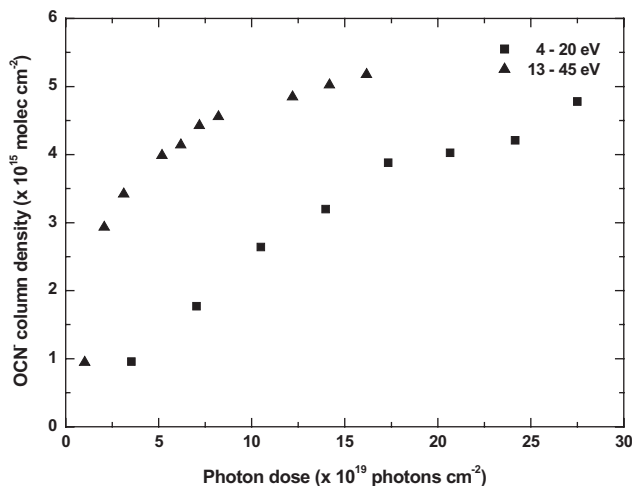
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Fig. 6.   Plot of the column density of OCN$^-$ as a function of the 4–20 eV (squares) and 13–45 eV (triangles) photon doses.

3.6, 2.2 and 1.9 times higher than the corresponding yields for the 4–20 eV experiment (squares) after an integrated photon dose of approximately 1×10^{20} photons cm^{-2}. This result suggests that small C-bearing molecules are produced from the direct photo-dissociation of naphthalene, which is the only carbon- bearing compound in our starting mixtures, and confirm that the photo- dissociation efficiency for such small molecules increases with the photon energy.

Figures 4 and 5 also show that CO is produced with a higher efficiency than CO_2. The column densities for CO are about 3.5 and 5.8 times higher than those for CO_2 in the 4–20 and 13–45 eV experiments, respectively. This can be understood because CO_2 is most likely a secondary photo-product, formed via the photolysis of CO. A possible mechanism of formation of CO_2 from CO would be the photo-excitation of CO and the subsequent reaction with CO[29]:

$$CO + h\nu \rightarrow CO^*(A^1\Pi, a^3\Pi)$$
$$CO^* + CO \rightarrow CO_2 + C\bullet,$$
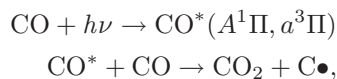
where $A^1\Pi$ and $a^3\Pi$ denote excited states of CO. The carbon atom released in this mechanism does not remain free in the medium, and may react with another CO molecule to produce C_2O. This mechanism is supported by the

presence of two IR features of C_2O at 1898 and $1902\,\text{cm}^{-1}$ in the irradiated samples[23] (see Fig. 2 and Table 1).

CO_2 can also be formed from the reaction between CO and the HO radical, which is produced from photo-dissociation of H_2O[30]:

$$H_2O + h\nu \rightarrow HO\bullet\ + H\bullet$$
$$HO\bullet\ + CO \rightarrow \bullet COOH \rightarrow CO_2 + H\bullet\ .$$

The photolysis of CO to form CO_2 and COOH radicals constitute the first steps for the formation of complex organic molecules. In particular, reactions between the parent molecules and their photo-products including radicals such as H, HO, C_nH_{2n+1} ($n \geq 1$) (alkyl radicals), COOH, NH, NH_2 at low temperature could lead to the production of molecules as complex as amino acids in such experiments, but also in astrophysical environments.

4. Conclusion

We have investigated the effects of the irradiation of $H_2O+NH_3+C_{10}H_8 =$ 1:1:1 ice mixtures with 4–20 eV (UV/near EUV) and 13–45 eV (EUV) photons. In the IR spectra of these samples, we have identified the characteristic features of several photo-products, namely CH_4, C_2H_6, C_3H_8, CO, CO_2, HNCO and OCN^-. Methyl amidogen (CH_2N), C_2O and the benzyl radical ($C_6H_5CH_2$) have also been tentatively identified. Our work also shows that on the one hand small hydrocarbons such as C_2H_6, C_3H_8 and the benzyl radical are significantly produced during the 4–20 eV irradiation experiment, and that on the other hand the production yields of CO, CO_2 and OCN^- are significantly higher in the 13–45 eV irradiation experiment. Therefore, the photo-products and their production yields strongly depend on the photon energy.

The present work shows that EUV photons can efficiently photo-dissociate naphthalene and probably other PAHs at low temperature. This has important implications on the photochemical evolution of PAHs in astrophysical environments, where the carbon reservoir could contribute significantly to the production of complex organic molecules including amino acids, the building blocks of proteins in all living beings on Earth.

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Acknowledgments

References

1. R. W. Russell, B. T. Soifer and S. P. Willner, *Astrophys. J.* **217** (1977) L149.
2. K. Sellgren, M. W. Werner and H. L. Dinerstein, *Astrophys. J.* **271** (1983) L13.
3. J. D. Bregman, H. L. Dinerstein, J. H. Goebel, D. F. Lester, F. C. Witteborn and D. M. Rank, *Astrophys. J.* **274** (1983) 666.
4. J. P. Simpson, J. D. Bregman, M. Cohen, F. Witteborn and D. H. Wooden, *Bull. AAS* **16** 523 (1984).
5. A. Léger, L. d'Hendecourt and D. Défourneau, *Astron. Astrophys.* **293** (1995) L53.
6. F. M. Johnson, *Bulletin of the Am. Astron. Soc.* **33** (2000) 716.
7. J. L. Puget and A. Léger, *Annual Review of Astron. Astrophys.* **27** (1989) 161.
8. G. Mulas, G. Malloci and P. Benvenuti, *Astron. Astrophys.* **410** (2003) 639.
9. L. J. Allamandola, D. M. Hudgins and S. A. Sandford, *Astrophys. J.* **511** (1999) L115.
10. E. Peeters, A. L. Mattioda, D. M. Hudgins and L. J. Allamandola, *Astrophys. J.* **617** (2004) L65.
11. J. M. Cannon and 24 co-authors, *Astrophys. J.* **647** (2006) 293.
12. R. G. Smith, K. Sellgren and A. T. Tokunaga, *Astrophys. J.* **344** (1989) 413.
13. K. Sellgren, T. Y. Brooke, R. G. Smith and T. R. Geballe, *Astrophys. J.* **449** (1995) L69.
14. J. D. Bregman, Th. L. Hayward and G. C. Sloan, *Astrophys. J.* **544** (2000) L75.
15. J. D. Bregman and P. Temi, *Astrophys. J.* **554** (2001) 126.
16. L. J. Allamandola, S. A. Sandford and B. Wopenka, *Science* **237** (1987) 56.
17. S. J. Clemett, C. R. Maechling, R. N. Zare, P. D. Swan and R. M. Walker, *Science* **262** (1993) 721.
18. M. P. Bernstein, S. A. Sandford, L. J. Allamandola, J. S. Gillette, S. J. Clemett and R. N. Zare, *Science* **283** (1999) 1135.
19. M. P. Bernstein, J. P. Dworkin, S. A. Sandford and L. J. Allamandola, *Meteoritics & Planetary Science* **36** (2001) 351.

20. S. A. Sandford, M. P. Bernstein and L. J. Allamandola, *Astrophys. J.* **607** (2004) 346.
21. C.-Y. R. Wu, D. L. Judge, B.-M. Cheng, W.-H. Shih, T.-S. Yih and W.-H. Ip, *Icarus* **156** (2002) 456.
22. T.-F. Hsieh, L.-R. Huang, S.-C. Chung, T.-E. Dann, P.-C. Tseng, C.-T. Chen and K.-L. Tsang, *J. Synchrotron Rad.* **5** (1998) 562.
23. M. Jacox and D. E. Milligan, *J. Chem. Phys.* **43** (1965) 3734.
24. E. G. Baskir, A. K. Maltsev, V. A. Koroler, V. N. Khabasheska and O. M. Nefedov, *Russ. Chem. Bul.* **42** (1993) 1438.
25. D. M. Hudgins, S. A. Sandford, L. J. Allamandola and A. G. G. M. Tielens, *Astrophys. J. Suppl. Ser.* **86** (1993) 713.
26. M. P. Bernstein, A. L. Mattioda, S. A. Sandford and D. M. Hudgins, *Astrophys. J.* **626** (2005) 909.
27. P. A. Gerakines, W. A. Schutte, J. M. Greenberg and E. F. van Dishoeck, *Astron. Astrophys.* **296** (1995) 810.
28. L. B. d'Hendecourt and L. J. Allamandola, *Astron. Astrophys Suppl. Ser.* **64** (1986) 453.
29. H. Okabe, *Photochemistry of small molecules* (Wiley, New York, USA, 1978).
30. N. Watanabe and A. Kouchi, *Astrophys. J.* **571** (2002) L173.