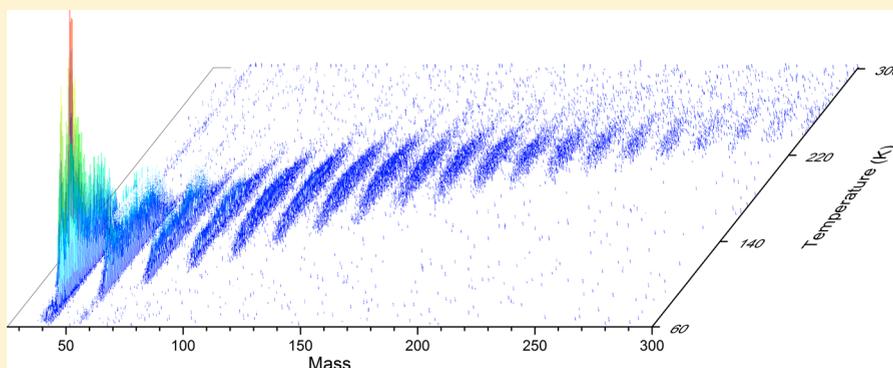


Application of Reflectron Time-of-Flight Mass Spectrometry in the Analysis of Astrophysically Relevant Ices Exposed to Ionization Radiation: Methane (CH₄) and D₄-Methane (CD₄) as a Case Study

Brant M. Jones* and Ralf I. Kaiser*

W.M. Keck Research Laboratory in Astrochemistry and Department of Chemistry, University of Hawaii at Mānoa, Honolulu, Hawaii 96822, United States



ABSTRACT: Methane ices have been detected on ice-coated interstellar grains and on the surface of Kuiper belt objects. These ices are chemically altered by ionizing radiation in the form of energetic photons and charged particles, leading to complex organic molecules. Despite decades of research, the chemical makeup of these newly synthesized molecules has not been completely understood to date. Here, we present a novel application of reflectron time-of-flight mass spectrometry coupled to soft photoionization to probe the molecular formulas of the molecules formed upon interaction of ionizing radiation with simple methane and D₄-methane ices. Our study depicts clear evidence of high-molecular-weight hydrocarbons of up to C₂₂, among them alkanes, *alkenes*, and *alkynes/dienes*, with those product classes in *italics* identified for the first time on line and in situ. These studies are particular timely as they provide laboratory data of methane-processed ices, which can be compared to actual data from the *New Horizons* mission on route to Pluto.

SECTION: Environmental and Atmospheric Chemistry, Aerosol Processes, Geochemistry, and Astrochemistry

Methane ice (CH₄) is ubiquitous not only within our solar system but also in cold molecular clouds,^{1–4} with methane observed toward over 25 young stellar objects.⁴ Within our solar system, methane has been detected on Triton,^{5–7} Orcus,^{8–10} Eris,^{7,11,12} Pluto,^{7,12–14} Makemake (2005 FY₉),^{15,16} Quaoar,^{17,18} and 2007 OR₁₀,¹⁹ with evidence for areas of pure methane for the surfaces of Pluto,¹⁴ Eris,¹¹ and Quaoar;²⁰ further evidence suggests that hitherto unspecified “higher-order hydrocarbons” are present on Quaoar¹⁷ and 1993SC.²¹ Furthermore, methane ice clouds are also thought to be present in the upper atmospheres of Uranus and Neptune.²² These objects are continuously being exposed to ionizing radiation in the form of UV photons and charged particles from the solar wind and galactic cosmic rays (GCRs), inducing both chemical and physical modifications of the nascent methane ice. Indeed, during the last decades, countless experiments have been conducted on the processing of methane ices with high-energy ions,^{23–30} high- and low-energy electrons,^{31,32} broad-band UV photons,^{24,33} and γ -radiation.^{34,35} The intent of this Letter is not an in-depth review of all of the past experimental findings, but instead, highlights novel observations. The

irradiated ices were mainly analyzed by Fourier transform infrared (FTIR) spectroscopy and converged on the identification of acetylene (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆), and propane (C₃H₈) as foremost radiolysis products. However, several groups presented compelling evidence suggesting “larger hydrocarbons” were formed as well. The photolysis of methane with broad-band UV light implicated “high-order volatiles” possibly up to C₇ hydrocarbons.³⁶ Vibrational modes characteristics of di- and trisubstituted benzenes were observed in the MeV proton- and α -particle-irradiated methane ice, indicating the presence of polycyclic aromatic hydrocarbons (PAHs) naphthalene, phenanthrene, and anthracene.²⁶ In addition, this study was the only one to monitor the products as they sublimed into the gas phase following a temperature-programmed desorption (TPD), detecting saturated hydrocarbons from C₈H₁₈ to C₁₄H₃₀. Thus far, only a single study exploited Raman spectroscopy to examine the effects on the

Received: March 29, 2013

Accepted: May 21, 2013

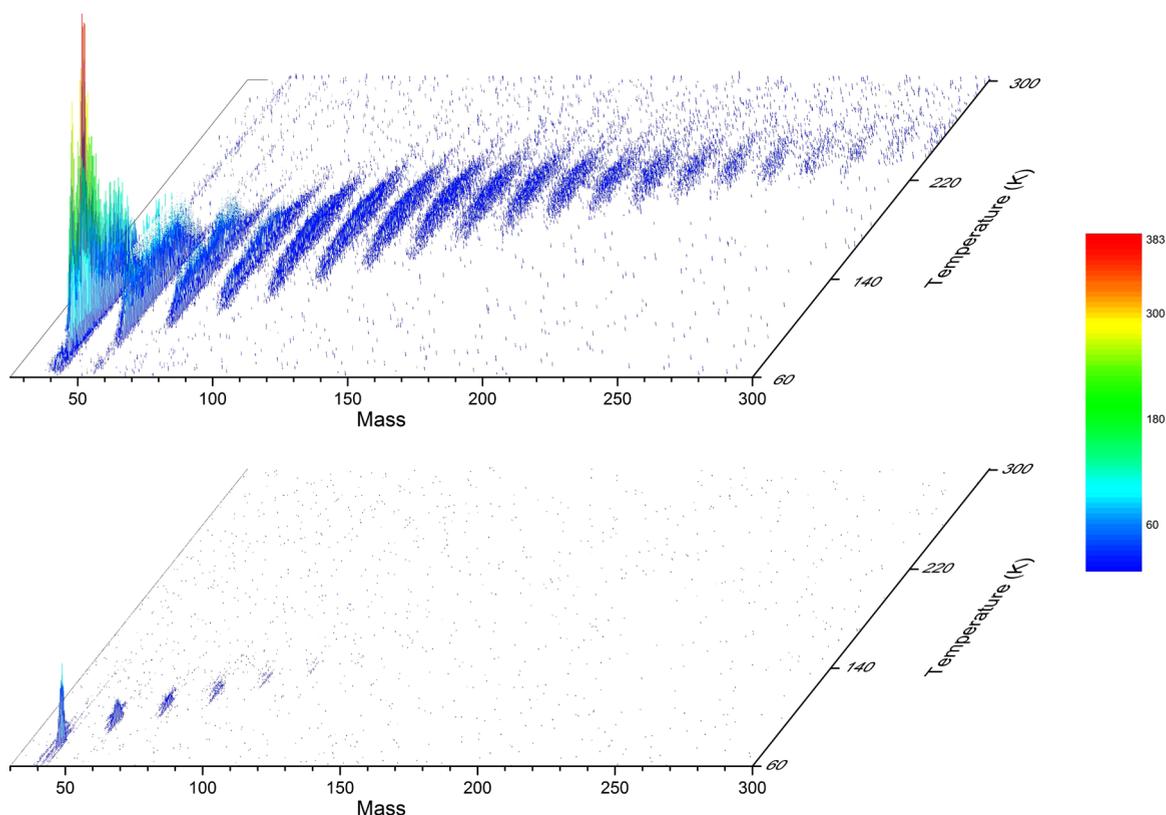


Figure 1. Reflectron time-of-flight mass spectra as a function of temperature of the newly formed hydrocarbon species subliming into the gas phase from the processed methane ices. (Top) High-dose experiment (12.5 eV per molecule); (bottom) low-dose experiment (1.5 eV per molecule). The ratio of the peak intensities for the C_3H_6 isomers (high-dose versus low-dose) shows a relative yield of 4:1 in the total amount formed.

organics synthesized within the ion irradiation of pure methane ice. The energy dose was quite extensive (1000 eV per molecule), and only a broad band was observed corresponding to the $C=C$ stretching mode of amorphous carbon.²⁵ Finally, a single experiment monitored the UVVIS reflectance spectra upon the irradiation of methane; unfortunately, this study only focused on the slope of the reflectance curve and the relationship of this to the observed colors of Centaurs and Trans-Neptunian objects; no products were identified.³⁷

The experiments summarized above have two commonalities. First, propane was the largest hydrocarbon distinctly identified *in situ* upon energetic processing of amorphous methane ice.^{23,24,28,33} Second, TPD studies of irradiated methane ices were able to only observe saturated hydrocarbons.^{26,27} This is a direct consequence of using a quadrupole mass spectrometer (QMS) coupled with electron impact ionization with 100 eV electrons, leading to extensive fragmentation of the parent molecule. In addition, the few experiments, that examined the organic residues^{30,34,35} employed *ex situ* and off line chromatography analysis (GC-MS; HPLC), with evidence of high-molecular-weight hydrocarbons.

With this Letter, we present a novel application of reflectron time-of-flight (ReTOF) mass spectrometry coupled to soft photoionization to probe the formulas of the molecules formed upon interaction of ionizing radiation with simple methane and D4-methane ices on line and *in situ*. Our study presents clear evidence of high-molecular-weight hydrocarbons of up to C_{22} , among them alkanes, alkenes, and alkynes/dienes giving an alternative route to their formation in often overlooked solid-state mechanistic in comparison to gas-phase reactions

involving poorly studied ion–molecule reactions. This study further provides a proof-of-concept for the novel adaptation of ReTOF mass spectrometry (ReTOF-MS) with single-photon (10.49 eV) soft photoionization to observe molecules, which are formed under conditions analogous to astrophysical environments of icy bodies upon exposure to ionizing radiation and then sublime upon a controlled-temperature desorption. Note that adaptations of TOF-MS have been implemented in the past to analyze astrophysically relevant surfaces.^{38–42} However, these experiments typically exploit highly focused small-power laser pulses or electrons to desorb the molecules from the solid into the gas phase. We, as of current, are not aware of any group photoionizing the molecules as they directly sublime following TPD under controlled conditions.

The success of our method is clearly demonstrated in Figure 1. Here, the mass spectrum as a function of temperature displays the intensity of the products subliming into the gas phase at a well-defined temperature during the warm-up phase after irradiating the methane sample with an average dose of 12.5 (top portion) and 1.5 eV per molecule (bottom portion). The first key variation to note between the high- and low-dose exposure is the distinctly diverse molecular composition of the newly formed molecules in the processed ices. The low-dose experiment yielded hydrocarbons only up to C_7H_{16} ($m/z = 100$ amu), whereas the most complex hydrocarbon group observed sublimating in the high-dose experiment corresponds to the C_{22} isomers, which sublimed around 220 K. Due to the extremely low count rates, we cannot clearly identify specific mass to charge ratios beyond the C_{13} hydrocarbon group. This limitation is most likely due to the extraction field not being uniform between the sample and first ion lens, a consequence

of the shape of the copper mask surrounding the silver target, which has been designed to minimize temperature gradients on the silver wafer from blackbody radiation from the main chamber. However, the instrument has sufficient capability to resolve specific mass to charge ratios for hydrocarbon groups between C_3 and C_{13} . Furthermore, signal corresponding to the hydrocarbons methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), acetylene (C_2H_2), and propane (C_3H_8) were not observed in the ReTOF experiments as their ionization energies are above the 10.49 eV threshold as set by our VUV light source. However, methane, ethane, and propane could be detected in the residual gas analyzer via electron impact ionization.

At this point, we would like to stress that the molecules within each hydrocarbon group (referred to as C_n) would not have been observed utilizing standard quadrupole mass spectroscopy coupled with electron impact ionization. Here, upon electron impact ionization, the fragmentation pattern and fragment masses of the saturated hydrocarbon (C_nH_{2n+2}) would conceal the parent ions of the unsaturated hydrocarbon analogues such as C_nH_{2n} and C_nH_{2n-2} . This is demonstrated here by selecting propane (C_3H_8 ; 44 amu) as a typical example (Figure 2). Here, the onsets of the ion counts for the C_3H_6 ($m/z = 42$) and C_3H_4 ($m/z = 40$) isomers are masked by the fragmentation ions from the propane parent (44 amu) formed upon electron impact ionization of propane. (Note that the mass 43 was shown here for clarity as the background signal from CO_2 is observed.) In addition, the largest mass observed in the QMS corresponded to isomers of pentane (C_5H_{12} , $m/z = 72$). The derived sublimation temperatures (onsets, not peaks) are plotted in Figure 3. Although the experimental error associated with the derived sublimation temperatures is ± 1 K, the rate of sublimation depends on the interaction between the substrate and the intramolecular interactions with surrounding species that may be present in the matrix.⁴³ Consequently, a table of sublimation temperatures is not reported here, and values should be taken as approximate in comparison to those of actual astrophysical ices. However, these temperatures are used here as a distinct identifier pertaining to a unique hydrocarbon group. From the results of this study, several trends are observed. First, the sublimation temperature increases with growing mass. Second, the saturated hydrocarbon (C_nH_{2n+2}) and unsaturated and/or cyclic hydrocarbon containing one double bond equivalent (C_nH_{2n}) have similar sublimation temperatures. Conversely, hydrocarbons with higher degrees of unsaturation (C_nH_m , where $m < 2n$) have significantly higher sublimation temperatures. This observation can be rationalized in terms of the stronger dipole–dipole interactions possibly taking place between the π -electrons of carbon–carbon double and triple bonds with the surrounding organic matrix. Last, albeit rather surprisingly, there was no strong indication of a temperature difference in the sublimation profiles between the deuterated and nondeuterated hydrocarbon analogues. This is shown in Figure 3, where the blue points represent the sublimation temperature for the deuterated compounds (shifted to their standard mass analogue for clarity), circles show derived points using the quadrupole mass spectrometer, and squares are the sublimation temperatures derived from the ReTOF mass spectrometer. The observation of similar sublimation temperatures for deuterated and nondeuterated hydrocarbon analogues was true as well for the high-dose experiments.

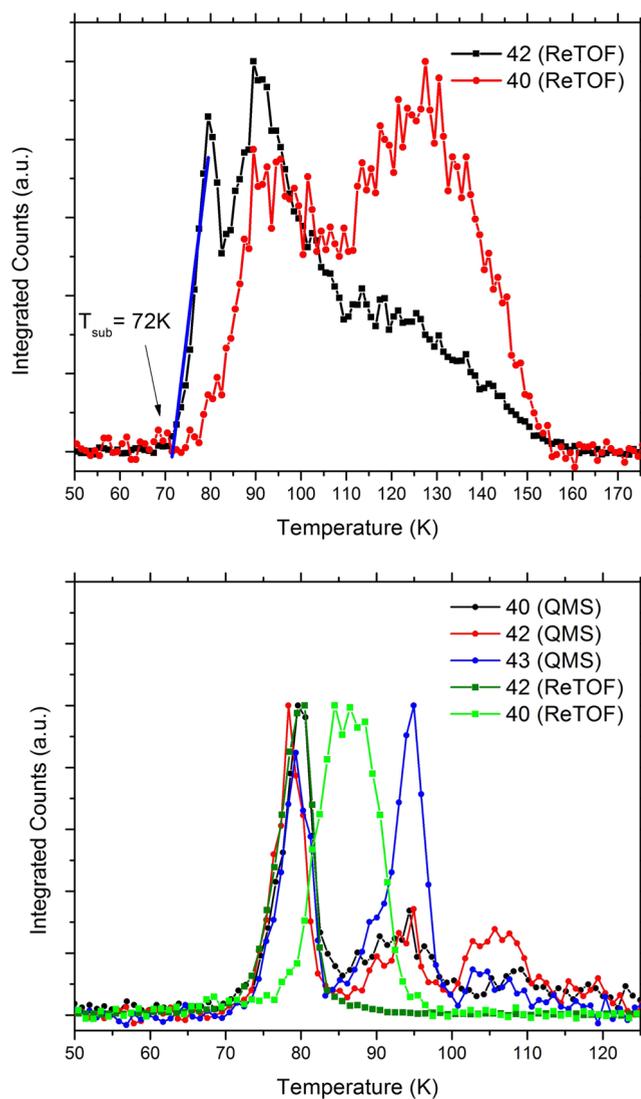


Figure 2. Normalized sublimation profiles of integrated ion counts at $m/z = 40$ and 42 corresponding to C_3H_4 and C_3H_6 isomers, respectively. The top portion of the figure originates from the high dose (12.5 eV per molecule), whereas the lower portion corresponds to the products observed from the low-dose experiment (1.5 eV per molecule). The sublimation temperature onsets were derived by fitting a line through the rise profile, as demonstrated for mass 42 (top portion, blue line). Both data sets have identical onsets within the error limits; however, the sublimation curves of the high-dose experiments show a broader sublimation range up to 150 K, suggesting a “hindered” sublimation from the ices due to an organic residue formed in the experiments, as previously observed.⁵⁵ QMS traces for ions at $m/z = 40$, 42 , and 43 are shown as well in the bottom portion to illustrate that no temperature difference can be resolved for C_3H_4 and C_3H_6 isomers in the QMS.

Another interesting feature is that the sublimation temperatures corresponding to masses 54, 56, and 58 amu (C_4H_6 , C_4H_8 , and C_4H_{10} isomers), formed within the C_4 hydrocarbon family, exhibited similar sublimation temperatures consistent in both the high- and low-dose experiments, implying the possibility that masses 54 and 56 amu are photofragments of the parent hydrocarbon, butane. In an effort to examine this possibility, the mass spectrum as a function of temperature for pure *n*-butane (C_4H_{10}) was collected under the identical experimental parameters. The mass spectrum as a function of

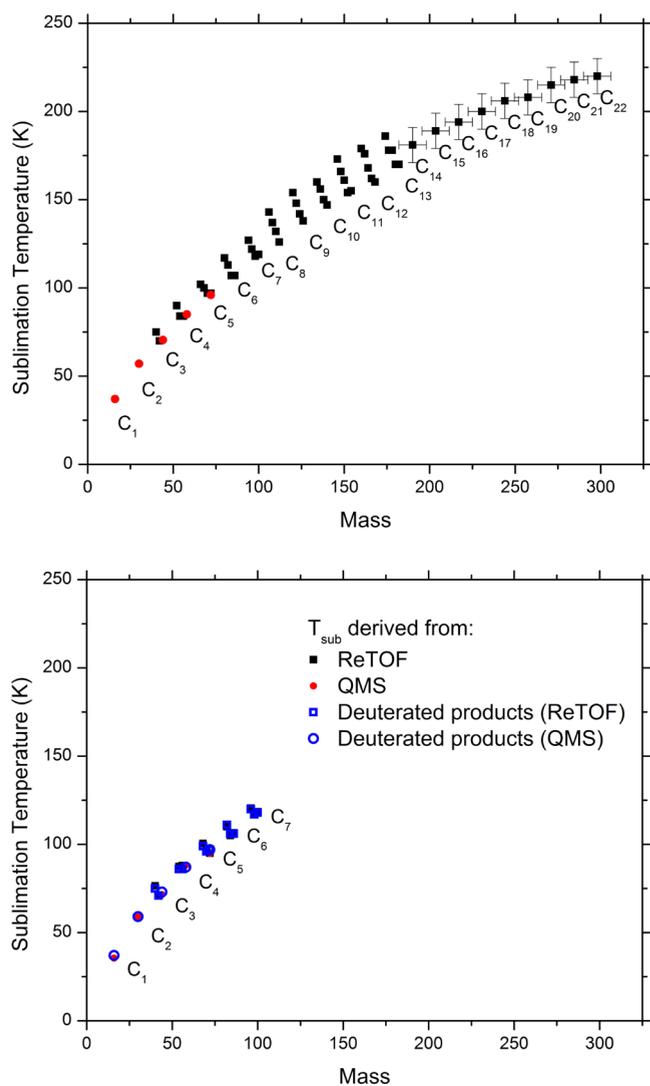


Figure 3. Sublimation temperatures for the observed hydrocarbons as a function of mass. Squares represent temperatures derived from the data collected utilizing the ReTOF mass spectrometer; circles represent temperatures derived from data collected utilizing the QMS operating in the standard residual gas analyzing mode. Blue colors represent the sublimation temperatures of the deuterated analogues, shifted in mass for comparison. The deuterated analogues did not exhibit a different sublimation temperature with respect to their standard isotopologues. We have chosen to leave out data points pertaining to the high-dose irradiation of deuterated methane for the sake of clarity (top portion). The sizes of the points correspond to the error of 1 K. The reflectron mass spectrometer was no longer able to resolve individual masses after 200 amu, which is reflected in the horizontal error bars. The top portion is from irradiating methane at 12.5 eV per molecule, while the bottom portion is from irradiation of methane at 1.5 eV per molecule.

temperature showed no signal at mass-to-charges of 54 or 56, indicating at the very least that isomers of molecular formula C₄H₈ are actually desorbed. Unfortunately, we cannot say with absolute certainty that C₄H₆ does not present a photofragment from butene isomers (C₄H₈) because these isomers were not explored. Similarly, the possibility of photofragmentation can be discounted for hydrocarbons with a high degree of unsaturation as these showed different sublimation temperatures larger than the reported uncertainties.

Although no distinct structural isomer of the hydrocarbon molecules was identified in this study, we can contemplate potential structures. Long-chain (aliphatic) hydrocarbons have a mode near 720 cm⁻¹, which is characteristic for carbon-carbon chains holding at least four carbon atoms; this absorption was not observed in this study, indicating that aliphatic hydrocarbons are not likely formed in the experiments. On the other hand, this conclusion implies that branched hydrocarbons with side chains of less than four hydrocarbons are likely synthesized. Similarly, none of the previous experiments identified the 720 cm⁻¹ band in processed methane ices, further implying that large, linear hydrocarbons are not formed in the processed ices. Further evidence can be inferred from the absorption ratios of the peak intensities for the asymmetric carbon-hydrogen stretch from the methyl group (R-CH₃) at 2960 cm⁻¹ and from the methylene group (R-CH₂-R) at the 2850 cm⁻¹ band. The intensity ratios of the integrated absorptions are consistent throughout the overall sublimation process, indicating that branched hydrocarbons are likely formed following irradiation and warm up.³⁶ Interestingly, a recent study demonstrated that unidentified infrared emission (UIR) spectral features might be associated with amorphous organic solids holding aromatic units randomly linked together with aliphatic hydrocarbon chains, thus suggesting that polycyclic aromatic hydrocarbons (PAHs) might not be the primary source.⁴⁴

To summarize, high-mass hydrocarbons of up to C₂₂ are easily formed upon irradiating methane ices with low irradiation doses, and their presence is masked within FTIR spectroscopy due to the similar group frequencies of their vibrational modes. Here, we have identified over 50 hydrocarbons with distinct *m/z* ratios containing up to 22 carbon atoms, with further evidence implying even more complex hydrocarbons synthesized based on single-photon ionization of the subliming molecules. A simple search on the NIST database for any of the observed isomers within the C₁₂H_{*n*} (26 > *n*_{even} > 18) group alone yields over 900 isomers.⁴⁵ Despite the numerous experimental investigations probing the effect of ionizing radiation on simple hydrocarbon astrophysical ice analogues, there is still a vast quantity of information to be gained. Utilizing the experimental techniques described above, we may finally be able to make considerable progress toward deciphering what compounds of the numerous possible isomers formed by exploiting the ReTOF spectroscopic technique. Moreover, future experiments involving in situ probing via soft laser ablation⁴⁰ coupled with molecule-specific ionization schemes such as resonance-enhanced multiphoton ionization (REMPI) will be conducted in order to elucidate the possible formation of PAHs.⁴⁶⁻⁴⁸ Finally, our pulsed coherent VUV light source has been designed to generate tunable VUV photons utilizing resonance-enhanced nonlinear four wave mixing, which will be implemented in future studies to aid in the identification of specific isomers based upon their distinctive ionization energies. In conclusion, our investigation has shown that the information contained in the previously mentioned experiments summarized above actually represents only a minor fraction of that possible, so that, given the available technology and established techniques, we may finally probe further into a door that may have been prematurely closed.

EXPERIMENTAL SECTION

The experiments were conducted in a contamination-free ultrahigh vacuum (UHV) stainless steel chamber (Figure 4),

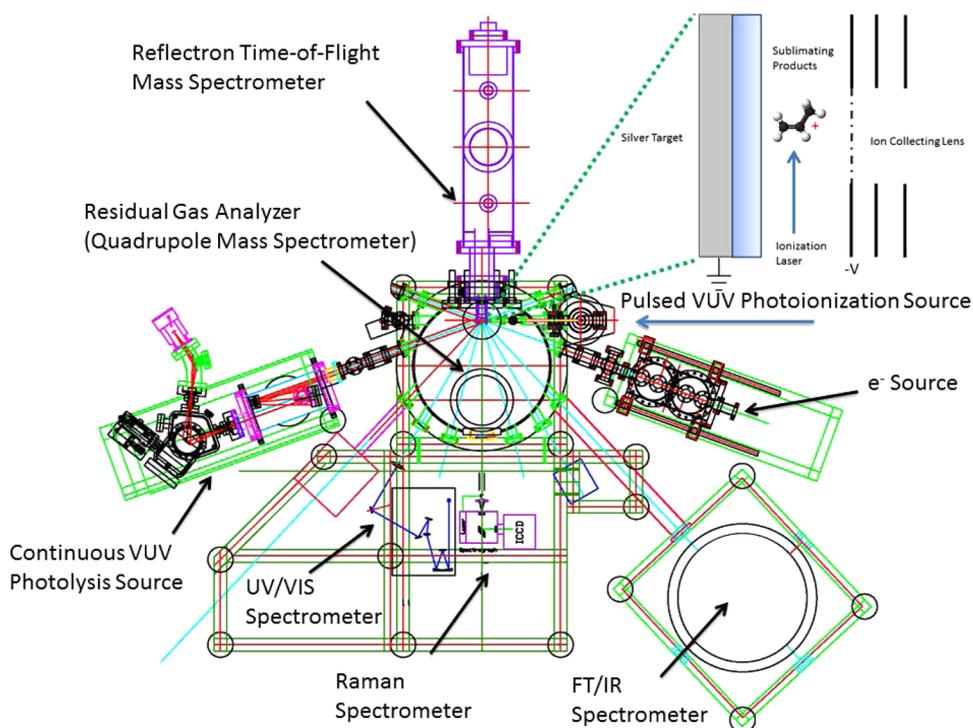


Figure 4. Top view schematic of the main chamber including the cryogenic target (point of converging lines), analytical instruments, and ionizing radiation modules. The irradiation sources are aligned with respect to the low-temperature target to allow for the simultaneous in situ monitoring of IR, Raman, and UV–vis spectroscopies (not discussed in this Letter). Upon exposing the astrophysical ice analogue to ionizing radiation, the cold head is rotated 180° to face the ReTOF mass spectrometer and heated, allowing the newly formed products to sublime where upon they were ionized and mass analyzed. The inset (top right) shows the geometry of the ReTOF ion source lens with respect to the target and ionization laser.

which can be evacuated to a base pressure of typically 5×10^{-11} Torr using oil-free magnetically suspended turbomolecular pumps and dry scroll backing pumps. A closed-cycle helium refrigerator cools a silver mirror to an ultimate temperature of 5.5 ± 0.1 K; this mirror acts as a substrate of the ices and is freely rotatable within the horizontal center plane of the chamber. Methane (Specialty Gases of America, 99.999%) or D4-methane (CDN Isotopes, 99.9% D) gas was then introduced through a glass capillary at a pressure of 5×10^{-8} Torr for approximately 5 min, yielding an ice sample of 500 ± 50 nm. The thickness of the sample was determined in situ using laser interferometry;⁴⁹ an index of refraction of 1.329 was used.⁵⁰ The methane and D4-ices were irradiated with 5 keV electrons isothermally at 5.5 ± 0.1 K in one set of experiments for 3 h at 92 nA (high dose) and in a second set of experiments for 1 h at 30 nA (low dose) over an area of 0.9 ± 0.1 cm² and an angle of incidence of 70° relative to the surface normal. The average dose per molecule deposited into the sample was determined from Monte Carlo (CASINO) simulations.⁵¹ The total energy deposited into the amorphous ice was calculated at 12.5 ± 0.8 eV per molecule (CH₄) [9.6 ± 1.0 eV per molecule (CD₄)] for the high-dose experiments and 1.5 ± 0.2 eV per molecule (CH₄) [1.2 ± 0.4 eV per molecule (CD₄)] and for the low-dose experiments. It should be noted here that in determining the thickness of the pristine D4-methane ice and consequently the dose, a density of 0.674 g cm⁻³ for D4-methane²⁶ was used and that the index of refraction was assumed to be identical to that of methane (1.329). These doses correspond to approximately 10³ (low dose) and 10⁴ (high dose) years for outer solar system ice bodies at 40 AU⁵² and 10⁵–10⁶ years for an interstellar ice grain.⁵³ During the irradiation, the chemical modifications of the ices were

monitored in situ via a Fourier transform infrared (FTIR) spectrometer (Nicolet 6700), with spectra collected every two minutes in the range of 6000–400 cm⁻¹ at a resolution of 4 cm⁻¹. A quadrupole mass spectrometer (Extrel, Model 5221) operating in residual-gas analyzer mode in the mass range of 1–500 amu was employed, allowing for the detection species in the gas phase via electron impact ionization (100 eV). After the irradiation, the sample was heated at a rate of 0.5 K min⁻¹. The sublimed products were also monitored after single-photon ionization (10.49 eV) in a ReTOF spectrometer.

Pulsed coherent vacuum ultraviolet (VUV) light at 118.2 nm (10.49 eV) was generated via a frequency tripling process ($\omega_{\text{vuv}} = 3\omega_1$) utilizing xenon as the nonlinear medium. Here, ω_1 represents the fundamental frequency from the third-harmonic (354.6 nm) output of a high-power pulsed neodymium-doped yttrium aluminum garnet laser (Nd:YAG, Spectraphysics, PRO-250) operated at 30 Hz. The pulsed xenon gas jet was housed in a mixing chamber evacuated by a 400 L/s turbomolecular pump. Typical operating pressures during VUV generation are on the order of 3×10^{-4} Torr. The pulsed valve was connected to the middle entrance of a T-shaped channel with a 1 mm diameter at 25 mm in length. Here, xenon (99.999%) released by the pulsed valve enters the T-shaped adapter and exits symmetrically, thereby forming a pulsed mixing “cell” in line with the propagating ω_1 pulse. The ω_1 laser beam was empirically focused into the adapter on the valve to yield optimal VUV intensity. From here, the generated VUV radiation was separated from the fundamental ω_1 beam, utilizing an off-axis lithium fluoride (LiF) plano-convex lens⁵⁴ (ISP Optics, LF-PX-38–150), and directed to about 1 mm above the ice surface, where the VUV light photoionizes the subliming molecules. The ReTOF spectrometer (Jordan TOF

Products, Inc.) with a customized electrostatic lens setup for the ion source assembly was utilized to identify the ionized product molecules after sublimation via their arrival times. Typically, ions are extracted into the focusing region with a repeller plate (positive voltage) and an extraction plate (negative voltage). However, as the silver target is sandwiched to the cold head with indium foil to ensure optimum thermal conductivity, no voltage can be applied to the silver target without floating the entire chamber as they have a common ground. To overcome this, the field between the repeller and extractor plate was simply held at an overall negative potential while compensating for the electrostatics lens downstream. Once the molecules thermally sublimated and were ionized by the VUV light (10.49 eV) via single-photon ionization, the ions were then resolved into their respective mass-to-charge ratios based on their arrival times. The ions were detected utilizing a multichannel plate with a dual chevron configuration. From here, the signals were amplified using a fast preamplifier (Ortec 9305) and shaped with a 100 MHz discriminator. The ReTOF spectra were recorded with a personal-computer-based multichannel scaler (FAST ComTec, P7888-1 E) using a bin width of 4 ns, triggered at 30 Hz (Quantum Composers, 9518) with 3600 sweeps per mass spectrum per 1 K change in temperature. The calibration of the ReTOF was done with the following molecules: ammonia (NH₃), hydrogen sulfide (H₂S), allene (C₃H₄), propene (C₃H₆), 1,3-butadiene (C₄H₆), *n*-butane (C₄H₁₀), *n*-pentane (C₅H₁₂), *n*-hexane (C₆H₁₄), vinyl bromide (C₂H₃Br), and iodotrifluoromethane (CF₃I). (The observation of butane is either from nonresonant multiphoton ionization, as the ionization energy of butane (10.53 eV) is slightly above the VUV energy used in this study, or a lowering of the ionization energy due to a dc field induced Stark shift.) No evidence of photofragmentation was observed for any of the above-mentioned species. A mass resolution ($m/\Delta m$) of 80 for the spectrometer was calculated based on the observed, fwhm (0.5) at $m/z = 40$ and fwhm (1.5) at $m/z = 180$, profiles.

AUTHOR INFORMATION

Corresponding Author

*E-mail: brantmj@hawaii.edu (B.M.J.); ralfk@hawaii.edu (R.I.F.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the W.M Keck Foundation and the University of Hawaii for their financial support and the reviewers for their insightful and helpful comments.

REFERENCES

- (1) Lacy, J. H.; Carr, J. S.; Evans, N. J., II; Baas, F.; Achtermann, J. M.; Arens, J. F. Discovery of Interstellar Methane — Observations of Gaseous and Solid CH₄ Absorption toward Young Stars in Molecular Clouds. *Astrophys. J.* **1991**, *376*, 556–560.
- (2) Boogert, A. C. A.; Schutte, W. A.; Tielens, A. G. G. M.; Whittet, D. C. B.; Helmich, F. P.; Ehrenfreund, P.; Wesselius, P. R.; de Graauw, T.; Prusti, T. Solid Methane Toward Deeply Embedded Protostars. *Astron. Astrophys.* **1996**, *315*, L377–L380.
- (3) Gibb, E. L.; Whittet, D. C. B.; Boogert, A. C. A.; Tielens, A. G. G. M. Interstellar Ice: The Infrared Space Observatory Legacy. *Astrophys. J. Suppl. Ser.* **2004**, *151*, 35–73.
- (4) Öberg, K. I.; Boogert, A. C. A.; Pontoppidan, K. M.; Blake, G. A.; Evans, N. J.; Lahuis, F.; Dishoek, E. F. v. The c2d Spitzer

Spectroscopic Survey of Ices around Low-Mass Young Stellar Objects. III. CH₄. *Astrophys. J.* **2008**, *678*, 1032–1041.

- (5) Cruikshank, D. P.; Roush, T. L.; Owen, T. C.; Geballe, T. R.; de Bergh, C.; Schmitt, B.; Brown, R. H.; Bartholomew, M. J. Ices on the Surface of Triton. *Science* **1993**, *261*, 742–745.

- (6) Brown, R. H. Surface Composition and Photometric Properties of Triton. In *Neptune and Triton*; Cruikshank, D. P., Ed.; University of Arizona: Arizona, 1995.

- (7) Tegler, S. C.; Grundy, W. M.; Olkin, C. B.; Young, L. A.; Romanishin, W.; Cornelison, D. M.; Khodadadkouchaki, R. Ice Mineralogy across and into the Surfaces of Pluto, Triton, and Eris. *Astrophys. J.* **2012**, *751*, 76–86.

- (8) Barucci, M. A.; Merlin, F.; Guilbert, A.; de Bergh, C.; Alvarez-Candal, A.; Hainaut, O.; Doressoundiram, A.; Dumas, C.; Owen, T.; Coradini, A. Surface Composition and Temperature of the TNO Orcus. *Astron. Astrophys.* **2008**, *479*, L13–L16.

- (9) Trujillo, C. A.; Brown, M. E.; Rabinowitz, D. L.; Geballe, T. R. Near-Infrared Surface Properties of the Two Intrinsically Brightest Minor Planets: (90377) Sedna and (90482) Orcus. *Astrophys. J.* **2005**, *627*, 1057–1065.

- (10) Delsanti, A.; Merlin, F.; Guilbert-Lepoutre, A.; Bauer, J.; Yang, B.; Meech, K. J. Methane, Mmonia, and Their Irradiation Products at the Surface of an Intermediate-Size KBO? *Astron. Astrophys.* **2010**, *520*, A40.

- (11) Merlin, F.; Alvarez-Candal, A.; Delsanti, A.; Fornasier, S.; Barucci, M. A.; DeMeo, F. E.; de Bergh, C.; Doressoundiram, A.; Quirico, E.; Schmitt, B. Stratification of Methane Ice on Eris' Surface. *Astron. J.* **2009**, *137*, 315–328.

- (12) Tegler, S. C.; Cornelison, D. M.; Grundy, W. M.; Romanishin, W.; Abernathy, M. R.; Bovyn, M. J.; Burt, J. A.; Evans, D. E.; Maleszewski, C. K.; Thompson, Z.; et al. Methane and Nitrogen Abundances on Pluto and Eris. *Astrophys. J.* **2010**, *725*, 1296–1305.

- (13) Cruikshank, D. P. The Surface of Pluto and Charon. In *Pluto and Charon*; Stern, S. A., Tholen, D. J., Eds.; University of Arizona: Arizona, 1997.

- (14) Douté, S.; Schmitt, B.; Quirico, E.; Owen, T. C.; Cruikshank, D. P.; de Bergh, C.; Geballe, T. R.; Roush, T. L. Evidence for Methane Segregation at the Surface of Pluto. *Icarus* **1999**, *142*, 421–444.

- (15) Brown, M. E.; Barkume, K. M.; Blake, G. A.; Schaller, E. L.; Rabinowitz, D. L.; Roe, H. G.; Trujillo, C. A. Methane and Ethane on the Bright Kuiper Belt Object 2005 FY9. *Astron. J.* **2007**, *133*, 284–289.

- (16) Licandro, J.; Pinilla-Alonso, N.; Pedani, M.; Oliva, E.; Tozzi, G. P.; Grundy, W. M. The Methane Ice Rich Surface of Large TNO 2005 FY₉: A Pluto-Twin in the Trans-Neptunian Belt? *Astron. Astrophys.* **2006**, *445*, L35–L38.

- (17) Schaller, E. L.; Brown, M. E. Detection of Methane on Kuiper Belt Object (50000) Quaoar. *Astrophys. J. Lett.* **2007**, *670*, L49–L51.

- (18) Dalle Ore, C. M.; Barucci, M. A.; Emery, J. P.; Cruikshank, D. P.; Dalle Ore, L. V.; Merlin, F.; Alvarez-Candal, A.; de Bergh, C.; Trilling, D. E.; Perna, D.; et al. Composition of KBO (50000) Quaoar. *Astron. Astrophys.* **2009**, *501*, 349–357.

- (19) Brown, M. E.; Burgasser, A. J.; Fraser, W. C. The Surface Composition of Large Kuiper Belt Object 2007 OR₁₀. *Astrophys. J. Lett.* **2011**, *738*, L26.

- (20) Brown, M. E. The Compositions of Kuiper Belt Objects. *Annu. Rev. Earth Planet. Sci.* **2012**, *40*, 467–494.

- (21) Brown, R. H.; Cruikshank, D. P.; Pendleton, Y.; Veeder, G. J. Surface Composition of Kuiper Belt Object 1993SC. *Science* **1997**, *276*, 937–939.

- (22) Samuelson, R. Atmospheric Ices. In *Solar System Ices*; Schmitt, B., de Bergh, C., Festou, M., Eds.; Kluwer Academic: The Netherlands, 1998.

- (23) de Barros, A. L. F.; Bordalo, V.; Seperuelo Duarte, E.; da Silveira, E. F.; Domaracka, A.; Rothard, H.; Boduch, P. Cosmic Ray Impact on Astrophysical Ices: Laboratory Studies on Heavy Ion Irradiation of Methane. *Astron. Astrophys.* **2011**, *531*, A160–169.

- (24) Baratta, G. A.; Leto, G.; Palumbo, M. E. A Comparison of Ion Irradiation and UV Photolysis of CH₄ and CH₃OH. *Astron. Astrophys.* **2002**, *384*, 343–349.
- (25) Ferini, G.; Baratta, G. A.; Palumbo, M. E. A Raman Study of Ion Irradiated Icy Mixtures. *Astron. Astrophys.* **2004**, *414*, 757–766.
- (26) Kaiser, R. I.; Eich, G.; Gabrysch, A.; Roessler, K. Theoretical and Laboratory Studies on the Interaction of Cosmic-Ray Particles with Interstellar Ices. II. Formation of Atomic and Molecular Hydrogen in Frozen Organic Molecules. *Astrophys. J.* **1997**, *484*, 487–498.
- (27) Kaiser, R. I.; Roessler, K. Theoretical and Laboratory Studies on the Interaction of Cosmic-Ray Particles with Interstellar Ices. III. Suprathermal Chemistry-Induced Formation of Hydrocarbon Molecules in Solid Methane (CH₄), Ethylene (C₂H₄), and Acetylene (C₂H₂). *Astrophys. J.* **1998**, *503*, 959–975.
- (28) Baratta, G. A.; Domingo, M.; Ferini, G.; Leto, G.; Palumbo, M. E.; Satorre, M. A.; Strazzulla, G. Ion Irradiation of CH₄-Containing Icy Mixtures. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2003**, *209*, 283–287.
- (29) Brunetto, R.; Barucci, M. A.; Dotto, E.; Strazzulla, G. Ion Irradiation of Frozen Methanol, Methane, and Benzene: Linking to the Colors of Centaurs and Trans-Neptunian Objects. *Astrophys. J.* **2006**, *644*, 646–650.
- (30) Lecluse, C.; Robert, F.; Kaiser, R.-I.; Roessler, K.; Pillinger, C. T.; Javoy, M. Carbon Isotopes of Irradiated Methane Ices: Implications for Cometary ¹²C/¹³C ratio. *Astron. Astrophys.* **1998**, *330*, 1175–1179.
- (31) Bennett, C. J.; Jamieson, C. S.; Osamura, Y.; Kaiser, R. I. Laboratory Studies on the Irradiation of Methane in Interstellar, Cometary, and Solar System Ices. *Astrophys. J.* **2006**, *653*, 792–811.
- (32) Huels, M. A.; Parenteau, L.; Bass, A. D.; Sanche, L. Small Steps on the Slippery Road to Life: Molecular Synthesis in Astrophysical Ices Initiated by Low Energy Electron Impact. *Int. J. Mass Spectrom.* **2008**, *277*, 256–261.
- (33) Gerakines, P. A.; Schutte, W. A.; Ehrenfreund, P. Ultraviolet processing of Interstellar Ice Analogs. *Astron. Astrophys.* **1996**, *312*, 289–305.
- (34) Davis, D. R.; Libby, W. F. Positive-Ion Chemistry: High Yields of Heavy Hydrocarbons from Solid Methane by Ionizing Radiation. *Science* **1964**, *144*, 991–992.
- (35) Davis, D. R.; Libby, W. F.; Meinschein, W. G. Chemistry of Positive Ions. VI. Positive-Ion Chemistry in Solid Methane. *J. Chem. Phys.* **1966**, *45*, 4481–4492.
- (36) Gerakines, P. A.; Schutte, W.; Ehrenfreund, P. Ultraviolet Processing of Interstellar Ices. *Astron. Astrophys.* **1996**, *312*, 389–305.
- (37) Baratta, G. A.; Brunetto, R.; Leto, G.; Palumbo, M. E.; Spinella, F.; Strazzulla, G. Raman Spectroscopy of Ion-Irradiated Astrophysically Relevant Materials. *J. Raman Spectrosc.* **2008**, *39*, 211–219.
- (38) Toftmann, B.; Rodrigo, K.; Schou, J.; Pedrys, R. High Laser-Fluence Deposition of Organic Materials in Water Ice Matrices by “MAPLE”. *Appl. Surf. Sci.* **2005**, *247*, 211–216.
- (39) Ricketts, C. L.; Contreras, C. S.; Walker, R. L.; Salama, F. The Coupling of a Reflectron Time-of-Flight Mass Spectrometer with a Cosmic Simulation Chamber: A Powerful New Tool for Laboratory Astrophysics. *Int. J. Mass Spectrom.* **2011**, *300*, 26–30.
- (40) Gudipati, M. S.; Yang, R. In-Situ Probing of Radiation-Induced Processing of Organics in Astrophysical Ice Analogs—Novel Laser Desorption Laser Ionization Time-of-Flight Mass Spectroscopic Studies. *Astrophys. J. Lett.* **2012**, *756*, L24–L29.
- (41) Chen, Y.; Aleksandrov, A.; Orlando, T. M. Probing Low-Energy Electron Induced DNA Damage Using Single Photon Ionization Mass Spectrometry. *Int. J. Mass Spectrom.* **2008**, *277*, 314–320.
- (42) Getty, S. A.; Brinckerhoff, W. B.; Cornish, T.; Li, X.; Floyd, M.; Arevalo, R.; Elsil, J.; Callahan, M. P. Two-Step Laser Time-of-Flight Mass Spectrometry to Elucidate Organic Diversity in Planetary Surface Materials. 44th Lunar and Planetary Science Conference, 2013; p 2676.
- (43) Collings, M. P.; Anderson, M. A.; Chen, R.; Dever, J. W.; Viti, S.; Williams, D. A.; McCoustra, M. R. S. A Laboratory Survey of the Thermal Desorption of Astrophysically Relevant Molecules. *Mon. Not. R. Astron. Soc.* **2004**, *354*, 1133–1140.
- (44) Kwok, S.; Zhang, Y. Mixed Aromatic-Aliphatic Organic Nanoparticles as Carriers of Unidentified Infrared Emission Features. *Nature* **2011**, *479*, 80–83.
- (45) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. *Neutral Thermochemical Data*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2010.
- (46) Messenger, S.; Amari, S.; Gao, X.; Walker, R. M.; Clemett, S. J.; Chillier, X. D. F.; Zare, R. N.; Lewis, R. S. Indigenous Polycyclic Aromatic Hydrocarbons in Circumstellar Graphite Grains from Primitive Meteorites. *Astrophys. J.* **1998**, *502*, 284–295.
- (47) Spencer, M. K.; Hammond, M. R.; Zare, R. N. Laser Mass Spectrometric Detection of Extraterrestrial Aromatic Molecules: Mini-Review and Examination of Pulsed Heating Effects. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18096–18101.
- (48) 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* **1993**, *262*, 721–725.
- (49) Fulvio, D.; Sivaraman, B.; Baratta, G. A.; Palumbo, M. E.; Mason, N. J. Novel Measurements of Refractive Index, Density and Mid-Infrared Integrated Band Strengths for Solid O₂, N₂O and NO₂:N₂O₄ Mixtures. *Spectrochim. Acta, Part A* **2009**, *72*, 1007–1013.
- (50) Brunetto, R.; Caniglia, G.; Baratta, G. A.; Palumbo, M. E. Integrated Near-Infrared Band Strengths of Solid CH₄ and Its Mixtures with N₂. *Astrophys. J.* **2008**, *686*, 1480–1485.
- (51) Hovington, P.; Drouin, D.; Gauvin, R. CASINO: A New Monte Carlo Code in C Language for Electron Beam Interaction — Part I: Description of the Program. *Scanning* **1997**, *19*, 1–14.
- (52) Cooper, J. F.; Christian, E. R.; Richardson, J. D.; Wang, C. Proton Irradiation of Centaur, Kuiper Belt, and Oort Cloud Objects at Plasma to Cosmic Ray Energy. *Earth, Moon, Planets* **2003**, *92*, 261–277.
- (53) Strazzulla, G.; Johnson, R. E. Irradiation Effects on Comets and Cometary Debris. In *Comets in the Post-Halley Era*; Newburn, R. L., Jr., Neugebauer, M., Rahe, J., Eds.; Springer: The Netherlands, 1991; Vol. 167, pp 243–275.
- (54) VonDrasek, W. A.; Okajima, S.; Hessler, J. P. Efficient Monochromator to Isolate VUV Light Generated by Four-Wave Mixing Techniques. *Appl. Opt.* **1988**, *27*, 4057–4061.
- (55) Kaiser, R. I.; Maksyutenko, P.; Ennis, C.; Zhang, F.; Gu, X.; Krishtal, S. P.; Mebel, A. M.; Kostko, O.; Ahmed, M. Untangling the Chemical Evolution of Titan’s Atmosphere and Surface—From Homogeneous to Heterogeneous Chemistry. *Faraday Discuss.* **2010**, *147*, 527–552.