

An evolutionary connection between interstellar ices and IDPs? Clues from mass spectroscopy measurements of laboratory simulations

Jason P. Dworkin ^{a,*}, J. Seb Gillette ^b, Max P. Bernstein ^{c,d}, Scott A. Sandford ^c,
Louis J. Allamandola ^c, Jamie E. Elsila ^b, Donald Ryan McGlothlin ^d, Richard N. Zare ^b

^a NASA's Goddard Space Flight Center, Code 691.0, Greenbelt, MD 20771, USA

^b Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA

^c NASA's Ames Research Center, Mail Stop 245-6, Moffett Field, CA 94035-1000, USA

^d The SETI Institute, 2035 Landings Drive, Mountain View, CA 94043, USA

Received 28 April 2003; received in revised form 4 August 2003; accepted 18 August 2003

Abstract

We present mass spectra of the residual organic matter that results from the ultraviolet photolysis of realistic interstellar ice analogs in the laboratory. The mass spectra show that this residue is a complex mixture of high molecular weight organic molecules, reminiscent of those reported for interplanetary dust particles (IDPs) – asteroidal and cometary dust. This represents a further characterization of the material for which we have already reported amphiphilic properties (Dworkin et al., 2001). If we assume that the compounds observed are conjugated hydrocarbons, the mass spectra of the organics are consistent with organic compounds of up to 22 carbon atoms. Heating in air at low-pressure up to 1470 K as a simulation of atmospheric entry increases the molecular masses detected by $\mu\text{L}^2\text{MS}$, resulting in a spectrum similar to those of the IDPs Florianus, and Aurelian. The results presented here are consistent with the notion that some of the large organic molecules delivered to the Earth on IDPs could have had their origin in low-temperature ice chemistry.

Published by Elsevier Ltd on behalf of COSPAR.

1. Introduction

Comparison of infrared (IR) telescopic observations of cold interstellar environments with low temperature laboratory ices suggest that interstellar and protostellar ices are often composed of H_2O mixed with 5–15% CO , CO_2 , CH_3OH , and NH_3 (Ehrenfreund and Charnley, 2000 and references therein). In most environments where such mixed-molecular ices are observed, radiation is also expected. For example, interstellar ices should be exposed to significantly enhanced UV fields in star-forming regions, and ices near young stars in their T-Tauri phase should be exposed to the high energy particle fluxes and UV radiation (Giampapa and Imhoff, 1985). Even in dense molecular clouds with high visual

extinction, radiative processing of these ices is expected from cosmic rays and cosmic ray-induced UV (Prasad and Tarafdar, 1983). Thus, astronomical mixed-molecular ices are predicted to experience energetic processing. Laboratory studies have shown that processing of relevant ice analogs in the laboratory by UV photolysis (Bernstein et al., 1995) and ion irradiation (Moore et al., 1996) produces organic compounds more complex than the simple starting materials.

Some of our past studies have shown that there are similarities between the organic compounds produced by energetic processing of ices and the molecules found in primitive meteorites (Bernstein et al., 2001, 2002, 2003). Of special relevance to this report is that the UV photolysis of an interstellar/protostellar/cometary ice analog with a composition of $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 100:50:1:1$ yields both fluorescent and amphiphilic compounds that can spontaneously self-assemble into

* Corresponding author.

E-mail address: jason.p.dworkin@nasa.gov (J.P. Dworkin).

vesicles (Dworkin et al., 2001). These vesicles have very similar morphologies to those produced by amphiphiles found in primitive meteorites like the Murchison carbonaceous chondrite (Deamer and Pashley, 1988) and such structures may have been preserved in the Tagish Lake meteorite (Nakamura et al., 2002). High precision liquid chromatographic (HPLC) analysis of the laboratory material reported (Dworkin et al., 2001) showed dozens of unidentified peaks indicating a diverse population of fluorescent and UV-absorbing compounds. In this paper we present mass spectra of the ice analog derived organic mixture that formed vesicles before and after simulated atmospheric entry heating, and compare these to the mass spectra of two IDPs. Together, this suggests that the amphiphiles in meteorites and the organics in IDPs may have derived from radiative processing of interstellar or protostellar ices at very low temperatures. An interstellar origin of the organic matter in meteorites and interplanetary dust particles (IDPs) is consistent with the presence of deuterium enrichments, suggestive of low temperature processes (Sandford et al., 2001). Additionally, the mass spectra of the unheated residues indicate the presence of hundreds, rather than dozens, of compounds extending the richness of the organic material formed through these simulations.

2. Methods

The preparation techniques for the simulated interstellar ice photolysis residue samples are described in detail elsewhere (Allamandola et al., 1988; Dworkin et al., 2001). The starting gas-mixture ($\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 100:50:1:1$) roughly reflects the composition and concentrations of the major ice components observed in interstellar dense molecular clouds along the line of sight to high-mass protostars (d'Hendecourt et al., 1999). Different concentrations of the same mixture (all H_2O -rich) have also been studied and produce similar results. The gas mixture was deposited onto a rotatable, 15 K brass or aluminum substrate mounted in a vacuum chamber. Prior to each experiment, substrates were cleaned by one of the following three methods with no change in results: buffing with steel wool, followed by a wash with HPLC grade methanol; buffing with cotton, followed by a wash with HPLC grade methanol; or heating aluminum substrates to 550 °C in air for 18 h. Sample gases were deposited onto the cold substrate at a rate of ~ 0.02 mmol/h. During deposition, the substrate/sample was simultaneously photolyzed with vacuum UV from a hydrogen plasma lamp (hydrogen Lyman α -line at 121.6 nm) and a 20 nm wide molecular transition centered near 160 nm) to simulate the processing of icy grains in dense molecular clouds. By simultaneously depositing ice while photolyzing, an optically thin layer of ice is

photolyzed before being buried by more ice. This enables more material to be processed than previously employed techniques (e.g., Allamandola et al., 1988). It has been determined that no significant reactions occur due to photolysis of material in the gas phase during the deposit (Gudipati et al., 2003). Furthermore, in the solid phase the time that elapses between photons arriving at the same molecular site was ~ 13 orders of magnitude longer than molecular relaxation times, so only single-photon processes are relevant. Deposition with simultaneous photolysis was continued for up to two days in each experiment. After this time, deposition and photolysis was stopped and the ice was allowed to slowly warm to room temperature under static vacuum.

The warming process, which typically took several hours, allowed volatile ice components to sublime, keeping the ice thin, which served several purposes. First, a thin ice insures a more homogeneous temperature. Second, by minimizing the amount of volatile compounds, the risk of losing large quantities of residue from explosive sublimation of ice is diminished. The samples were warmed under static vacuum to diminish the loss of compounds of moderate volatility. After warming to room temperature there is a thin organic film on the substrate. At this time the chamber was then re-evacuated and the substrate with residue re-cooled to 15 K, followed by the next two-day cycle of deposition with photolysis and subsequent warm-up under static vacuum. A layer of ice was deposited on top of the residue to insure that the *residue* is not photolyzed. (Photolysis of the residue is interesting as well, but was not performed in this case, some fluorescence data regarding this can be found in Gudipati et al. (2003).) The cycles of deposit and photolysis followed by warm-up was repeated up to ten times for a typical total sample preparation period of about five weeks.

After the final warm-up air was let into the vacuum chamber and the substrate with its organic film was removed. Samples on aluminum foil substrates were then cut into five strips. One of the strips was placed in the sample chamber of a microprobe laser-desorption laser-ionization mass spectrometer ($\mu\text{L}^2\text{MS}$; located in the Chemistry Department, Stanford University) and the mass spectrum of the sample was recorded, using the technique described in greater detail elsewhere (Clemett and Zare, 1997). The other samples strips were used for parallel analyses described elsewhere (Dworkin et al., 2001). The $\mu\text{L}^2\text{MS}$ technique is very sensitive for the detection of compounds with conjugated bonds, such as aromatic hydrocarbons, but will not detect species that are not ionized by photons at the wavelengths of the ionization laser.

In several experiments we used a Model 5530-L “hotspot” infrared spot heater to pulse heat our residues. Different aliquots of the same sample were pulse

heated to peak temperatures of 295 (unheated), 610, 870, 1160, and 1470 K. The samples were heated in ~ 50 mTorr of air and peak temperatures were held for only 2–4 s to simulate atmospheric entry conditions. (Note. These temperatures are in K so the equation presented later works and for consistency of units throughout the paper.)

3. Results and discussion

3.1. Sample analysis

Fig. 1 shows the $\mu\text{L}^2\text{MS}$ of the non-volatile organic residue synthesized by the UV photolysis of a $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3:\text{CO} = 100:50:1:1$ ice mixture at 15 K in comparison to control experiments. It is seen that high molecular weight compounds are formed by the UV photolysis of simple ices at low temperature. The overall shape of the mass distribution is always found to be very similar for a given set of conditions. All UV photolyzed ice samples produce mass spectra having a distribution of peaks (one at every mass) peaking around 225 amu and stretching for approximately 100 amu in either direction (Fig. 1b). Atomic masses in this range would correspond to conjugated C_{22} hydrocarbons, which indicates a considerable increase in molecular complexity compared to the one carbon atom

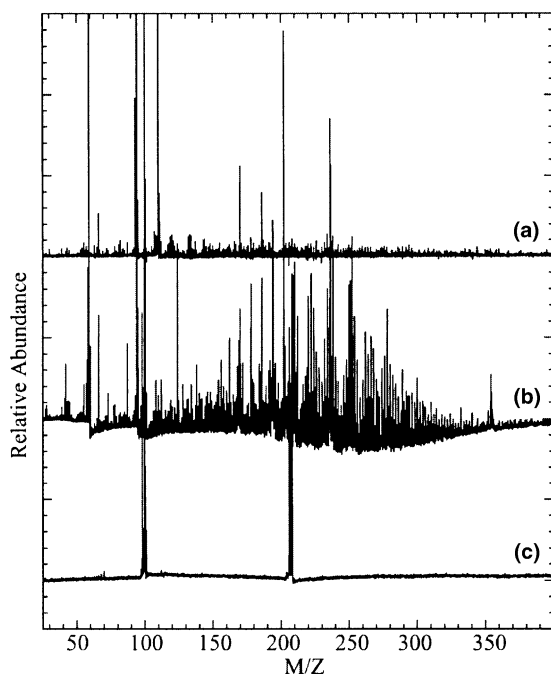


Fig. 1. The $\mu\text{L}^2\text{MS}$ mass spectra of an ice photolysis residue and two controls. Trace a is the mass spectrum of a control of water deposited and photolyzed as described in the text. Trace b is the mass spectrum of a typical sample. Trace c is the mass spectrum of an unphotolyzed sample. (Note. The peak at 100 M/Z is D_{10} -toluene that was added during analysis as a standard and the peaks at 204, 206, 207 and 208 correspond to lead desorbed from the brass substrate.)

ice starting materials. Naturally, the presence of exclusively hydrocarbons is not expected given the presence of hetero-atoms in the ice mixtures.

Many control experiments were performed to eliminate the possibility of contamination and to ensure that the residue produced by ice photolysis is responsible for the species detected. Each analysis was performed blind (i.e., the Stanford group did not know identity of a given sample). In one control the gas mixture was deposited for three weeks according to the same procedure described above except the lamp was never turned on. After warm-up of the sample $\mu\text{L}^2\text{MS}$ on the substrate failed to detect a significant mass envelope – the peaks at 100 and $\sim 200 M/Z$ correspond to an internal standard and lead from the brass sample platter (the lead is not normally seen, however since the Stanford group did not know it was a control they increased the desorption laser power until they saw a signal) (Fig. 1c). Similar negative results were found in a control which contained only H_2O (Fig. 1a), as well as for $\text{H}_2\text{O}:\text{NH}_3 = 100:1$, and $\text{H}_2\text{O}:\text{NH}_3:\text{CO} = 100:1:1$ photolyzed ices (which are not shown).

Each control experiment was bracketed by an experiment under typical conditions to ensure that there was minimal carry-over between experiments and that the lack of a signal was not due to a defect in the instruments, reagents, or protocols. These controls, particularly the photolysis of H_2O (Fig. 1a) and the deposition of the gas mixture without photolysis (Fig. 1c), demonstrate that the residual organic material is unlikely to be a contaminant from the vacuum pumps or any other part of the sample preparation apparatus, generated by the photolysis of such a contaminant in a H_2O matrix, nor is it an artifact of our sample analysis protocols.

The $\mu\text{L}^2\text{MS}$ technique is particularly sensitive for polycyclic aromatic hydrocarbons (PAHs). We determined that if the vacuum sample preparation system used to make these residues had been used for PAH research in the past, some of these PAHs and their oxidized and reduced products (Bernstein et al., 1999, 2003) would appear in the $\mu\text{L}^2\text{MS}$ mass spectra. To remove this concern, we only prepared samples in a dedicated PAH-free system for the results reported here.

The experiment was repeated numerous times. All the mass spectra from the different samples are similar, but they often show modest differences in detail, both between different samples and between different spots on the same sample substrate. These modest differences are presumably due to slight differences in deposition flow rates across the substrate (and hence, differences in total UV exposure), deposition angles, etc., as well as to possible phase separations occurring within the sample during warm-up and ice sublimation. In an extreme case we observed that when the gas flow was increased by a factor of ten, diminishing the average UV dose by a

factor of ten, the center of the mass envelope diminishes by a factor of two. This sample was heated (see below) to generate Fig. 3d.

The spectra are complex (see, for example, Fig. 2), making assignments of specific compounds very difficult. A lower power for the $\mu\text{L}^2\text{MS}$ desorption laser did not significantly change the spectra. This fact suggests that the majority of the peaks (particularly above 100 M/Z) are not fragments of larger compounds. Isotopic labeling experiments with $^{15}\text{NH}_3$ or where all carbon-containing materials were labeled with ^{13}C resulted in clear shifting upward within the mass spectrum. However, the extraordinary complexity of the spectra precluded any easy determination of the shifting of individual mass peaks.

3.2. Comparison with IDPs: preliminary results

Mass spectra of IDPs can display a bimodal distribution of peaks (Fig. 3a and b, Clemett et al., 1993). The mass spectra of our photolysis residues reproduce only the lower (up to 300 amu) mass envelope seen in the mass spectra of IDPs (Fig. 3c). However, after heating intended to simulate the affects of atmospheric entry, an increase in the overall mass distribution observed by $\mu\text{L}^2\text{MS}$ (Fig. 3d), making the appearance similar to those of IDPs (in Fig. 3 compare spectrum d to a and b).

Heating resulted in an increase in the center of the observed mass distribution, with higher temperatures yielding larger upward shifts. In one trial, the center of the mass envelope (M) follows the relationship: $M \approx 0.16T + 75$, but additional experiments will be

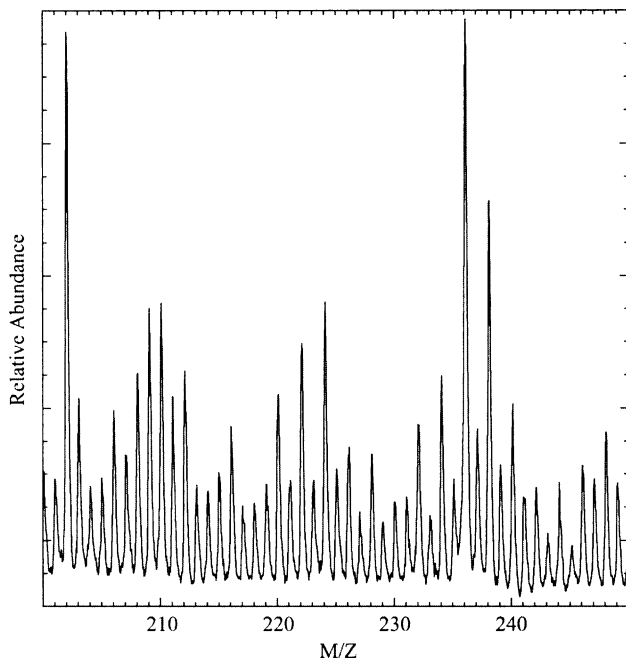


Fig. 2. Detail of Fig. 1b showing the complex peak pattern of the residue's mass spectrum and the presence of a peak at every mass.

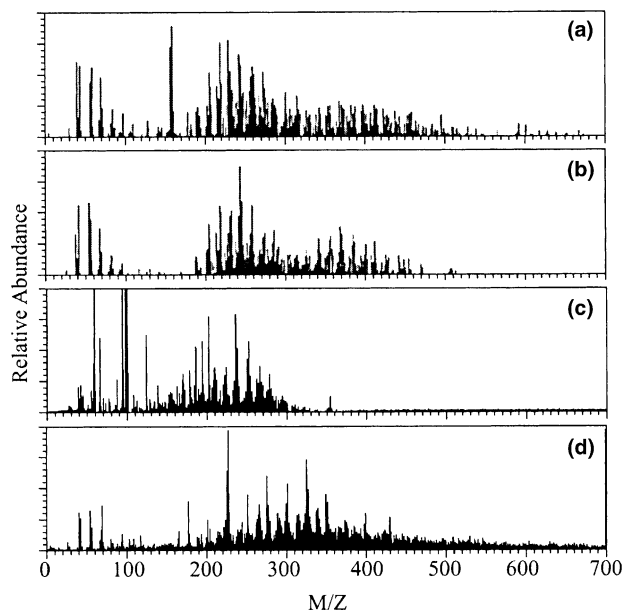


Fig. 3. Comparison of the $\mu\text{L}^2\text{MS}$ mass spectra of two IDPs (a,b) (Clemett et al., 1993) with that of (c) a typical UV ice photolysis residue, and (d) a photolysis residue heated to 1470 K for ~ 2 s in 50 mTorr of air. Note that the starting residue used to produce spectrum d was produced using a much lower total UV fluence than that used to produce the residue in spectrum c. As a result, the center of the mass distribution in the spectrum of the unheated residue in d (not shown) occurred at about 1/2 the mass value of residue c, i.e., near 100–125 amu. Thus, heating of the residue shown in d resulted in the center of the mass distribution moving up by about a factor of 2.

necessary to determine whether this relationship is generally valid, and how it depends on specific conditions of the heating and sample composition. The highest temperature heating (1470 K) was necessary to produce large enough shifts in the $\mu\text{L}^2\text{MS}$ of the laboratory material that the center of the mass distribution moved into the range of the higher mass envelope seen in the IDP mass spectra.

4. Conclusions and implications

We have presented two-step laser desorption mass spectra of the organic mixture produced in laboratory experiments designed to reproduce the photochemistry of realistic interstellar/protostellar/cometary ices both before and after heating designed to simulate atmospheric entry. This study represents a further molecular characterization of the same material for which fluorescent and amphiphilic properties had already been reported (Dworkin et al., 2001). We find that our laboratory organic material formed by UV photolysis of ice at low temperature is composed of a very complex mixture of organic molecules with high molecular weight components. Because the $\mu\text{L}^2\text{MS}$ analytic technique is sensitive to UV-absorbing (i.e., aromatic or conjugated) compounds, this suggests that the fluorescent and

UV-absorbing peaks detected by HPLC by Dworkin et al. (2001) could correspond to species as large as $\sim C_{22}$ conjugated hydrocarbons. Laboratory simulations of the heating of atmospheric entry lead to an increase in the molecular masses detected by μL^2MS , resulting in a spectrum comparable to those of the IDPs Florianus, and Aurelian. This finding supports the hypothesis originally suggested by Clemett et al. (1993) that the lower mass envelope in IDPs might be from materials indigenous to the IDP, whereas the higher mass envelope might be produced by “sintering” during atmospheric heating. The presence of two peaks in IDPs, rather than just the higher mass peak would then presumably be the result of kinetic chemical effects. These observations are all consistent with the possibility that some of the organic molecules in meteorites and IDPs may have derived from low-temperature ice photochemistry.

Acknowledgements

We very gratefully acknowledge Bob Walker for his excellent technical support, without whom these long duration experiments would not have been possible. This work was supported by NASA's Exobiology (Grant 344-38-12-04), Astrobiology (Grant 344-50-92-02), and Origins of Solar Systems (Grant 344-37-44-01) Programs.

References

- Allamandola, L.J., Sandford, S.A., Valero, G. Photochemical and thermal evolution of interstellar/pre-cometary ice analogs. *Icarus* 76, 225–252, 1988.
- Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Chang, S., Scharberg, M.A. Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophys. J.* 454, 327–344, 1995.
- Bernstein, M.P., Moore, M.H., Elsil, J.E., Sandford, S.A., Allamandola, L.J., Zare, R.N. Side group addition to the PAH coronene by proton irradiation in cosmic ice analogs. *Astrophys. J.* 582, L25–L29, 2003.
- Bernstein, M.P., Dworkin, J.P., Sandford, S.A., Cooper, G.W., Allamandola, L.J. Racemic amino acids from the ultraviolet photolysis of interstellar ice analogs. *Nature* 416, 401–403, 2002.
- Bernstein, M.P., Dworkin, J.P., Sandford, S.A., Allamandola, L.J. Ultraviolet irradiation of naphthalene in H₂O Ice: implications for meteorites and biogenesis. *Meteor. Planet. Sci.* 36, 351–358, 2001.
- Bernstein, M.P., Sandford, S.A., Allamandola, L.J., Gillette, J.S., Clemett, S.J., Zare, R.N. UV irradiation of polycyclic aromatic hydrocarbons in ices: production of alcohols, quinones, and ethers. *Science* 283, 1135–1138, 1999.
- Clemett, S.J., Zare, R.N. In: van Dishoek, E.F. (Ed.), *Molecules in Astrophysics: Probes and Processes*. International Astronomical Union, Dordrecht, Netherlands, pp. 305–320, 1997.
- Clemett, S.J., Maechling, C.R., Zare, R.N., Swan, P.D., Walker, R.M. Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* 262, 721–725, 1993.
- Deamer, D.W., Pashley, R.M. Amphiphilic components of carbonaceous meteorites. *Orig. Life Evol. Biosph.* 19, 21–38, 1988.
- Dworkin, J.P., Deamer, D.W., Sandford, S.A., Allamandola, L.J. Self-assembling amphiphilic molecules: synthesis in simulated interstellar/precometary ices. *Proc. Natl. Acad. Sci. USA* 98, 815–819, 2001.
- Ehrenfreund, P., Charnley, S.B. Organic molecules in the interstellar medium, comets and meteorites: a voyage from dark clouds to the early Earth. *Ann. Rev. Astron. & Astrophys.* 38, 427–483, 2000.
- Giampapa, M.S., Imhoff, C.L. In: Blac, D.C., Matthews, M.S. (Eds.), *Protostars and Planets II*. University Arizona Press, Tucson, pp. 386–404, 1985.
- Gudipati, M.S., Dworkin, J.P., Chillier, X.D.F., Allamandola, L.J. Luminescence from VUV irradiated cosmic ice analogs and residues. *Astrophys. J.* 583, 514–523, 2003.
- d'Hendecourt, L.B., Jourdain de Muizon, M., Dartois, E., Demyk, K., Ehrenfreund, P., Heras, A. In: Cox, P., Kessler, M.F. (Eds.), *The Universe as Seen by ISO*. ESA Publications Division, Noordwijk, Netherlands, pp. 589–597, 1999.
- Moore, M.H., Ferrante, R.F., Nuth, J.A. Infrared spectra of proton irradiated ices containing methanol. *Planet. Spa. Sci.* 44, 927–935, 1996.
- Nakamura, K., Zolensky, M.E., Tomita, S., Nakashima, S., Tomeoks, K. Hollow organic globules in the Tagish Lake meteorite as possible products of primitive organic reactions. *Int. J. Astrobiol.* 179–189, 2002.
- Prasad, S.S., Tarafdar, S.P. UV radiation field inside dense clouds: its possible existence and chemical implications. *Astrophys. J.* 267, 603–609, 1983.
- Sandford, S.A., Bernstein, M.P., Dworkin, J.P. Assessment of the interstellar processes leading to deuterium enrichment in meteoritic organics. *Meteor. Planet. Sci.* 36, 1117–1133, 2001.