Photochemistry of caged molecules: CD_3Cl@Ice

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(Received 19 December 2002; accepted 2 April 2003)

Hydrocarbons formation following UV photo-induced dissociation of CD_3Cl trapped and caged inside thin amorphous solid water (ASW) layers on Ru(001) has been measured for the first time under well-defined UHV conditions. Stable products such as C_2D_6, CHD_3, CD_3CD_2Cl, CD_3OH were detected via post-irradiation temperature programmed desorption. Specific reactivity pathways for the various photo-products were identified based on excitation wavelengths, ASW layer thickness, and parent molecules initial coverage dependence. Cross sections of $(1-6)\times10^{-19}$ cm^2 and $(1-3)\times10^{-20}$ cm^2 at 193 nm and 248, respectively, were measured. These photo-induced phenomena of caged molecules are discussed as a possible mechanism for the formation of hydrocarbons in interstellar space. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1577534]

I. INTRODUCTION

The origin of hydrocarbons in interstellar space as a possible initial step for the origin of life has fascinated researchers for ages, therefore, has been the subject of intensive research by various disciplines of science.[1–7] Among the ideas that have been considered, UV light-induced reactions at the bulk of molecular ice such as H_2O, CH_3OH, CO_2, NH_3, that have gradually accumulated on the surface of submicron size solid particles (grains) in interstellar space is particularly interesting and can be reproduced in laboratory conditions.[2,5] These studies have very recently resulted in the remarkable discovery of the formation of amino acids, the essential molecular components of living organisms on Earth.[6,7] Most of the model laboratory studies performed so far have investigated relatively thick layers of molecular ice; therefore, details of the molecular structure at or near the solid surface were often missing.

Photochemical events reported in the literature to take place on bare metallic or oxide surfaces under ultrahigh vacuum (UHV) conditions[8,9] included intact molecular desorption or dissociation. In the latter, fragments are often ejected to the gas phase; therefore no significant bond rearrangement can occur to form new molecular species. Bimolecular systems, on the other hand, such as CH_3Br and CH_3I coadsorbed with CCl_4 on Ag(111), were demonstrated to result in actual bonds rearrangement to form CH_3Cl.[10]

Caging of weakly bound adsorbates within thin layers of amorphous solid water (ASW) or ice on solid surfaces was recently reported. The trapped molecules explosively desorb upon heating, having an extremely narrow temperature programmed desorption (TPD) peak width of 2 K near the onset of ice desorption at 165 K. The first demonstration of a caged molecular system was that of N_2@Ice on Ru(001),[11] and later the same behavior was shown for CCl_4,[12] O_2,[13] and CD_3Cl.[14] The last example represents a case of strong hydrophobic, repulsive interactions between dipolar adsorbates having an almost identical dipole moment: CD_3Cl and H_2O. It results in the compression, reorientation, and eventually encapsulation and caging of the methyl chloride within the accumulating water layers.[14]

In this paper we describe the unique and rich photochemistry that takes place when dipolar molecules—methyl chloride in this case, compressed and caged inside ASW layers, are exposed to UV irradiation at 248 and 193 nm. The hydrocarbons formed as a result of hot methyl radical chemistry, such as CHD_3, C_2D_6, CD_3OH, and CD_3CD_2Cl, following photodissociation of the parent methyl chloride inside the cage, are discussed as a possible pathway for the formation of interstellar hydrocarbons.

II. EXPERIMENT

The photochemistry experiments described below were performed in an ultrahigh vacuum (UHV) apparatus, described elsewhere in detail.[15] It is equipped with LEED/Auger, and a quadrupole mass spectrometer (QMS) that is glass shrouded with a 3 mm aperture to improve sensitivity and selectivity to molecules desorbing only from the sample. This instrumentation enables the determination of sample cleanliness and long range order and high sensitivity ΔP-TPD studies. Adsorbates orientation could be determined by means of a Kelvin probe, operated in a $\Delta\varphi$-TPD mode, as explained elsewhere in detail.[14] In addition, a mini excimer laser provides 2.5 ns long pulses at 248 and 193 nm of about 1 mj/pulse, and variable repetition rate up to 100 Hz for the photo-excitation studies. The analysis of the photo-products was based on post-irradiation ΔP-TPD. The simultaneous detection of up to 12 masses could be performed in a single TPD run. The Ru(001) sample, oriented to within 0.5° of the (001) plane, could be cooled down to 82 K by pumping over a liquid nitrogen reservoir. Temperature was determined via a C-type thermocouple (W5%Re/W26%Re) and controlled to within 1° using an ac resistive heating routine.

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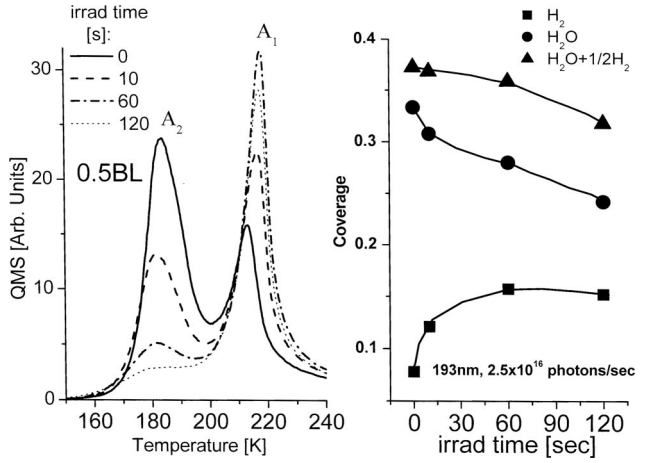

FIG. 1. A TPD of 0.5 BL H_2O/Ru(001) following irradiation times of 0–120 s of 193 nm photons. The heating rate was 1 K/s. To the right are the resulting coverages of hydrogen and water. The lines through the data points are as a guide to the eye. The sum of $\theta(H_2O)+1/2\ \theta(H_2)$ suggests that up to 60 s the dominant process is dissociation.

III. RESULTS AND DISCUSSION

The cage formation process of CD_3Cl under gradually thicker layers of (ASW) on Ru(001) was recently described in detail.[14] Briefly, for water coverage of more than ~3 bilayers (BL), a narrow TPD peak emerges near 165 K, at the onset of ice desorption. This peak of caged molecules eventually contains all the methyl chloride preadsorbed on the surface, with no sign of low-temperature desorption of molecules that are directly bonded to the metallic surface. The encapsulated methyl chlorides desorb only as parent molecules, with no sign of any thermal reactivity such as dissociation. This conclusion is reached from the lack of mass 4 (D_2) in the resulting TPD, an expected product if CD_3 radicals were accumulated on the surface as a result of parent molecule thermal dissociation on the Ru(001) surface.[15]

Before discussing the photochemistry within the cage, it is important to note that the cage material, namely water molecules undergo photodissociation at an excitation wavelength of 193 nm. At a photon wavelength of 248 nm, no photodissociation of adsorbed water takes place.

Irradiating the first bilayer of water adsorbed on Ru(001) at 82 K, by UV photons at 193 nm results in molecular desorption from and dissociation at the A_2 TPD sites within the first bilayer, leading to practically total removal of water molecules from this site following exposure to more than 5×10^{18} photons. All this is demonstrated in Fig. 1. The removal of the A_2 water molecules is associated with an increase in the intensity of the A_1 desorption peak. This increase, together with the accumulation of hydrogen on the ruthenium surface (calculated from the integrated hydrogen TPD peak near 300 K, see Fig. 1) as a result of photodissociation of water molecules in the A_2 sites, accounts well for the diminishing A_2 TPD peak up to 60 s of irradiation time (equivalent to 1.5×10^{18} 193 nm photons). Beyond this exposure time to the UV photons, water molecules seem to undergo a preferential photodesorption. This observation is supported by the saturation in the hydrogen uptake beyond this exposure time. It is interesting to note a recent report,[18] where it was suggested, based on DFT calculations, that the A_1 TPD peak is associated with the presence of OH_{ad} and H_{ad} fragments on the surface. As shown in Fig. 1, the clear increase of the A_1 peak following photodissociation is an indirect support for this observation. The presence of hydrogen atoms near the caged methyl chloride molecules and on the ruthenium surface can explain some of the photoproducts we obtained that will be discussed below.

Once the CD_3Cl@Ice cage has been prepared and is stable at 82 K, it was irradiated by photons at 248 or 193 nm. Typical pulse energy used for these measurements was less than 2 mJ/cm^2, leading to a transient surface heating of less than 5° during the laser pulse duration. This is calculated using the standard procedure, based on heat diffusivity/conductivity and the known optical absorption coefficient of Ru at this wavelength.[16,17] The small temperature increase due to the absorbed laser pulse can rule out any thermal reactivity/desorption of the trapped molecules, as discussed above.

Post-irradiation ΔP-TPD spectra are shown in Fig. 2 at several different masses, for two initial CD_3Cl coverages. These spectra are obtained after subtracting a baseline, which is the QMS signal measured without laser irradiation, thus extracting the net effect of photochemistry. This baseline signal always follows the parent molecules' TPD, including the CD_3Cl TPD signal obtained from the pure molecules without the water cage. We conclude that this signal arises from cracking of the parent molecule at the ionizer of the QMS.

The initial stage following 193 nm photon absorption by methyl chloride involves photofragmentation to ''hot'' CD_3 and Cl. Stable molecules that are photochemically produced as a result of dissociation at a wavelength of 193 nm (6.4 eV photon energy) are as follows: The most abundant product is found at mass 19 (CHD_3, methane), the result of a direct reaction of ''hot'' methyl with water molecules that surround it. Mass 36 (C_2D_6)—a reaction between two methyl radicals; Mass 69 (CD_3CD_2Cl)—formed via an insertion of a CD_2 fragment into a parent molecules' C–Cl bond. Mass 52 could be an exchange of hydrogen with deuterium in CD_3Cl, resulting in CD_2HCl, or a more chemically feasible reaction between a chlorine atom and water to produce HOCl and hydrogen. Mass 33 (CD_2OH) is a fragment of methanol while the methanol signal itself, at mass 35, is masked by the strong background signal of chlorine from the parent CD_3Cl molecule. This assignment was confirmed as the same product was found also when CD_3Cl was replaced by CD_3Br, where the background at mass 35 does not exist. All these molecules explosively desorb at 165 K together with the parent molecules at the onset of ice desorption. In several of the product molecules, a fraction of the molecules may find their way to directly interact with the metallic substrate during the TPD heating process. As a result, in addition to the narrow explosive desorption of caged products, we find them also at a higher desorption temperature. An example is the signal at mass 33, associated with methanol, that desorbs also around 280 K. Another example is found in mass 3 (DH), where the majority of the molecules desorbs at their ''normal'' temperature range of recombinative desorption near 300 K. In this case, however, there is also a unique desorption peak at

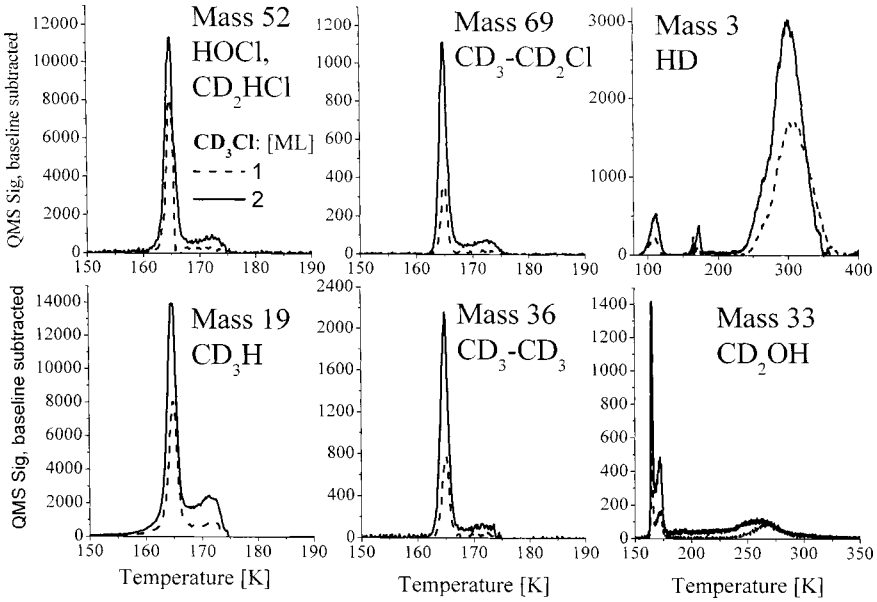

FIG. 2. Post-irradiation TPD, at the indicated masses. Caged CD_3Cl molecules inside the ASW layer were irradiated by 6×10^{18} photons at a wavelength of 193 nm. The amplitudes of the TPD peaks reflect relative yields of the products. The cage preparation conditions were fixed for all six frames: The indicated CD_3Cl coverage first, then 10 ASW layers.

very low temperature, 115 K. This low-temperature appearance may be explained by the presence of hydrogen atoms throughout the ASW layer as a result of water photodissociation at 193 nm that was discussed above. Indeed, irradiation at 248 nm, in which water molecules do not photodissociate, does not produce mass 3 (HD) at the low temperatures discussed above. Other masses (not shown) include 20 (CD_4), 32 (C_2D_4 or CD_2O) and 30 (a fragment of mass 32).

There are several possible structural configurations in which the methyl halide molecules could be encapsulated and caged by the ASW layers.[14] These possibilities are schematically illustrated in Fig. 3. The cage could consist of (a) isolated, single CD_3Cl molecules surrounded by ASW, similar to rare gas matrix isolation experiments [Fig. 3(a)]; (b) Small three-dimensional (3D) clusters of methyl chloride, each molecule is still in contact with surrounding water molecules [Fig. 3(b)]; (c) large 3D clusters in a cage [Fig. 3(c)]. In the case of large clusters, CD_3Cl molecules occupy two types of sites that should affect the photoproduct formation mechanism: (1) Molecules at the outermost layer (surface) of the cage that are in contact with ASW; (2) molecules at the bulk of the cage that are surrounded by other methyl chloride molecules.

If all the parent CD_3Cl molecules were isolated within the ASW matrix, then doubling the initial coverage of CD_3Cl should double the amount of photoproducts. Solvated molecules of this kind, however, cannot explain the formation of, e.g., ethane (C_2D_6), if we assume a negligible probability for methyl fragments produced from parent molecules that are far apart from each other to diffuse and react. Increasing the initial coverage of the parent molecules, therefore, is expected to result in a gradual increase of the fraction of large clusters. One expects a different behavior of the photochemical products' yield with changing parent molecules initial coverage. This behavior depends on the specific reaction mechanism for the formation of each of these photoproducts. Specifically, one expects a different dependence on the cage/molecular-cluster size and shape. Assuming spherical (large) cages, their volume would be proportional to R^3 (R is the average radius of the cage) and to the initial coverage of CD_3Cl (θi). The density at the outermost layer or surface of these spheres is proportional to R^2. Consequently, photoproducts that can only be formed at the edges of the cage based on reaction mechanism that requires direct contact with the surrounding water molecules should follow a $\theta_i^{2/3}$ dependence on the initial coverage of the parent molecules. This is exactly the behavior of the product at mass 52 (HOCl) as coverage increases; see Fig. 4(a).[19] Other photoproducts that are formed inside the cage, such as CD_3CD_3 (mass 36) follow a perturbed bimolecular channel, namely, $\theta_i^{(3/2\pm1/2)}$ dependence on initial coverage [Fig. 4(b)].

The origin of all the reactions described above is the photodissociation of caged CD_3Cl molecules. Two excitation mechanisms are possible: Direct photon absorption by the parent CD_3Cl molecules and dissociative electron attachment

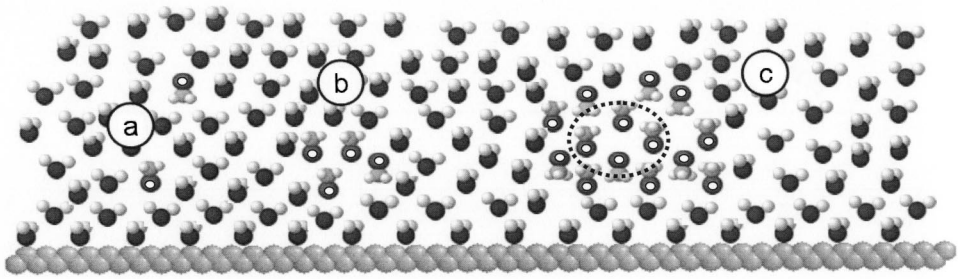

FIG. 3. A schematic of the possible cages of CD_3Cl formed inside ASW layers: (a) Isolated, solvated molecules. (b) Small 3D cages. (c) Large 3D cages. Molecules outside the dashed circle are expected to lead to the photoproducts yield that changes as $\theta_i^{2/3}$; see the text.

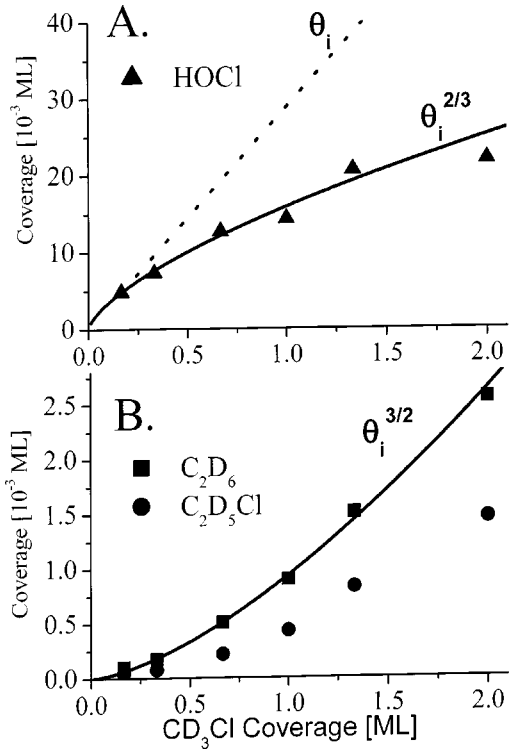

FIG. 4. The dependence of the photoproducts' yield (solid symbols) on the parent molecules initial coverage (θ_i). The solid and dotted lines are calculated values based on the indicated dependence on θ_i. Irradiation conditions were as in Fig. 2.

(DEA).[20,21] Both mechanisms produce "hot" methyl and chlorine radicals, which lead to most of the chemistry we observe. An important difference between the two excitation mechanisms is the state of the nascent post-irradiation chlorine—in DEA it is a chloride anion, while in the direct photoabsorption process it is a chlorine radical. A DEA process takes place when electrons in the metal[22] are excited by the UV laser, in our case at photon energies of 5.0 and 6.4 eV. Low-energy electrons generated this way subsequently attach to the CD_3Cl molecules, forming an excited negatively charged ion, after traveling through the layers of ASW that can be considered a neutral spacer.[20,21] As was shown before,[23] one may expect that the DEA rate will be suppressed if the CD_3Cl molecules are separated from the metal surface by gradually thicker ASW layers, while the direct photon absorption process should remain unchanged. In the current experiments 2–10 ASW spacer layers were deposited first, then a fixed amount of CD_3Cl (0.6 ML), and then caging with an additional 10 ASW layers of water. We observed that the production rate of masses 19 (CHD_3), 36 (C_2D_6), and 3 (HD) was clearly attenuated by the thicker spacer layers, indicating a DEA process. All other photoproducts, being insensitive to the ASW spacer layer thickness, are formed by direct photoabsorption of the parent molecules, as long as photon energy is 6.4 eV.

Another difference between photodissociation via direct photon absorption of UV photons by the parent molecule and DEA should be noted. This is the kinetic energy content of the nascent methyl and the chlorine species immediately following the C–Cl bond rapture event. The direct absorption process should produce far "hotter" methyl and chlorine than the DEA channel, since the electrons generated in the solid bulk are far slower, overcoming the binding energy to the metal.

In order to define the threshold energy for the direct absorption mechanism of the adsorbed methyl chloride, we have changed the laser wavelength to 248 nm (5.0 eV). In the gas phase, this is at the edge of the absorption band of methyl chloride, therefore direct absorption by adsorbed CD_3Cl at 248 nm can be neglected. This conclusion is reached from the fact that photoproducts that were insensitive to the ASW spacer layer thickness, e.g., HOCl (mass 52) and CD_3CD_2Cl (mass 69), as long as photon energy was 6.4 eV, were totally absent in the post-irradiation TPD at 248 nm. We conclude that somewhere between 5.0 and 6.4 eV photon energy, is the threshold for direct photodissociation of adsorbed methyl chloride, consistent with its gas phase absorption spectrum.

The yield of the various stable photochemically produced molecules discussed above was studied as a function of irradiation time at a fixed laser power. This in order to extract an apparent production rate and cross section for each of the individual products formed, at 193 and 248 nm excitation wavelengths. The cross sections were obtained from the curves of the integrated QMS signal as a function of irradiation time for the various masses, as shown in Fig. 5. The largest cross sections $(5\pm1)\times10^{-19}$ cm^2 were found for the initial formation of masses 52 (HOCl) and 36 (C_2D_6), although their formation rates saturate after irradiation of more than 10^{19} photons at 193 nm. Most other molecules were formed at a cross section of the order of $(1.0\pm0.5)\times10^{-19}$ cm^2 at this wavelength. As a reference, the gas phase cross section at electron energy near 1 eV was reported to be 2×10^{-21} cm^2.[24] In addition to the absence of any direct absorption at 248 nm, the cross sections for the (substrate mediated) photo-induced processes at 248 nm is reduced by more than an order of magnitude, to the range of $(1.5\pm0.5)\times10^{-20}$ cm^2.

The cross section found for the formation of ethane, for example, at photon energy of 6.4 eV, is smaller than those reported for the DEA of methyl chloride inside the solid matrix of krypton by more than two orders of magnitude.[20,21] It suggests that ASW as the caging material substantially suppress the overall DEA process and thus the photoreactivity that results from it. The observation that some of the products' formation rate saturate above a photon dosage of $\sim10^{19}$ must relate to the question of whether a direct photochemical reaction takes place *during the laser pulse*, or is it a subsequent process that occurs following sample heating of the caged photofragments.

The absence of longer chain hydrocarbons is somewhat surprising considering the presence of chlorine radicals that can initiate chain reactions. It may relate to the low temperature in which all the reactions inside the cage take place. These conditions and the small size of the methyl chloride cages seem to favor termination reactions at the level of ethane, thus avoiding longer chains. These important mechanistic questions need further investigation and will be addressed in future studies.

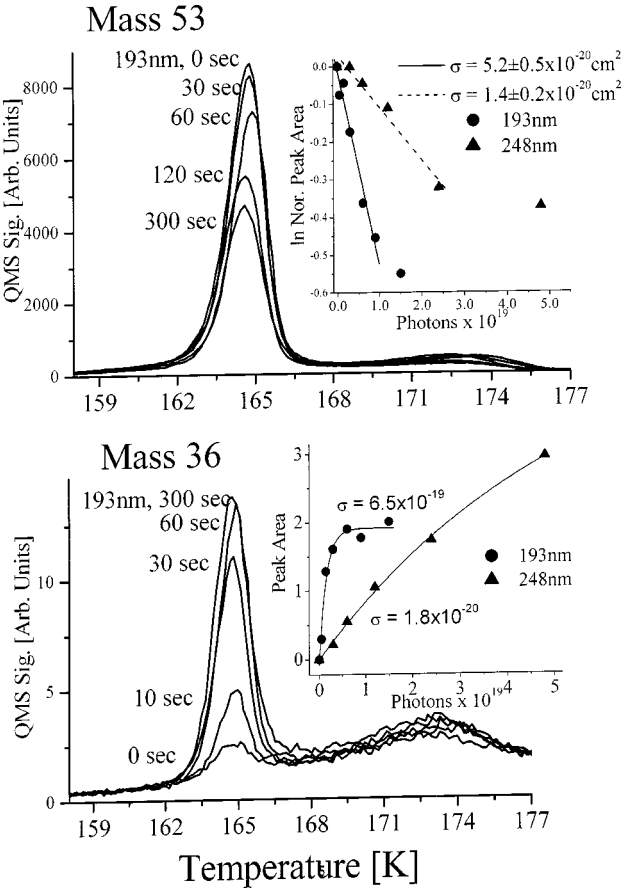

FIG. 5. The photochemical yield for the depletion of CD_3Cl and the formation of C_2D_6 following the irradiation of caged CD_3Cl molecules within a 10 BL thick ASW layer by 193 nm photons. The resulting cross sections are shown for both 193 and 248 nm.

It is interesting to discuss the relevance of the observations described above to the possible formation of hydrocarbons at the interstellar space. This issue is at the focus of intense research within the astrophysical–astrochemical community,[1–7] where hydrocarbons in general and amino acids in particular[7] are thought to be the necessary precursor molecules for the origin of life on our planet.[1b] Although alkyl halides are hardly expected to be present in interstellar clouds, ''hot'' methyl radicals generated photochemically, that are the source of reactivity in the present system, can be formed by other routes such as methanol.[1] The gradual accumulation of ice on solid grains (mostly oxide particles) that result in the formation of preadsorbed molecular cages as described in this and our previous report,[14] is quite reasonable to occur also on these interstellar grains. Since these particles are irradiated continuously by UV and vacuum-UV photons, photochemical event, mostly via direct photodissociation, as those described in this paper, can gradually take place over time. In order to release the trapped molecules, the solid grains should be wormed occasionally up at least to the ice desorption onset on solid surfaces near 165 K. Free hydrocarbons are thus released this way to the interstellar space. These chemicals may eventually contribute to the materials incorporated into planets, asteroids and comets.

IV. CONCLUSIONS

Photoinitiated reactions that take place within cages of methyl chloride molecules inside ASW-CD_3Cl@Ice has been studied in molecular level mechanistic details, for the first time. This system may be viewed as a model for the formation of hydrocarbons in interstellar space. Photochemical processes of methyl chloride inside ASW proceed along the following pathways: Hot methyl groups are generated either as a result of the dissociative electron attachment (DEA) process or via direct molecular absorption, at photon energy 6.4 eV. In addition to methyl, hydroxyl and hydrogen radicals are also formed as a result of the dissociation of water. These radicals are constrained and compressed within a high-density cage formed by ASW layers. Radical reactions within the cage with a small or no activation barrier take place, leading to reactions such as, e.g., $2CD_3 \rightarrow C_2D_6$. The reaction of chlorine atoms with the surrounding water molecules to form HOCl is observed as well, although this channel is blocked at a photon energy of 5.0 eV, indicative of a direct molecular absorption pathway. The partial dissociation of water leads to the formation of HCD_3 and CD_3OH molecules as well. Cross sections for these photoinitiated reactions of caged molecules at a photon energy of 6.4 eV are of the order of $(3\pm2)\times10^{-19}$ cm^2. This number is smaller than those reported for the DEA of methyl chloride in a solid matrix of krypton by more than two orders of magnitude.[20,21] It suggests that cage walls made of ASW substantially suppress the overall DEA process and thus the photoreactivity that results from it. At a photon energy of 5.0 eV the cross sections are about an order of magnitude smaller than these at 6.4 eV.

The unique photochemical processes of molecules trapped and caged within ASW layers based on ''hot'' methyl chemistry, open the way for deeper understanding of interstellar photochemical pathways.[1] Similar processes are expected to take place on ASW covered solid grains exposed to UV radiation[1–7] and may have contributed to the presence of hydrocarbons in outer space and perhaps also help us to understand some elements of the origin of life.[1(b)]

ACKNOWLEDGMENTS

This work was partially supported by a grant from the The US–Israel Binational Foundation, German Israel Foundation, and the Israel Science Foundation. The Farkas center is supported by the Bundesministerium fur Forschung und Technologie and the Minerva Gesellschaft fur die Forschung mbh.

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