

Photon-induced processes in model interstellar ices

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Introduction

Emission features attributable to polycyclic aromatic hydrocarbons (PAHs) have been detected toward a wide variety of astronomical objects. They are considered to be ubiquitous throughout the interstellar medium (ISM), and provide an important sink for elemental carbon^[1]. In regions of the ISM such as dense molecular clouds and planetary nebulae where the temperature is low enough for volatile species to condense into icy mantles on dust grains, it is expected that PAHs will be mixed in such ices.

Photodesorption is a significant process in various astrophysical environments, and is often included in astrochemical models to account for higher than expected gas phase abundances^[2]. However, there are only a few examples where photodesorption has been experimentally studied in an astrophysical context^[3]. These have generally focussed on measurements of photodesorption rates, without examining the energetics of the process. Here, we study photodesorption from astrophysically relevant ice films, using benzene as a 'model' PAH.

Discussion

Ultra-thin films of benzene (2 nm) and water (16 nm) were deposited onto a sapphire crystal held at approximately 80 K in an ultrahigh vacuum chamber. These films were irradiated with the frequency doubled output of a nanosecond pulsed Nd³⁺-YAG pumped dye laser, operated with a pulse frequency of 10 Hz and pulse energies of either 1.8 mJ or 1.1 mJ, focussed onto a spot of 0.5 mm². An 'on-resonance' wavelength of 250.0 nm was chosen to excite a vibronic component of the B_{2u} ← A_{1g} transition of the $\pi(1e_{1g}) \rightarrow \pi^*(1e_{2u})$ transition of pure benzene ice. Absorption by benzene is also significant at the 'near-resonance' wavelength of 248.8 nm, which corresponds to a local minimum in the absorption cross section, but is negligible at the 'off-resonance' wavelength of 275 nm. Absorption by water is negligible over this entire wavelength range, although sapphire shows significant absorption at each wavelength. Desorbed molecules were detected by a pulse counting quadrupole mass spectrometer, and the time-of-flight (ToF) profile was measured by a multichannel scaler triggered by each laser pulse. The ToF profiles were averaged over 15-30 spots, and then fitted with a density weighted Maxwell-Boltzmann (M-B) function^[4] to determine the translational temperature, T_t.

Figure 1 displays on-resonance (250.0 nm) ToF profiles for benzene and water desorption as a function of the layer configuration. A small desorption peak is evident following irradiation of water adsorbed alone on the sapphire (S/W). This desorption peak is attributed to a substrate-mediated mechanism, in which the sapphire is heated by the laser pulse. The desorption peak observed following irradiation of a layer of benzene alone (S/B) is much larger, and demonstrates that benzene is photodesorbed by a direct adsorbate-mediated mechanism. When a layer of water is deposited over the benzene layer (S/B/W), the rate of benzene photodesorption is substantially decreased. The water overlayer acts as a barrier, limiting the escape of excited benzene molecules. The S/B/W system shows a slight enhancement in the rate of

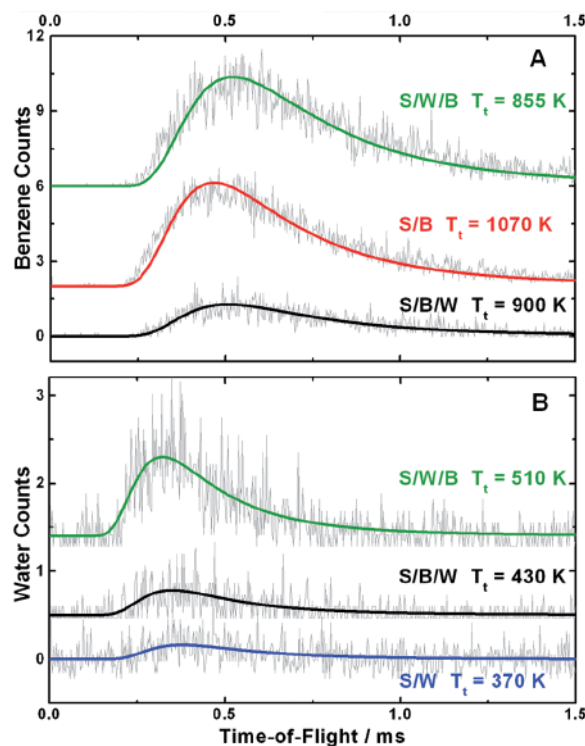


Figure 1. ToF profiles for (A) benzene and (B) water desorption from varying layer configurations, laser pulse energy = 1.8 mJ, $\lambda = 250$ nm. Thin grey lines: raw data. Thick lines: single component M-B fits. Profiles have been offset for clarity.

photodesorption of water compared to the S/W system. Therefore, energy absorbed by benzene molecules must be transferred to neighbouring water molecules, leading to an indirect adsorbate-mediated desorption process. This transfer occurs at the interface between the benzene and water layers. Therefore, excited water molecules must escape through the thick water layer. The enhancement in water photodesorption is greater when benzene is adsorbed over a pre-deposited water layer (S/W/B), since the benzene layer is thinner and provides less of a barrier to excited water molecules escaping from the water-benzene interface.

The ToF profiles in figure 1 have been fitted with a single component M-B distribution. However, it is apparent that such a fit is not perfect, particularly at the leading edges of the benzene profiles. Figure 2 displays ToF profiles for benzene and water as a function of laser wavelength. Benzene desorption from the S/B system is evident following off-resonance (275.0 nm) irradiation where absorption by benzene is negligible. This confirms the presence of a substrate-mediated desorption mechanism. A single component M-B fit gives a T_t of 530 K for the desorbed benzene molecules. As expected, there is a slight enhancement of the benzene desorption rate for near-resonance (248.8 nm) irradiation, and a large enhancement for on-resonance (250.0 nm) irradiation. Since the absorption by sapphire is relatively constant over the 248–275 nm range, the substrate-mediated mechanism is expected to be similarly active at each wavelength.

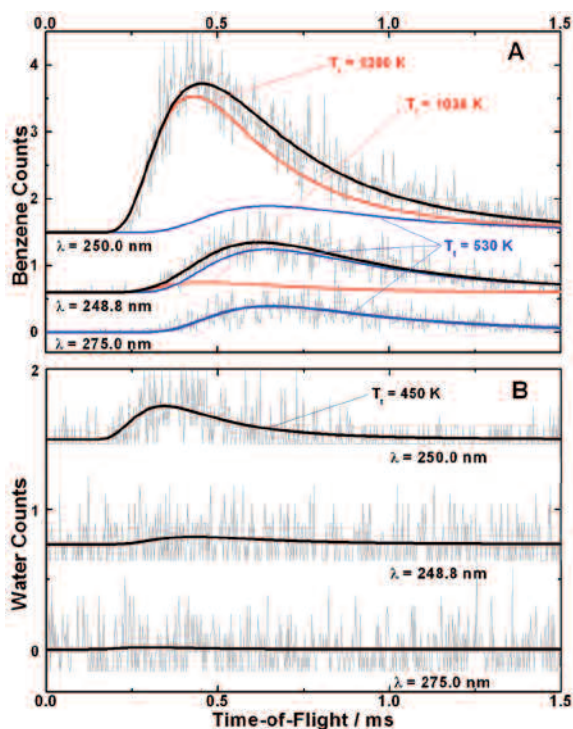


Figure 2. (A) ToF profiles of benzene desorption from the S/B system at varying photon wavelength; laser pulse energy = 1.1 mJ; thin grey lines: raw data; thick lines: M-B fits, one component fixed at $T_t = 530$ K (blue), one free component (red) and the sum of the two components (black). (B) ToF profiles of water desorption from the S/W/B system at varying photon wavelength; laser pulse energy = 1.1 mJ; thin grey lines: raw data; thick lines: single component M-B fits. Profiles have been offset for clarity.

Therefore, we applied a two-component M-B fit to the near and on-resonance profiles, in which the T_t of one component was fixed at 530 K, but the T_t of the second component and the size of both were free variables. This provides an improved fit to the experimental data. The T_t of the free component, attributed to the direct adsorbate-mediated desorption, was above 1000 K for the near and on-resonance experiments. At the lower laser power employed for these experiments, the desorption of water was barely detectable in the near and off-resonance experiments. However, in the on-resonance experiment, a single component M-B fit gives a T_t of 450 K.

Conclusions

These experiments have identified three distinct photodesorption mechanisms for layered benzene and water ices – the direct adsorbate-mediated desorption of benzene, the indirect adsorbate-mediated desorption of water, and the substrate-mediated desorption of benzene and water. A two component M-B fit was applied to all of the benzene desorption profiles, giving a T_t of 1200 ± 200 K and 530 ± 100 K for the direct adsorbate-mediated photodesorption and the substrate-mediated photodesorption of benzene respectively. The T_t of the indirect adsorbate-mediated and substrate-mediated desorptions of water could not be separated, and were found to be 450 ± 100 K. These values of T_t are much higher than the thermal desorption temperatures of benzene and water (130 K and 160 K respectively), and very much higher than the temperature of icy mantles in the ISM (10 K). The injection of excited molecules into the gas phase via any of these photodesorption mechanisms may have significant impact on gas phase chemistry, since these molecules may have sufficient energy to overcome otherwise insurmountable reaction barriers. The astrophysical implications are discussed elsewhere^[5].

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References

- For example: D. M. Hudgins, and L. J. Allamandola, in *IAU symposium* **231**, Ed. D. C. Lis, G. A. Blake, and E. Herbst (Cambridge, CUP), 433 (2005).
- For example: C. Dominik, C. Ceccarelli, D. Hollenbach, and M. Kaufman, *Astrophys. J.* **635**, L85 (2005).
- (a) M. S. Westley, R. A. Baragiola, R. E. Johnson, and G. A. Baratta, *Nature* **373**, 405 (1995), (b) K. I. Öberg, G. W. Fuchs, Z. Awad, H. J. Fraser, S. Schlemmer, E. F. van Dishoeck, and H. Linnartz, *Astrophys. J.* **662**, L23 (2007).
- F. M. Zimmerman, and W. Ho, *Surf. Sci. Rep.* **22**, 127 (1994).
- J. D. Thrower, D. J. Burke, M. P. Collings, A. Dawes, P. J. Holtom, F. Jamme, P. Kendall, W. A. Brown, I. P. Clark, H. J. Fraser, M. R. S. McCoustra, N. J. Mason, A. W. Parker, *submitted to Astrophys. J.*, astro-ph: 0705.2367.