Photon-stimulated processes in model interstellar ices

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Introduction

Balancing the universal carbon budget remains one of the outstanding problems in astrochemistry. The extra stability conferred to carbocycles by aromatisation suggests that polycyclic aromatic hydrocarbons (PAHs) and their heteroatomic analogues (HPAHs) may represent a significant sink for carbon in the interstellar medium (ISM). While there are no definitive identifications of (H)PAHs from observations of the ISM, there is increasing evidence, from studies of infrared absorption and emission in the 2.8 to 3.7 μm region that such species are likely to exist in high abundances [1].

Given their likely existence, small (H)PAHs will inevitably be adsorbed onto silicate grain surfaces and will be incorporated into icy grain mantles as they accumulate. Larger members of the PAH family may indeed even represent the core material in the carbonaceous grain population evidenced by the characteristic 217 nm bump in the interstellar extinction along many lines of sight [2]. Understanding the interaction of water and other ISM ice components with (H)PAHs is therefore an important issue in laboratory astrochemistry, as the (H)PAHs are known to absorb photons across a wide range of the near ultraviolet and visible wavelength region. Such absorption, as the NASA group of Allamandola and co-workers has demonstrated [3], can promote chemistry leading to the formation of complex species of pre-biotic nature.

However elegant these high vacuum (HV) experiments may be, they suffer from the same limitations as all HV studies of ice chemistry, as identified by Collings *et al.* [4]. Ultrahigh vacuum (UHV) experiments probing the photon-stimulated processes in (H)PAH/water ice systems, have, in contrast, the potential to more completely address the issue of where the photon energy goes once deposited in the (H)PAH molecule. By simplifying our choice of absorber by selecting benzene (C_6H_6) and by limiting our initial studies to water (H_2O) ice, we hope to quantify the distribution of energy that leads to both physical (morphological change and desorption) and chemical change. In this contribution, we describe our initial studies of the ultraviolet photon-stimulated desorption of C_6H_6/H_2O ice systems.

Discussion

Ultrathin films of C_6H_6 and H_2O of known thickness were grown on a cryogenically cooled sapphire substrate mounted in the CLF UHV system [5]. The films were irradiated with the frequency-doubled output of a nanosecond Nd^{3+}-YAG pumped dye laser. Irradiation wavelengths were chosen by consideration of the low temperature UV absorption spectra of C_6H_6 and H_2O, Figure 1, to represent on- and off-resonance situations, 248.8 and 275 nm respectively. Typically the laser peak power density employed was of the order of 1 to 10 MW cm^{-2}. Species desorbing from the films were detected by electron-impact quadrupole mass spectrometry (EI QMS) using appropriate pulse counting electronics to permit recovery of the desorbate time-of-flight.
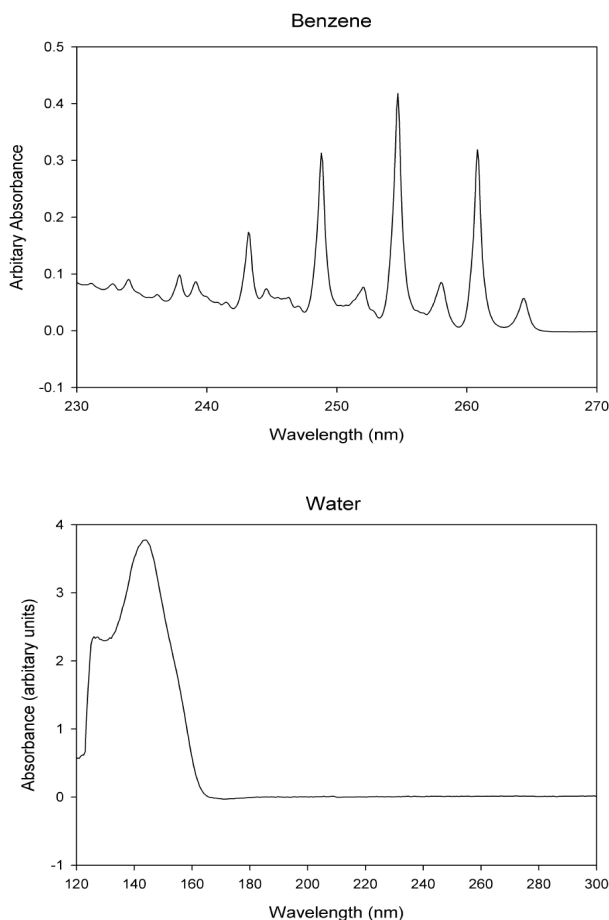

Figure 1. UV absorption spectra of thin solids films of benzene (C_6H_6) and water (H_2O) of about 100 nm thickness at around 100 K.

A typical time-of-flight spectrum for C_6H_6 desorbing from an ultrathin C_6H_6 film on our sapphire substrate, following on-resonance excitation, is shown in Figure 2. Analysis of the smoothed profile (solid red line) employing a suitable density weighted Maxwell distribution (solid green line) yields an effective gas temperature of around 2100 K. The thermal desorption of C_6H_6 from our substrate normally occurs around 130 K. Thus, the photon-stimulated desorbate is clearly non-thermal. However, carrying only around 17.5 kJ mol^{-1} of kinetic energy (cf. a photon energy equivalent to 480.9 kJ mol^{-1}), it is evident that much energy loss occurs into the adsorbed C_6H_6 layer prior to ejection of the desorbate. Further analysis of these time-of-flight data is on-going, with the aim of determining whether multiple Maxwell components are present in the empirical distribution.
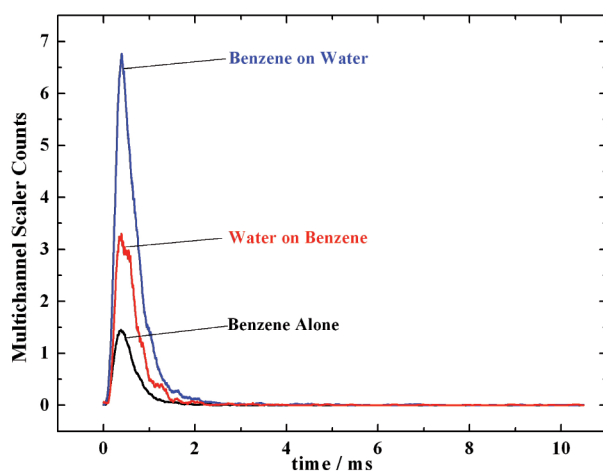

Figure 2. Time-of-flight data for benzene (C_6H_6) desorbing from a sapphire surface at around 100 K, following excitation at 248.8 nm. Raw data are in black. The solid red line represents a 54 point moving average smooth, and the solid green line is the fit to a density weighted Maxwell speed distribution for a gas temperature of 2100 K.

Investigation of the variation of the time-of-flight data with the nature of the excited adsorbate layer (C_6H_6 alone, C_6H_6 overlayers on H_2O and H_2O overlayers on C_6H_6) reveals a surprising increase in the desorption yield of C_6H_6 in the presence of H_2O layers following on-resonance excitation, as shown in Figure 3. Clearly, a greater propensity for C_6H_6 desorption in systems in which C_6H_6 overlays a H_2O layer may point to a less efficient coupling of energy out of the C_6H_6 layer and into the underlying sapphire substrate. However, this does not explain the inverse situation in which H_2O overlays C_6H_6. Perhaps, here, the growth mechanism of such films should be considered. It is likely that C_6H_6 grows on the sapphire substrate in the Stranski-Krastinov manner, i.e. island formation on top of layer-by-layer growth. Growth by island formation will result in a C_6H_6 film with a larger surface area than the obviously geometric. A H_2O overlayer on such a film will effectively be thinner, and C_6H_6 molecules at the C_6H_6/H_2O interface may experience interactions more akin to those of C_6H_6 molecules overlaying a H_2O layer. Consequently desorption occurs more readily. Such an assumption, however, demands a detailed off-line investigation of the growth of C_6H_6 films on sapphire using, for example, X-ray photoelectron spectroscopy.
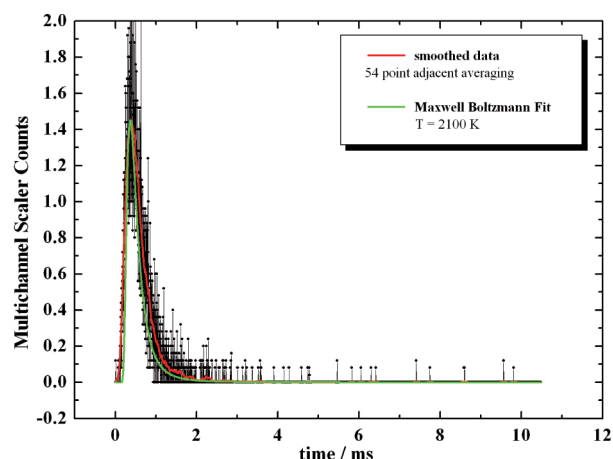

Figure 3. Comparison of the benzene (C_6H_6) time-of-flight spectra following desorption from benzene layers on a sapphire substrate in the absence of water and in the presence of under- and over-layers with of solid water (H_2O) at around 100 K.

Interestingly in all of our measurements recorded to date, photon-stimulated desorption of water as a consequence of excitation of adsorbed C_6H_6 is limited. Desorption of the C_6H_6 dominates. Further experiments are currently underway to investigate these observations.

Conclusions

These preliminary measurements have highlighted some fascinating physics in this simple model of interstellar ice. The enhancement of C_6H_6 desorption in the presence of adsorbed layers of water is surprising and may point to an additional mechanism of loss of complex organic species from icy grain mantles, limiting the potential for photon-driven prebiotic chemistry in such mantles. However, we must fully quantify the yield of such processes as a function of optical wavelength (i.e. address the issue of resonance in this mechanism) in order to understand this mechanism fully. In addition, the presence of hot photoproducts in the gas phase will inevitably induce local heating of the surrounding gas in the ISM. The effect of this local heating on the chemistry of the gas may be significant.

Acknowledgements

References

1. See for example: (a) L. J. Allamandola, A. G. G. M. Tielens, and J. R Barker, *Astrophys. J. Suppl. Ser.,* 1989, **71**, 733; (b) S. A. Sandford, L. J. Allamandola, A. G. G. M. Tielens, K. Sellgren, M. Tapia, and Y. Pendleton, Y. *Astrophys. J.* 1991, **371**, 607; (c) Y. J. Pendleton, S. A. Sandford, L. J. Allamandola, A. G. G. M. Tielens, and K. Sellgren, *Astrophys. J.* 1994, **437**,

683-696; (d) D. M. Hudgins, and L. J. Allamandola, *Astrophys. J.,* 1999, **513**, L69; (e) G. Mulas, G. Malloci, and P. Benvenuti, *Astron. Astrophys.,* 2003, **410**, 639; (f) M. P. Bernstein, S. A. Sandford, and L. J. Allamandola, *Astrophys. J. Suppl. Ser.,* 2005, **161**, 53

2. (a) W. W. Duley and S. Seahra, *Astrophys. J.,* 1998, **507**, 874; (b) S. Tomita, M. Fujii and S. Hayashi, *Astrophys. J.,* 2004, **609**, 220

3. See for example (a) M. P. Bernstein, J. P. Dworkin, S. A. Sandford and L. J. Allamandola, *Adv. Space. Res.,* 2002, **30**, 1501-1508; (b) M. P. Bernstein, J. E. Elsila, J. P. Dworkin, S. A. Sandford, L. J. Allamandola and R. N. Zare, *Astrophys. J.,* 2002, **576**, 1115-1120

4. M. P. Collings, H. J. Fraser, J. W. Dever and M. R. S. McCoustra, *Proc. NASA Lab. Astrophys. Workshop, Ames Laboratory, California, USA,* 2002, (NASA/CP-2002-21186, Moffet Field, CA., USA, 2002) pp192-197

5. F. Jamme, M. R. S. McCoustra, M. A. Chesters, I. P. Clark and A. W. Parker, *Central Laser Facility Annual Report 2004-2005,* (CCLRC, Didcot, 2005) pp239-240