Laboratory evidence for the formation of hydrogenated fullerene molecules

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Abstract. Experimental evidence for the formation of hydrogenated fullerene molecules is presented. Films of C_{60} were grown on a highly oriented pyrolytic graphite (substrate) and exposed to a beam of deuterium atoms. Thermal desorption combined with mass spectrometry was used to determine the deuterated fullerene products formed, revealing a maximum degree of deuteration corresponding to $C_{60}D_{36}$. Release of D_2 from the deuterated C_{60} film occurs at a much higher temperature than for D-saturated graphite.

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1. Introduction

Large carbon containing molecules such as PAHs and fullerenes account for a significant fraction of the carbon present in the interstellar medium (ISM). PAHs are widely detected among many lines of sight through their characteristic stretching and bending vibrational signatures in the infrared (IR) and are thought to account for around 10% of the carbon budget (Tielens 2013). Through their IR emission, C_{60} and C_{60}^+ have been been observed to be present in a variety of environments including planetary nebulae (Cami *et al.* 2010) and reflection nebulae (Sellgren *et al.* 2010; Berné, *et al.* 2013) as well as the diffuse ISM (Berné *et al.* 2017). In addition, two of the diffuse interstellar bands (DIBS) at 9577 and 9632 Å were tentatively attributed to electronic transitions of C_{60}^+ (Foing & Ehrenfreund 1994) - an assignment confirmed more recently through gas phase spectroscopic measurements (Campbell *et al.* 2015).

On the basis of infrared observations showing an increase in C_{60} abundance with increasing UV field strength, along with a decrease in PAH abundance, Berné *et al.* 2012 suggested a top down route to fullerenes through the UV induced dehydrogenation and folding of PAH molecules. Subsequent modelling (Berné *et al.* 2015) indicated the potential viability of such a route, with laboratory measurements confirming that laser irradiation of large PAHs can lead to fullerene formation (Zhen *et al.* 2014). The reverse process, *i.e.* the reformation of PAHs through the hydrogenation of fullerene species, may provide a further link between these two important classes of carbon bearing species.

The interaction between such carbon bearing molecules and the most abundant element, H, is of particular important in interstellar chemistry. The spatial correlation between H_2 formation rate and PAH emission in PDRs (Habart *et al.* 2003) lead to the

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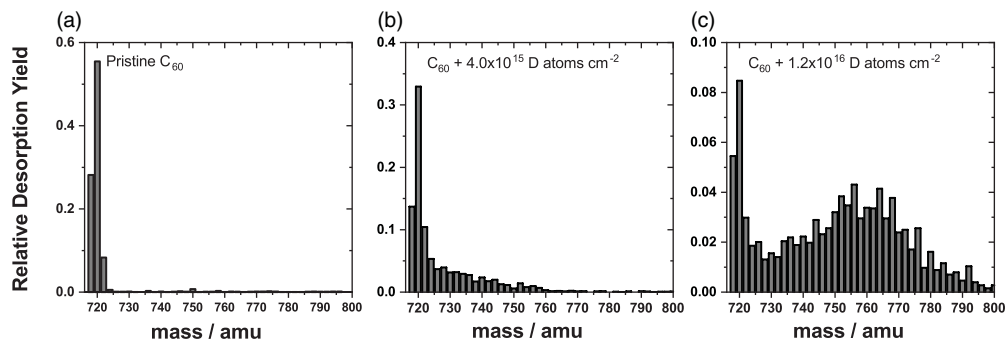
Figure 1. Mass spectra of desorption products for (a) Pristine C_{60} adsorbed on HOPG and (b-c) C_{60} on HOPG increased to increasing D-atom fluences.

suggestion that the hydrogenation of PAHs might lead lead to H_2 formation (Habart *et al.* 2004). A variety of experimental and theoretical studies have demonstrated the catalytic formation of H_2 through the hydrogenation of both neutral (Rauls & Hornekær 2008; Mennella *et al.* 2012; Thrower *et al.* 2012; Jensen *et al.* 2019) and cationic (Boschmann *et al.* 2012; Cazaux *et al.* 2016) PAHs *via* superhydrogenated PAH (HPAH) intermediates.

Here, we consider the interaction between C_{60} and atomic hydrogen, demonstrating experimentally that deuterated fullerenes, $C_{60}D_x$, can be formed through exposure of C_{60} adsorbed on graphite and to a gas phase beam of D-atoms. The formation of such species rapidly leads to a stabilization of the entire fullerene layer, as observed through a dramatic increase in the temperature required to thermally desorb the adsorbed molecules. In addition, D_2 evolution from deuterated C_{60} occurs at a significantly higher temperature than from graphite.

2. Experimental methods

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of *ca.* 5×10^{-10} mbar. The highly oriented pyrolytic graphite (HOPG) substrate was cleaved with adhesive tape immediately prior to transfer into UHV where it was annealed to > 1000 K between measurements to removed adsorbed contaminants. C_{60} (Sigma-Aldrich) was deposited onto the HOPG substrate using a home-built thermal evaporator operated at $360°$C. Exposure to atomic deuterium was performed using a hot capillary thermal cracking source (MBE Komponenten; (Tschersich 2000)). Thermal desorption measurements were performed by heating the HOPG substrate with a linear ramp of 1 Ks^{-1} in front of a pulse counting quadrupole mass spectrometer (QMS; Hiden EPIC 1000 series - 500 amu). C_{60} and $C_{60}D_x$ species were detected through their doubly charged ions formed in the ionization region of the mass spectrometer. The use of atomic deuterium to demonstrate the hydrogenation process ensured that the products appeared at integer values of mass-to-charge ratio. Desorption product mass spectra were obtained by integrating the desorption signal for each mass over the entire temperature range.

3. Results and Discussion

Figure 1 (a) shows the mass spectra obtained for *ca.* 1 monolayer (ML) of C_{60} deposited on HOPG and then thermally desorbed without exposure to D-atoms. As expected, the mass distribution is dominated by a peak at 720 amu corresponding to C_{60}. Small contributions to higher mass can be attributed to the natural abundance of ^{13}C while that at 718 amu is due to some degree of overlap between the mass channels resulting from a reduced resolution at high mass. Panels (b-c) in Figure 1 show the evolution of
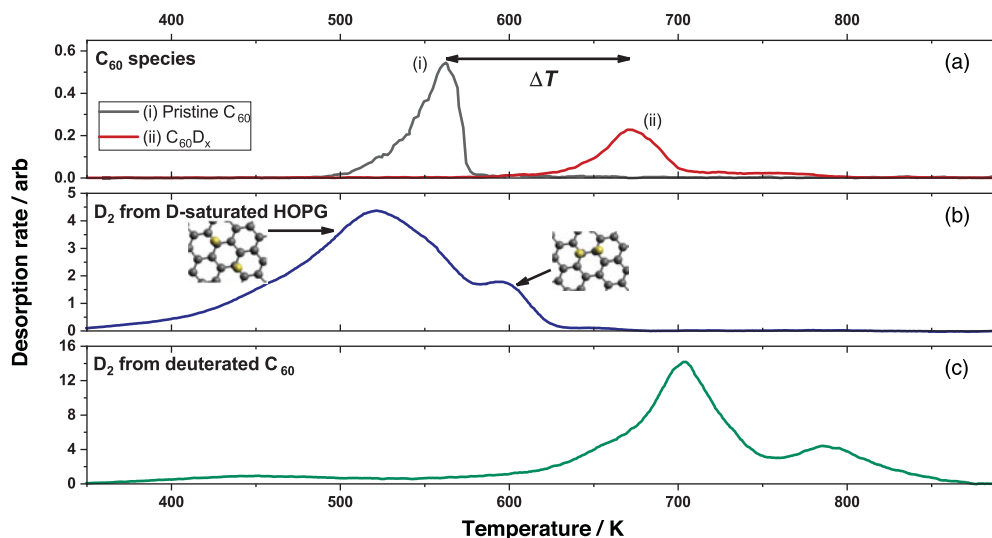
Figure 2. (a) (i) Thermal desorption of *ca.* 1 ML of pristine C_{60} from HOPG, (ii) summed desorption signal of all $C_{60}D_x$ species with $0 \leqslant x \leqslant 36$ for *ca.* 1 ML C_{60} on HOPG exposed to a D-atom fluence of 7.2×10^{17} cm^{-2}, (b) Thermal desorption of D_2 from D-saturated HOPG showing characteristic desorption peaks corresponding to para and ortho dimers as highlighted, (c) Thermal desorption of D_2 from corresponding to (i) in (a).

the product mass distribution for C_{60} adsorbed on HOPG and subsequently exposed to increasing D-atom fluences. As the exposure to D-atoms increases, the mass distribution shifts to higher mass indicating the formation of $C_{60}D_x$ species. The distribution shown in panel (c) represents the limiting case for high D-atom exposure, *i.e.* longer D-exposure times do not shift the distribution to higher mass. The mass distribution appears to peak at around 756 amu with the mass distribution extending to around 792 amu. These two masses correspond to the species $C_{60}D_{18}$ and $C_{60}D_{36}$ and are consistent the previously observed stable species $C_{60}H_{18}$ and $C_{60}H_{36}$ (Palit *et al.* 1998). The dominance of the lower mass species might result from the C_{60} being surface bound leading to a preference for single-sided deuteration, consistent with DFT calculations suggesting that the most stable isomer of $C_{60}H_{18}$ has H (or D) atoms bound one one side (Clare & Kepert 2003).

Curve (i) in Figure 2 (a) shows the thermal desorption of C_{60} from *ca.* 1 ML of C_{60} adsorbed on HOPG. The desorption peak shape is consistent with zero order desorption and shows a maximum at around 550 K. Curve (ii) in Figure 2 (a) shows the desorption profile summed over all $C_{60}D_x$ species with $0 \leqslant x \leqslant 36$ for C_{60} adsorbed on HOPG and subsequently exposed to a D-atom fluence of 7.2×10^{17} cm^{-2}. It is clear that the deuteration process leads to a significant stabilization of the $C_{60}D_x$ film with all species desorbing at a significantly higher temperature of around 650 K, as highlighted by ΔT in Figure 2 (a). A similar shift has been observed previously (Löffler *et al.* 2007) and suggests increased interactions between molecules in the hydrogenated film. Figure 2 (b) shows the D_2 thermal desorption signal obtained from a D-saturated HOPG surface showing two peaks associated with para and ortho dimers (Hornekær *et al.* 2006). As shown in Figure 2 (b), when *ca.* 1 ML of C_{60} on HOPG is exposed to a large D-atom fluence a much higher temperature D_2 desorption signal is observed, possibly suggesting hydrogen release from deuterated fullerenes at high temperature. Desorption of D_2 from defective graphite occurs over a similar temperature range (Güttler *et al.* 2004) which might indicate deuteration induced fragmentation of the C_{60} molecule.

4. Conclusions

We confirm the formation of deuterated fullerene molecules up to $C_{60}D_{36}$ when C_{60} films adsorbed on HOPG are exposed to a beam of deuterium atoms. The apparent preference to form $C_{60}D_{18}$ may result from single-sided deuteration when the C_{60} molecules are surface adsorbed. Deuteration leads to a significant stabilization of the entire molecular film, raising its desorption temperature by over 100 K, suggestive of increased interactions between molecules. Release of D_2 from the $C_{60}D_x$ films occurs at a significantly higher temperature than from deuterated graphite and may point to hydrogen induced fragmentation of the C_{60} molecules, warranting further investigation.

Acknowledgment

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