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Desorption of volatile molecules from the surface of interstellar carbonaceous dust analogs

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Abstract. The desorption of volatile molecules from dust grains in cold dense clouds is crucial for the chemical inventory in the various stages of cloud collapse. In this work we investigate the desorption of N_2, CO, CH_4 and CO_2 from surfaces of hydrogenated amorphous carbon (HAC), which, according to IR observations, is one of the main components of interstellar dust.

Keywords. Astrochemistry, ISM:dust, ISM:molecules

Interstellar dust grains consist mostly of silicates and carbonaceous materials. In the diffuse medium, carbonaceous dust produces a characteristic absorption band at 3.4 μm and weaker features in the 5.5-7.7 μm interval attributed to hydrogenated amorphous carbon (HAC) (Dartois *et al.* 2007). In the cold interior of dense clouds atoms and molecules freeze out on grain surfaces forming ice mantles dominated by water. CO_2 and CO are also present in large amounts. CH_4 and NH_3 have been detected too, and other species like N_2 and O_2 are assumed. Heating of the grains activates both, chemistry and desorption, in the hot core phase. In the outer regions of a forming star, volatiles can be retained on the grains and then incorporated to larger bodies like asteroids, planets and moons. Desorption studies, relevant for astrophysical conditions, have been carried out previously for surfaces of water-ice (Gálvez *et al.* 2008; Noble *et al.* 2012; Smith *et al.* 2016; He *et al.* 2016), graphite (Vidali *et al.* 1991; Ulbricht *et al.* 2006), graphene (Smith *et al.* 2016) and silicates (Noble *et al.* 2012; Collings *et al.* 2015). In this work we extend these studies to HAC surfaces taken as analogs of interstellar carbonaceous dust.

Two types of HAC samples were produced and deposited on Al substrates. One of these samples (HAC1) was a flat film generated in an inductive Radio Frequency (RF) discharge of CH_4/He. The second sample (HAC2) was made of dust particles produced by gas-phase polymerization between the parallel electrodes of a capacitive RF discharge of C_2H_2/Ar. SEM images of HAC2 showed a rough surface formed by 1-2 μm flakes made of particles with a narrow diameter distribution around $\approx$ 130 nm. In both cases the Al surface was completely covered by the carbonaceous deposit. IR spectra of the samples showed that the HAC1 film was essentially aliphatic and the HAC2 dust sample had both aliphatic and aromatic bands. The spectra of HAC2 were in better agreement with astronomical observations.

Thermal programmed desorption (TPD) measurements of N_2, CO, CH_4 and CO_2 from the two HAC surfaces were carried out in a UHV chamber with a closed-cycle He cryostat. Coverages $\leqslant 1$ monolayer (ML) were deposited on the HAC surfaces and then desorbed and detected with a quadrupole mass spectrometer (QMS), with a resolution better than 0.5 u, placed at $\approx$ 1 cm from the surface. As an illustration of the measurements, the TPD

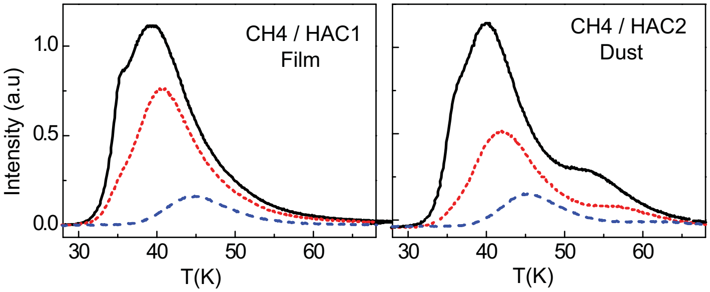

Figure 1. QMS signal of CH_4 (16 u) desorbed from HAC surfaces. Left panel: HAC1 film; right panel: HAC2 dust (see text). The black curves correspond to coverages of 1 ML.

spectra of CH_4 are shown in Fig. 1. The spectra from HAC2 have two broad maxima indicating two groups of desorption sites. Qualitatively similar spectra are also obtained for N_2 and CO. They correspond to 1st order desorption. TPD spectra of CO_2 have a different shape with just one peak and shared leading edge, characteristic for 0 order kinetics.

For the analysis of the desorption measurements we have employed the Polanyi-Wigner equation:

$$-\frac{d\theta}{dT} = \nu\theta^n\beta^{-1}\exp\left(-\frac{E_d}{kT}\right)$$

where θ is the coverage, n the desorption order, ν a pre-exponential factor, β the heating ramp (20K/min), and E_d the desorption energy. We have taken the ν factors given by Ulbricht *et al.* 2006 for desorption from graphite, namely: $\nu = 5\times10^{10\pm1}\ s^{-1}$, $2\times10^{14\pm1}s^{-1}$, $4\times10^{15\pm1}s^{-1}$, and $5\times10^{10\pm1}s^{-1}$ for N_2, CO, CH_4 and CO_2 respectively. From eq (0.1) and the TPD spectra we have derived average desorption energies, $\overline{E_d}$, for coverages of 1 ML. The $\overline{E_d}$ values (in kJ/mol) for desorption from the HAC1 film were: 7.8±0.6, 11.1±0.7, 14.0±0.8, and 24.9±1.5 for N_2, CO, CH_4 and CO_2, and those for the desorption from the HAC2 dust surface were: 8.3±0.7, 11.6±0.7, 14.8±0.9, and 27.0±1.8 for N_2, CO, CH_4 and CO_2 respectively.

The desorption energies for the two HAC samples are, in general, close to those reported in the literature for surfaces of graphite and graphene and are higher than those for ice or silicate analogs, indicating that carbonaceous surfaces, irrespective of their structure or composition, will retain volatiles for a longer time in the course of cloud collapse. The two peak shape in the TPD spectra of HAC2 points to two distinct groups of desorption sites that might be due to differences in the structure (aliphatic/aromatic) or morphology of the sample.

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