

Light-induced molecular processes on ice

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Chapter 7

Adsorption and the photochemistry of multilayer bromoform on ice

The adsorption and the 266 nm photochemistry of bromoform multilayers on and in amorphous solid water (ASW) are studied using reflection absorption infrared spectroscopy (RAIRS), temperature-programmed desorption (TPD), and time-of-flight (TOF) techniques. Regardless of the initial exposure, bromoform resides on top of the ASW layer. No migration of bromoform molecules into the ASW film is observed for adsorption on top of the water layer. The UV radiation results in significant desorption of photochemical fragments, reaction of photochemical products on the surface and light-induced molecular reorganization of the remaining CHBr₃, which is apparent from a comparison of pre- and post-irradiation TPD experiments. The ice-mediated C—C $(C_2H_2Br_2)$ and C—O (CHBrO) photoproducts desorb from both the ASW surface and the Pt surface. The photoproduct $C_2H_2Br_4$ is formed exclusively from multilayers of CHBr₃ and desorbs only from the Pt surface.

7.1 Introduction

It is well-established that halogen species are active in ozone depletion [1]. In the atmosphere, halogenated compounds interfere with and modulate many chemical processes. Heterogeneous reactions between halogen "reservoir compounds" on stratospheric ice particles are known to be sources of highly reactive halogen species that contribute to ozone depletion to various extents [2-4].

In the stratosphere, bromine and chlorine deplete ozone via a similar mechanism, namely the halogen oxide cycle [1]. Although the abundance of bromine in the stratosphere is much less than that of chlorine, its presence can have a significant effect on ozone depletion [1-3]. This is due to the relatively large ozone destruction potential of bromine; recent reports have estimated the ozone destruction potential of bromine to be up to two orders of magnitude higher than that of chlorine [5,6].

The ozone depletion problem has stimulated intense laboratory studies on the interactions of atmospherically relevant gases with ice surfaces [7], as this is the first step toward revealing the reaction pathways leading to ozone depletion. For this purpose well-defined ice layers are prepared on metal surfaces under ultrahigh vacuum (UHV) conditions, as the ice morphology can be controlled by adjusting several parameters [8]. Furthermore, ultraviolet (UV) photochemistry of atmospherically pertinent molecules on these ice films may provide detailed insights into the reaction pathways in the atmosphere.

Studies on stratospherically relevant halocarbon compounds adsorbed on the surface of ice films have revealed various degrees of interaction with the non-hydrogen-bonded surface hydroxyl groups, also known as "free" or "dangling" O—H bonds [9]. Similar interactions have been reported for a large series of halomethanes *co-adsorbed* with water ice [10]. Furthermore, the photochemistry of CD₃Cl trapped and caged inside thin (\leq 20 monolayers) amorphous solid water (ASW) layers on Ru(001) has been studied recently, with reports of new C—C

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and C—O bond containing species [11], whilst CFCl₃ adsorbed on both porous ASW and polycrystalline ice leads to Cl and CFCl₂ formation upon 193 nm irradiation [12,13].

Bromoform (CHBr₃) is an important source of active bromine to the stratosphere [14,15]. It is mainly produced by ice algae as a byproduct of the photosynthetic process [16] and by emissions from oceanic microalgae [17]. An unexpectedly high mobility of bromoform molecules adsorbed on ice surfaces, compared to the structurally identical chloroform, has been recently reported [18]. Moreover, a rich UV photochemistry of the monolayer CHBr₃ on ice surface has been revealed, with reports of direct Br formation, along with CHBr₂, Br₂, and CHBr species and ice-mediated C-C and C-O bond containing compounds [19].

Despite the increasing research on halocarbon compounds on ice, the adsorption behavior and the photochemistry of *multilayer* halocarbons on ice surfaces has yet to be explored. The adsorption structure, the chemistry of the photogenerated species, and the influence of UV irradiation on the molecular arrangement within multilayer halocarbon on ice are practically unknown. These may be relevant since halocarbon compounds may interact on the surface of ice particles in the polar stratospheric clouds. In addition, it is interesting to study halocarbon diffusivity into bulk ice, as ice bulk diffusion of hydrogen halide molecules has been reported for a wide range of exposures of HBr and HCl onto ice layers [20-22]. Although such studies do not exist on the solid water surface, there have been reports on the photochemistry of multilayer adsorbates on metal surfaces. The photochemistry of multilayers of CH₃Br on Ru(001) and on Cucovered Ru(001) has been found to be strongly influenced by the nature of the molecule–substrate interaction and the structure of the first layers of CH₃Br [23]. In contrast, the multilayer of phenol adsorbed on the Ag(111) surface is not affected by the UV irradiation, as only the chemisorbed layer in direct contact with the metal surface releases photogenerated products [24]. As the nature of the (insulating) ice surface is very different from that of these metal surfaces, it is not evident to what extent these previous results can be extrapolated to the haloform-ice system.

In this chapter, a study of the adsorption behavior of the multilayer CHBr₃ on ASW layers as well as its photochemistry upon 266 nm irradiation is described. Pre- and post-irradiation reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) results are compared and it is concluded that multilayer CHBr₃ resides on top of compact ASW regardless of the amount of bromoform dosed. Post-irradiation TPD spectra of CHBr₃ indicate a UV-induced molecular reorganization of the remaining bromoform. No caging effect of the CHBr₃ multilayers (up to 5 layers) is suggested by the time-of-flight (TOF) spectra of the direct Br photofragment. Distinctly different behavior of the ice-induced photochemical products is observed compared to the CHBr₃ monolayer [19]. Particular amounts of $C_2H_2Br_2$ and CHBrO find their way to directly interact with the Pt substrate during the TPD process. Moreover, a new C—C species ($C_2H_2Br_4$) desorbing exclusively from the Pt substrate, is formed upon UV irradiation of the multilayer CHBr₃.

7.2 Experimental

The experimental setup – a UHV chamber with a base pressure of 2×10^{-11} mbar – has been described in detail elsewhere [25,26]. Briefly, a triply differentially pumped, compact molecular beam line was used for dosing water onto an inert, single-crystal platinum substrate. This Pt(533) substrate is mounted on a liquid nitrogen cooled, temperature-controlled sample holder. Details of the substrate cleaning procedures can be found elsewhere [27].

Compact, non-porous ASW layers were prepared by depositing water (D_2O or H_2O) from the molecular beam under normal incidence at a substrate

temperature of 100 K (at a deposition rate of ~5 MLmin⁻¹). Uniform layers can be deposited, as the diameter of the molecular beam at the crystal position exceeds that of the crystal. One monolayer coverage is defined here as the dose of water necessary to form an ice-like bilayer on the Pt(533) substrate, as defined in Refs. [27,28]. The water coverage was determined from the area under the TPD peaks. H₂O was obtained from a Simplicity Millipore System (resistivity value > 18 MΩcm⁻¹), while D₂O (≥99.96%) was supplied by Aldrich. Both H₂O and D₂O were degassed with repeated freeze-pump-thaw cycles.

Bromoform (>99% Aldrich) was dosed at 100 K by background dosing, typically at a pressure of 1×10^{-7} mbar. The exposure was controlled by varying the dosing time. A dose of 10 L (we define 1 Langmuir (L): 1×10^{-6} mbar s) of CHBr₃ results in one ML (monolayer) on the ice surface. 1 ML of CHBr₃ is defined as the coverage above which the multilayer desorption peak starts appearing in the TPD spectrum. The reported pressures are not corrected for ion-gauge sensitivity.

Photochemical processes were initiated using irradiation at 266 nm, obtained by frequency-tripling the output of an 800 nm amplified Ti:sapphire laser (Quantronix GmbH). The laser provides pulses of 130 fs duration at 266 nm of about 90 μ J/pulse at a repetition rate of 1 kHz. The substrate was homogeneously irradiated at a 35⁰ angle with respect to the surface normal, using a spot size exceeding the substrate diameter. Unless otherwise mentioned, the 266 nm irradiation amounted to 8.9 × 10¹⁸ photons cm⁻². For a wide range of photon fluxes below 10²⁰ cm⁻², this number of photons resulted in highest yield of the CHBr₃ photoproducts. No different chemical species could be observed at different fluences.

It was verified experimentally that the resulting laser fluence ($<1 \text{ Jm}^{-2}$) was sufficiently low to avoid contributions from multiphoton processes. The (sequential) one-photon processes giving rise to the observed chemistry originates from direct excitation of bromoform molecules, and not from the

indirect excitation of the water or Pt substrate, as will be shown below. This can be understood by noting that ice is transparent to the 266 nm irradiation [29], and accordingly no change in the RAIR spectrum of D_2O is observed after irradiation (see Figure 7.1f). Also, absorption of 65% of the incident laser light by the substrate results in a transient substrate heating of less than 10 K and therefore any thermal reactivity of the adsorbed molecules can be ruled out.

Photodesorbed fragments were detected as a function of their flight time by a differentially pumped quadrupole mass spectrometer (QMS, Balzers QS 422) placed in a collinear geometry with the sample surface normal, amplified with a fast amplifier and counted with a multichannel scaler after a 70 mm flight path. The same mass spectrometer was used to record post-irradiation TPD spectra. Masses 18 (H₂O⁺), 20 (D₂O⁺), 108 (CHBrO⁺), 171 (CHBr₂⁺), 187 (C₂H₂Br₂⁺), 252 (CHBr₃⁺), and 345 (C₂H₂Br₄⁺) were simultaneously monitored. TPD spectra were typically recorded at a heating rate of 0.5 Ks⁻¹.

The RAIR spectra were recorded at 4 cm⁻¹ resolution under grazing incidence with a commercial FTIR spectrometer (Biorad FTS 175). For the RAIRS measurements, D_2O was used instead of H_2O , to prevent the C-H stretching vibration of CHBr₃ at 3017 cm⁻¹ of being obscured by the O-H stretching mode region of H_2O (3000-3700 cm⁻¹). We found no evidence for the photochemistry being dependent on the isotopic composition of the ice layer.

7.3 Results and discussion

Figure 7.1 shows RAIR spectra (at 100 K) in the frequency range 1800-3200 cm⁻¹ of (a) 100 L of CHBr₃ dosed on top of 22 ML of D₂O (i.e. *sequentially*), (b) 10 L of CHBr₃ dosed on top of 90 L of CHBr₃ adsorbed *simultaneously* with 22 ML of D₂O, and, for reference, (c) 22 ML of D₂O, without CHBr₃. The dosing temperature was 100 K. The corresponding post-irradiation RAIR spectra of the

samples (a) - (c) after irradiation by 8.9×10^{18} photons cm⁻² at a wavelength of 266 nm, are shown in Figure 7.1, curves d-f, respectively. The broad band at 2250-2650 cm⁻¹ is assigned to the O—D stretching vibration of D₂O [30,31], while CHBr₃ is reflected in the C-H stretching vibration at 3017 cm⁻¹. The RAIR spectra of the sequentially dosed CHBr₃-D₂O sample (Figure 7.1a) and the bare D₂O (Figure 7.1c) are very similar in the O—D stretching range, while the spectrum of the simultaneously dosed sample (Figure 7.1b) is very different. This clearly indicates that CHBr₃ adsorbed on top of ASW does not diffuse into the bulk ASW at 100 K. The interaction of CHBr₃ with the surface of the ASW film is further apparent from the shift of the non-hydrogen-bonded, surface "dangling" OD peak, from 2728 cm⁻¹ to 2678 cm⁻¹. (Note that in the case of the simultaneous exposure of CHBr₃ and D₂O also a monolayer of CHBr₃ is placed on top of ASW.) This shift is caused by the CHBr₃ interaction through lone pair donation from a bromine atom to a deuterium atom of the dangling O—D group [10]. Unlike CHBr₃ on compact ASW, the migration of HCl into the ASW bulk has been previously reported even at 100 K [20]. The highly porous ASW laver employed in those experiments presumably favors the bulk diffusion of the smaller HCl molecules.



Figure 7.1. Reflection absorption infrared (RAIR) spectra of (a) 100 L CHBr₃ dosed on top of 22 ML D₂O (sequential dosage), (b) 10 L CHBr₃ dosed on top of 22 ML D₂O and 90 L CHBr₃ simultaneously dosed on Pt(533), and (c) 22 ML D₂O adsorbed on Pt(533). (d-f) Post-irradiation RAIR spectra of case a-c, respectively, following irradiation by 8.9 x 10^{18} photons cm⁻² at a wavelength of 266 nm. All dosages and RAIRS measurements were performed at 100 K. The weak features in the spectra at ~2355 cm⁻¹ is due to the incomplete cancellation of gas phase CO₂ present in the optical path.

The OD stretching vibration of bulk D_2O in the sequentially dosed D_2O -CHBr₃ layer (Figure 7.1a) remains unchanged after illuminating the sample with 266 nm (Figure 7.1d), suggesting that the resulted photoproducts reside on top of the ASW layer. Apparently, there is no significant participation of the bulk ASW to the UV-induced photochemical processes in the sequentially obtained D_2O -CHBr₃ system. In contrast, the D_2O dosed simultaneously with CHBr₃ is affected by the 266 nm light, as evidenced by the altered shape of the post-irradiation OD stretching vibration of bulk D_2O (compare Figure 7.1b and 7.1e). Remarkably, the peak of the dangling OD bonds (2678 cm⁻¹) disappears upon 266 nm irradiation (Figure 7.1d and 7.1e). As the dangling OD peak is still visible in the post-irradiation RAIR spectrum of pure D_2O (Figure 7.1f), this indicates the involvement of the surface species of the underlying ASW in the CHBr₃ photochemistry. The UV-induced reaction of CHBr₃ is clearly reflected by the reduction of the C-H band intensity (3017 cm⁻¹) upon UV irradiation (Figure 7.1d and 7.1e). A new peak at 2136 cm⁻¹ is observed, due to CO formation [32], only in the post-irradiation RAIR spectra of the simultaneously dosed D₂O-CHBr₃ system (Figure 7.1e). As the C—O bonds are not observed in the sequentially dosed D₂O-CHBr₃ system, C—O bond appears to require the exposure of CHBr₃ molecules to the D₂O ice matrix. This is corroborated by other photogenerated C—O bond containing species observed in the post-irradiation TPD spectra (Figure 7.5c, see below).

The TPD spectra of D_2O (m/z 20) corresponding to the IR spectra of Figure 7.1, are shown in Figure 7.2 (curves a-f), together with the TPD spectra of CHBr₃ (m/z 252) for cases a and b, namely curves g and h. Remarkably, although the RAIRS spectrum of water is greatly affected, the presence of CHBr₃ within the water layer does not influence the desorption temperature of D_2O (curves b and c in Figure 7.2 are rather similar). If a thick layer of CHBr₃ is dosed on the ASW layer, the desorption temperature of D_2O is shifted to higher temperatures by ~10 K (Figure 7.2a), as water cannot desorb until the bromoform on top has desorbed (Figure 7.2g). The dependence of the D_2O desorption on the manner in which CHBr₃ is (co)adsorbed, is very different from that of the water-HBr system [21]. In the latter, the thermal desorption behaviour of H_2O is identical regardless of whether HBr is dosed in the center of a water layer or on top. The reason for this lies in the HBr migration into the bulk, driven by the formation of H_2O /HBr hydrates [21]. For CHBr₃, the formation of hydrates is clearly not favored, or it is kinetically hindered.



Figure 7.2. TPD signal for D₂O (m/z 20) from (a) 100 L CHBr₃ dosed on top of 22 ML D₂O, (b) 10 L CHBr₃ dosed on top of 22 ML D₂O and 90 L CHBr₃ simultaneously dosed on Pt(533), and (c) 22 ML D₂O adsorbed on Pt(533). (d-f) Corresponding postirradiation TPD signal for D₂O (m/z 20), respectively, following irradiation by 8.9×10^{18} photons cm⁻² at a wavelength of 266 nm. (g) TPD signal for CHBr₃ (m/z 252) from 100 L CHBr₃ dosed on top of 22 ML D₂O, (h) TPD signal for CHBr₃ (m/z 252) from 10 L CHBr₃ dosed on top of 22 ML D₂O and 90 L CHBr₃ simultaneously dosed on Pt(533). Dosing temperature was 100 K. The heating rate was 0.5 Ks⁻¹.

After UV irradiation, only the TPD trace for the simultaneously adsorbed D_2O -CHBr₃ system is changed: a new, double-peak structure is clearly visible in

the post-irradiation TPD of the D_2O co-adsorbed with CHBr₃ (Figure 7.2e). The desorption trace of D_2O from the sequentially obtained D_2O -CHBr₃ system (Figure 7.2d) and the pure D_2O layer (Figure 2f) remains essentially unchanged. This is in agreement with the post-irradiation RAIR spectra depicted in Figure 7.1, curves d-f, which indicate modified IR absorption solely for D_2O dosed simultaneously with CHBr₃. Although the number of water molecules actively involved in the bromoform chemistry constitutes only a small fraction of the total number, there is significant UV-induced rearrangement of the hydrogen-bonded water network, resulting in the new aspect of the post-irradiation TPD of D_2O molecules.

Although the TPD spectrum of D₂O for the sequential dosage case does not notably change upon 266 nm irradiation, the TPD trace of CHBr₃ is significantly different, as can be observed in Figure 7.3. Figure 7.3a shows the TPD spectra (at 0.5 Ks⁻¹ heating rate) of CHBr₃ (m/z 252) from 2 L, 5 L, 10 L, 15 L, 30 L, and 50 L, respectively, of CHBr₃ sequentially dosed (at 100 K) on top of 65 ML of ASW (H₂O). The corresponding post-irradiation TPD spectra following illumination by 8.9×10^{18} photons cm⁻² at a wavelength of 266 nm, are depicted in Figure 7.3b. Before irradiation, the sequentially dosed CHBr₃ mainly desorbs around the desorption temperature of the supporting H_2O (~183 K, Figure 7.3a). After UV irradiation (Figure 7.3b), CHBr₃ desorbs both from the surface and upon the crystallization of ASW layer at T = 160-180 K, depending on the precise coverage, i.e. before the underlying H₂O desorbs at 183 K. A lowering of the bromoform binding energy on the surface is apparently induced by the UV light. The common trailing edges observed for CHBr₃ desorption from the UV-irradiated samples (Figure 7.3b) is indicative of zeroth-order desorption kinetics. This indicates that desorption occurs preferentially from specific domains on the surface, with CHBr₃ being supplied from a reservoir [33], but it is not clear what physical situation that could correspond to.



Figure 7.3. TPD spectra, before (a) and after (b) irradiation (with 8.9 x 10^{18} photons cm⁻² at a wavelength of 266 nm), of CHBr₃ (m/z 252) dosed (at 100 K) on 65 ML ASW (H₂O). The initial exposure of CHBr₃ was 2 L, 5 L, 10 L, 15 L, 30 L, and 50 L, respectively. The dotted gray curve indicates the scaled desorption peak of 65 ML ASW (m/z 18). The heating rate was 0.5 Ks⁻¹.

An additional desorption peak at ~199 K, accompanied by a broad feature centered at ~214 K can be also observed in the TPD spectra of CHBr₃ dosed on top of the ASW layer (Figure 7.3a). These TPD features increase in intensity as the initial bromoform exposure increases, and are also visible in the post-irradiation spectra (Figure 7.3b). These correspond to CHBr₃ desorbing from the bare Pt(533) substrate after water has completely desorbed, as is apparent from a TPD of bromoform dosed directly on the Pt surface. At a heating rate of 0.5 Ks⁻¹,

a fraction of the CHBr₃ molecules finds their way to the metal substrate, as ASW crystallizes during the TPD process [18]. Analogous TPD peaks (i.e., following water desorption) have been reported for both the photoproducts of CD₃Cl trapped inside ASW layers [11] and ammonia adsorbed on crystalline ice surface [34].

RAIRS and TPD measurements provide information on the molecules left on the substrate after irradiation. However, no information is obtained about the species desorbing during the irradiation. Figure 7.4 shows time-of-flight (TOF) spectra of Br^+ (m/z 79) collected during the 266 nm irradiation of (a) 10 L and (b) 50 L of CHBr₃ dosed sequentially (at 100 K) on 65 ML of ASW. The TOF spectra are averages of 60.000 laser pulses, and can be well described by Maxwell-Boltzmann distributions [35], with the corresponding translational temperatures indicated in the graph. Within our experimental accuracy, the translational temperatures mentioned in Figure 7.4 are independent of initial thickness of the CHBr₃ layer. The ratio of the area under the two spectra (5:1)coincides with the ratio between the parent CHBr₃ exposures, indicating that caging of the light-induced Br fragments is not effective by a coverage up to 5 monolayers of CHBr₃ on thick ASW. In addition, this ratio corroborates that multilayers of CHBr₃ reside on top of the ASW layer. These results present further evidence that the photochemical mechanism is not mediated by the metal substrate, but direct absorption of 266 nm photons by the CHBr₃ adsorbed on ASW.

Chapter seven



Figure 7.4. TOF spectra of Br^+ (m/z 79), following irradiation of (a) 10 L and (b) 50 L CHBr₃ adsorbed (at 100 K) on 65 ML ASW (H₂O) by 60.000 laser pulses at 266 nm, at t = 0. The distribution of flight times of the Br^+ fragment from the surface to the mass spectrometer (70 mm from the surface) is characterized by translational temperatures indicated in the graph. These temperatures are obtained from a fit to a Maxwell-Boltzmann distribution, shown as solid black lines. Spectrum (b) is offset for clarity purposes.

In addition to the direct photofragments desorbing during the 266 nm irradiation of sequentially dosed CHBr₃ on top of the ASW layer (only Br shown here [19]), new C—C and C—O bond containing species can be observed in post-irradiation TPD spectra, shown as dotted curves in Figure 7.5 ((a) m/z 345 ($C_2H_2Br_4$), (b) m/z 187 ($C_2H_2Br_2$), and (c) m/z 108 (CHBrO)). TPDs were recorded for an initial exposure of 100 L of CHBr₃ on a 22 ML thick ASW (D_2O) layer, following irradiation by 8.9×10^{18} cm⁻² photons at 266 nm. The TPD signals from the simultaneously dosed CHBr₃:D₂O system (10 L of CHBr₃ dosed on 90 L of CHBr₃ adsorbed simultaneously with 22 ML of D₂O) are depicted as continuous curves in the same figure. The corresponding TPD traces of m/z 20 (D_2O) are depicted in Figure 7.5d, for comparison. Apparently two reaction pathways are involved in the formation of the ice-mediated photoproducts: (i)

dimerization, resulting in the formation of new C—C bonds ($C_2H_2Br_4$, $C_2H_2Br_2$) and (ii) the chemical reaction of the photofragments with the water molecules, resulting in the formation of new C—O bonds (CHBrO) [19]. Amongst the iceinduced photoproducts of CHBr₃, $C_2H_2Br_4$ shows a particular behavior (as will be shown in Figure 7.6): it is formed only upon *multilayer* exposures of parent CHBr₃ and it desorbs exclusively from the Pt substrate, after D₂O has completely desorbed (Figure 7.5a, dotted curve). Unlike $C_2H_2Br_4$, part of $C_2H_2Br_2$ desorbs from the outermost surface of the ASW layer at 151 K, as one can observe in Figure 7.5b (dotted curve). This particular desorption feature is the only observed in the TPD spectra of $C_2H_2Br_2$ obtained from *monolayer* CHBr₃ on ASW layer (see below, Figure 7.6). A rather weak, broad peak also appears in the TPD spectrum of $C_2H_2Br_2$ (Figure 7.5b, dotted curve) at the desorption temperature of D₂O (177 K). (Note that formation of $C_2H_2Br_2$ partially from $C_2H_2Br_4$ dissociation in the mass spectrometer can not be ruled out.)

CHBrO desorption appears to occur mainly upon both crystallization and consecutive desorption of the ASW (D₂O) (~177 K), as indicated by the TPD trace depicted in Figure 7.5c (dotted curve). This is not surprising if we take into account the active involvement of the ice matrix D₂O molecules in the formation of the photoproducts, as these have to provide the oxygen atoms. The area of the CHBrO peak is significantly higher in the case of the simultaneous dosage of CHBr₃ and D₂O (Figure 7.5c, continuous curve). Together with the CO formation exclusively upon UV irradiation of CHBr₃ dosed simultaneously with D₂O (Figure 7.1e, see above), this indicate that the C—O bond formation is enhanced by a larger exposure of CHBr₃ molecules to the D₂O ice matrix.



Figure 7.5. Post-irradiation TPD spectra at the indicated masses, following irradiation of 100 L CHBr₃ dosed on top of 22 ML D₂O (dotted curves) and 10 L CHBr₃ dosed on top of 22 ML D₂O and 90 L CHBr₃ simultaneously dosed on Pt(533) (continuous curves), by 8.9 x 10^{18} photons cm⁻² at 266 nm. Dosing temperature was 100 K. The heating rate was 0.5 Ks⁻¹.

Whereas bromoform-water interactions are enhanced by incorporation of bromoform into the water layer, bromoform-bromoform interactions are clearly enhanced for multilayer adsorption on the ice surface: the different behavior of multilayer CHBr₃ in comparison with monolayer CHBr₃ is illustrated in Figure 7.6. Post-irradiation TPD spectra of the ice-mediated photoproducts ($C_2H_2Br_4$,

 $C_2H_2Br_2$, CHBrO), following irradiation of CHBr₃ on 65 ML ASW by 8.9×10^{18} cm⁻² photons at 266 nm are shown. The initial exposures of CHBr₃ were 2 L, 5 L, 10 L (which corresponds roughly to 1 monolayer (ML) of CHBr₃ on the ice surface), 15 L, 30 L, and 50 L. One can observe in Figure 7.6 (left panel) that $C_2H_2Br_4$ forms exclusively upon UV irradiation of multilayer CHBr₃ and desorbs solely from the Pt surface, after ASW has desorbed. In contrast, $C_2H_2Br_2$ and CHBrO appear even at sub-monolayer CHBr₃ exposures and desorb from the surface of ASW (Figure 7.6, middle and right panel, respectively). As the dosage of parent CHBr₃ increases, part of these photoproducts percolates the ASW layer during TPD and desorbs also from the Pt substrate. Another possible explanation is that these molecules remain on top of the ice layer, while this is thinning during TPD, and reach the surface in that manner.



Figure 7.6. Post-irradiation TPD spectra at the indicated masses, following irradiation of CHBr₃ dosed (at 100 K) on top of 65 ML ASW (H₂O), by 8.9×10^{18} photons cm⁻² at 266 nm. The initial exposure of CHBr₃ was 2 L, 5 L, 10 L, 15 L, 30 L, and 50 L, respectively. The gray curve indicates the scaled desorption peak of 65 ML ASW (m/z 18). The heating rate was 0.5 Ks⁻¹.

To elucidate the mechanism of the photochemical changes, we performed similar experiments for analog co-adsorbed D₂O-CHBr₃ sample dosed on a purposely pre-adsorbed 50 ML thick ASW (D₂O) layer. At this thickness of the ASW spacer, it is known that the metal substrate plays no significant role in the photochemistry of CHBr₃ [19]. Since the TPD traces of the photoproducts are similar on Pt and on 50 ML of ASW, the role of the Pt substrate and the electrons from Pt in the formation of the indicated photoproducts appears to be negligible. This is rather surprising since dissociative electron attachment (DEA) [36,37] has been reported as the main mechanism driving the 248 nm photochemistry of CD₃Cl trapped into thin (\leq 20 ML) ASW layers [11]. Although DEA cannot be ruled out as a contribution to CHBr₃ photodissociation, our results suggest that C₂H₂Br₄, C₂H₂Br₂, and CHBrO are formed as a result of direct absorption of 4.5 eV photons by CHBr₃ molecules.

7.4 Conclusions

The adsorption behavior and the photochemistry of CHBr₃ multilayers on ASW are reported with RAIRS, TPD, and TOF techniques. CHBr₃ resides on top of the ASW layer regardless of its dose (up to a ratio CHBr₃:D₂O of 5:1). Diffusion of CHBr₃ into the bulk ice is not observed for CHBr₃ placed on the surface of a compact ASW layer, by comparison with the behavior of purposely mixed CHBr₃-water layers. UV irradiation induces a molecular reorganization of CHBr₃ on top of the ASW layer, as observed from the corresponding pre- and post-irradiation TPD spectra. TOF traces of direct photoproduct Br reflect no caging effect upon irradiation of the multilayer CHBr₃ (up to 5 molecular layers) on ASW. The ice-mediated C—C ($C_2H_2Br_2$) and C—O (CHBrO) photoproducts desorb from both the ASW surface and the Pt substrate; they apparently reach the Pt surface during the TPD process. Remarkably, the photoproduct $C_2H_2Br_4$ is

formed exclusively upon irradiation of multilayer $CHBr_3$ and desorbs only from the Pt substrate. Our results show that chemical interactions between bromoform and water in stratospherical processes are enhanced by insertion of the bromoform into the ice layer. This process may readily occur in the stratosphere: the high rate of water desorption and adsorption will lead to the encapsulation of bromoform within the ice layer.

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