

Photochemical studies of astrophysically relevant molecules on a carbon surface

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Introduction

The space between the stars, the interstellar medium (ISM), comprises clouds of gas and dust containing molecules, which play a crucial role in star formation. Studies show that gas-surface chemistry is essential to rationalise the abundance of many of these molecules. In the ISM, molecules freeze out on the cold (10 K) surfaces of grains, forming molecular ices containing both simple and more complex species, indicative of the processing of the ices by exposure to ultra-violet (UV) light and low energy electrons.

The exact composition of interstellar ices depends on the environment. However, observations show that the ices are dominated by H₂O (60-70%) with other abundant constituents including CO, CO₂, CH₃OH, CH₄ and NH₃¹. These molecules are also precursors for the formation of complex molecular species (e.g. methyl formate and glycolaldehyde^{2,3}) detected in gas and condensed phases. Sulphur-bearing molecules are also found in interstellar ices. A range of sulphur-bearing species have been detected in the ISM, including SO₂, H₂S and OCS. Since H₂S has been detected in the gas phase, but not in ices^{4,5}, OCS is thought to be the main reservoir of sulphur in ices⁶. In particular it is thought that photochemical processes may lead to the destruction of H₂S in ices.

The dust grains on which these ices freeze out play a pivotal role in chemical processes in the ISM⁷, opening up reaction pathways to species accreted on the grains that are not available in the gas-phase⁸. In particular molecular ices frozen out on the grains can undergo chemical and physical transformation *via* numerous routes, including UV irradiation.

Despite extensive laboratory studies of model interstellar ices⁹, the role of UV irradiation in molecular formation and photo-desorption has received considerably less attention^{2,10}. Similarly, the photochemical pathway is often overlooked in computational models, despite the fact that photo-excited states generated within ices or originating from the gas-phase, would provide sufficient energy to surpass otherwise insurmountable reaction energy barriers.

To date, most UV studies of ices have focused on resonant photon-induced processes within the ices, i.e. irradiating ices at wavelengths at which the parent molecules within the ice absorb light, leading to electronically excited states facilitating desorption or dissociation^{2,10}. These experiments have been performed on insulators¹⁰ and metals² and neglect substrate-mediated effects that lead to photo-desorption and photodissociation¹¹. Furthermore, these surfaces do not truly reflect the nature of dust grains, which are known to be siliceous and carbonaceous in nature.

To investigate the effect of substrate-mediated photochemical processes on interstellar dust grains, we have therefore studied the irradiation of various astrophysically relevant molecules adsorbed on highly oriented pyrolytic graphite (HOPG) over the wavelength range 220-232 nm. HOPG is known to have an absorption at around 218 nm¹². For glycolaldehyde and methyl

formate, irradiation at 280 nm and 263 nm were additionally studied, in order to investigate direct molecular absorption by these molecules. For the sulphur-containing molecules, OCS has its maximum absorption in the 220-230 nm wavelength range¹³ and hence it is expected that this molecule should show strong photochemistry in this region.

Methodology

Model interstellar ices of known thickness were grown on an HOPG sample, cooled to ~ 20 K to mimic low ISM temperatures. The low pressure conditions of the ISM were simulated by mounting the sample in an ultrahigh vacuum (UHV) apparatus, equipped with a pulse counting quadrupole mass spectrometer. A range of model interstellar ices grown on the HOPG substrate were investigated, including ices containing simple molecules such as CO₂ and CH₄, sulphur-containing species (OCS, H₂S and SO₂), the alcohols CH₃OH, CH₃CH₂OH, propan-2-ol and more complex organic species (the C₂H₄O₂ isomer family of glycolaldehyde, methyl formate and acetic acid). In the case of the complex isomers, the photochemical behavior of the pure species and the species mixed with water ice was investigated.

Samples were irradiated with a Nd³⁺-YAG pumped dye laser at a repetition rate of 10 Hz. In order to study substrate-mediated photo-processes, samples were irradiated over the 220-232 nm wavelength range. In the case of methyl formate and glycolaldehyde, the samples were also irradiated at 263 nm and 280 nm respectively, to additionally investigate direct molecular absorption. Direct molecular absorption was also expected for OCS, which shows a maximum absorption at around 220-230 nm¹³.

The laser beam was incident on the sample at 45°. The absolute laser power measured outside the window into the UHV chamber was of the order of 1-4.4 mW over the 220-232 nm range, giving an energy of 0.1-0.44 mJ pulse⁻¹. Beam energies were considerably higher at 263 and 280 nm, and hence the power was attenuated to give similar powers to those achieved at 224 nm (typically 0.3 - 0.4 mJ pulse⁻¹). Desorbing species were monitored with a pulse counting quadrupole mass spectrometer to give photo-induced desorption (PID) traces. Post-irradiation temperature programmed desorption (pi-TPD) spectra were also recorded, in order to characterise any photo-reactions that took place during laser irradiation.

For all molecules, the effect of surface coverage on the photochemistry was studied. Methyl formate was found to be particularly photoactive and hence the effect of irradiation time, irradiation wavelength over the 220 - 232 nm range, and of surface coverage, were all investigated for this molecule.

Results and discussion

For all molecules investigated, PID was observed. For some molecules, additional photo-induced dissociation was also observed. Below we report results for three classes of molecules: the C₂O₂H₄ isomers, a series of alcohols and finally for sulphur-containing molecules.

1. Photochemistry of the C₂O₂H₄ isomers

All three isomers, glycolaldehyde (GA), methyl formate (MF) and acetic acid (AA), gave rise to PID when irradiated over the 220 – 232 nm wavelength range, as seen for MF in Figure 1A. Of these three molecules, MF was observed to be the most photo-active with the parent molecule being depleted by between 15-25% depending on coverage, irradiation time and irradiation wavelength (Figure 1B). AA was the least photo-active, giving rise to sharp and very low intensity PID signals. Evidence of the photo-dissociation of MF into HCO and CH₃O fragments was seen following laser irradiation (Figure 1D), as well as further evidence for the formation of CH₃ and CO₂ fragments. These two sets of fragments can be formed by the breaking of either of the C-O bonds in the MF molecule (Figure 2), suggesting that photo-reaction/dissociation occurs.

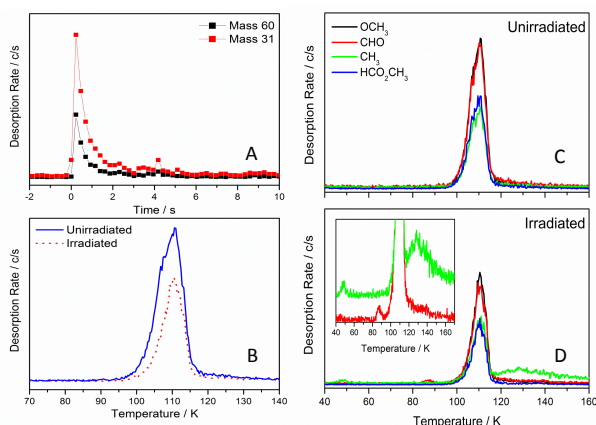


Figure 1: A shows PID data for the irradiation of MF at 224 nm, showing the desorption of the parent molecule. B shows pi-TPD spectra following that irradiation, showing the depletion of the molecule. C and D show TPD spectra for the unirradiated and irradiated MF respectively, showing the dissociation of MF into various molecular fragments.

Analysis of the ratios between the integrated TPD area of the parent MF molecule (mass 60) and the CHO and CH₃O fragments, both pre and post-irradiation, provides further evidence that dissociation occurs in addition to desorption. For example, following irradiation of a 4 L dose of MF for 8 minutes at 224 nm, the CHO/parent ratio increases from 1.51 (un-irradiated) to 1.85 (irradiated). The increase in this ratio is indicative of larger amounts of CHO in the mass spectrometer, thus providing clear evidence for the dissociation of the parent molecule.

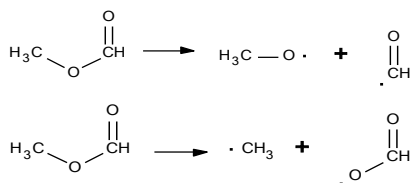


Figure 2: Possible photo-dissociation routes for MF.

To further investigate the observed photo-desorption and photo-dissociation of MF, and to try to distinguish between adsorbate and substrate-mediated processes, further irradiation of MF was performed at 263 nm (MF has a strong absorption at 259 nm in the gas phase¹⁴). Initial indications from these data show that the depletion of the parent molecule is less at 263 nm, and not as much fragmentation takes place, indicating that substrate mediated photo-processes are responsible for a large part of the observed MF photochemistry. Unfortunately this is complicated by the possibility of a weak molecular absorption for MF at 224 nm in the gas phase¹⁴.

For all three isomers, the effects of co-adsorbing the isomer with water ice were also investigated and in all cases it was found that water inhibited both the desorption and the dissociation (where this was observed). It is not clear exactly what the mechanism for this inhibition is, however clear effects were observed when the isomers were co-deposited with water ice, in addition to clear desorption of water molecules during irradiation

For MF, the laser irradiation data were also compared with data for irradiation of the molecule using a 40 W continuous wave Xe arc lamp, operating at 280 nm. Despite the large difference in the flux of the two different UV sources, similar effects were observed with photo-dissociation of the MF being observed in both cases. This is particularly important in terms of relating the laser results to an interstellar situation, since UV sources in the interstellar case are much less intense than the laser source used for the investigations described here. However, the similarity between the laser and lamp data gives confidence that the results obtained with a laser can be applied to interstellar situations and can hence be used in modeling of UV processes in an interstellar context.

2. Photochemistry of alcohols adsorbed on HOPG

In contrast to the isomers already described, the alcohols studied are transparent in the 220-232 nm wavelength region and hence only substrate-mediated photo-processes were observed. PID was observed for all three alcohols investigated (methanol, ethanol and propan-2-ol). For methanol, some evidence of photo-induced dissociation was observed, with the formation of CH₃ being seen in pi-TPD spectra. In contrast, ethanol and propan-2-ol showed only photo-induced desorption.

3. Irradiation of sulphur-containing model interstellar ices

The sulphur-containing molecules investigated (OCS, SO₂ and H₂S) were found to be particularly photo-active when irradiated over the 220-232 nm wavelength range. SO₂ and H₂S are transparent in this wavelength region (the main SO₂ absorption is at 294 nm¹⁵ and that for H₂S occurs at 187 nm in the gas phase¹⁶), however OCS shows a strong absorption in the 220-230 nm wavelength range in the gas phase¹³. For all three molecules, relatively large PID signals were observed as shown in Figure 3. The largest amount of photo-induced desorption was seen for H₂S, as can be seen from the pi-TPD data (right hand side, Figure 3) which shows that around 60-70% of the adsorbed H₂S desorbs following laser irradiation for 4 minutes at 224 nm.

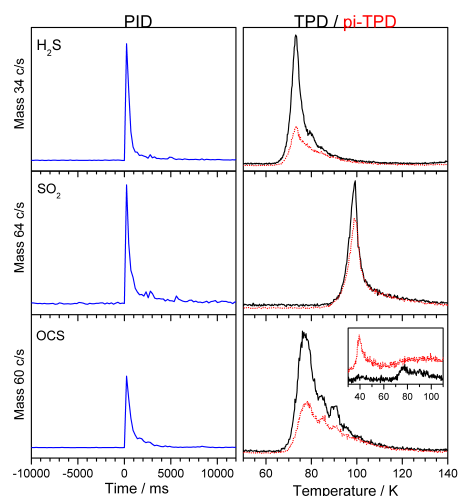


Figure 3: PID (left hand side) and pre (black trace)- and post-irradiation (red trace) TPD spectra (right hand side) for the irradiation of H₂S, SO₂ and OCS adsorbed on the HOPG surface. The inset in the OCS TPD trace shows the signal for CO (mass 28), showing that photo-dissociation of OCS occurs. The SO₂ PID trace has been multiplied by 4 to increase its size on the scale of the other PID traces.

The exact amount of photo-desorption of each molecule varied as a function of surface coverage, but in all cases active photo-desorption was observed.

For H₂S, there is no evidence of photo-dissociation seen in pi-TPD. However for OCS, CO is clearly seen in the post-irradiation TPD spectrum (right hand side, Figure 3) in a peak that is not associated with the main TPD peak (ie not a mass spectrometer cracking fragment of the OCS). This clearly shows that photo-dissociation, as well as photo-desorption, takes place for OCS. Since OCS has a strong absorption in the 220-230 nm wavelength range¹³ it is likely that the observed OCS photochemistry arises from a combination of adsorbate and substrate-mediated processes. For SO₂, there is some evidence of a small amount of photo-dissociation, with the possible observation of O₂ in pi-TPD.

Conclusions

Laser irradiation of interstellar ice analogues over the wavelength range of 220-232 nm was performed in order to investigate substrate-mediated photochemistry. For all molecules investigated, photo-desorption was observed, indicating that substrate-mediated processes are important for these adsorbate systems. For some molecules, photo-dissociation was also observed. In the case of methyl formate, the molecule was observed to dissociate along either of the C-O bonds and for OCS the molecule dissociated into CO and S. In both of these cases, the observed photochemistry could be ascribed to a mixture of adsorbate and substrate-induced processes. In the case of methyl formate, additional irradiation was also performed at 263 nm, where the molecule is known to have a weak molecular absorption, and again photo-desorption and dissociation were observed, although not as strongly as that seen at 224 nm.

These investigations have shown that substrate-mediated photochemistry is an important processing route for model interstellar ices adsorbed on carbonaceous surfaces, and hence it is clearly important to include this mechanism in models of ISM chemistry. Further analysis of the data obtained will allow detailed UV absorption cross-sections to be determined, which can then be incorporated into astrochemical models.

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