

New experiments and interpretations concerning the “XCN” band in interstellar ice analogues

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Received 7 October 1999 / Accepted 12 January 2000

Abstract. Evidence for the formation of OCN^- in interstellar ice analogues is summarized with an emphasis on the recent experiments of Demyk et al. (1998). Their experiments are reinterpreted in terms of two different types of chemical reactions, acid-base and oxidation-reduction. New spectra of UV-photolyzed and p^+ -irradiated ices are presented, and reasons for similarities considered. The role of e^- and H^+ scavengers in revealing ice photo- and radiation chemistries is stressed, and it is concluded that electron-transfer reactions may play a more important role than commonly thought.

Key words: infrared: ISM: lines and bands – ISM: molecules – ISM: abundances – molecular processes – ISM: dust, extinction

1. Introduction

A recent paper of Demyk et al. (1998) addresses the important issue of the 2160 cm^{-1} ($4.62\ \mu\text{m}$) IR band in interstellar ices. This feature has been reported in several protostellar sources by a number of observers, most recently in sources studied with the Infrared Space Observatory (ISO). As there is some uncertainty in the assignment of this band, it has often been labeled as “XCN” with the species responsible being either the cyanate ion, OCN^- , or a neutral nitrile or isonitrile molecule. The XCN band is currently one of two rather prominent unidentified features in ISO spectra of protostellar sources, the other being a feature at $6.85\ \mu\text{m}$.

Laboratory studies have shown that an IR absorption at 2160 cm^{-1} can be readily produced by UV photolysis of $\text{CO} + \text{NH}_3$ mixtures near 15 K (Grim & Greenberg 1987). The purpose of the paper of Demyk et al. (1998) was to demonstrate that this 2160 cm^{-1} feature in laboratory mixtures is, in fact, due to OCN^- . To this end, a set of experiments was presented on photolyzed mixtures of $\text{CO} + \text{NH}_3$, $\text{CO} + \text{NH}_3 + 2\text{-methyltetrahydrofuran}$, $\text{CO} + \text{NH}_3 + \text{CCl}_4$, and $\text{CO} + \text{NH}_3 + \text{SF}_6$. Spectra of these photolyzed mixtures were compared to an ISO spectrum of RAFGL 7009S, a protostellar source, and used to argue for the presence there of both OCN^- and NH_4^+ .

The UV photolysis experiments reported by Demyk et al. (1998) are both elegant and informative, and it is doubtful that we could improve on them in any substantial way. However the *interpretations* attached to those experiments are incomplete, somewhat puzzling, and, at times, contradictory. For example, 2-methyltetrahydrofuran (MTHF) was described as an “electron donor” that raises the abundance of OCN^- , although no explanation was given for how this occurs. The molecules CCl_4 and SF_6 were described as “electron acceptors” which would reduce the abundance of OCN^- , but again no explanation was provided. In all, four nitrogen-containing products were observed in the photolyzed mixtures, namely OCN^- , NH_4^+ , HNCO , and HC(O)NH_2 , but no reactions were supplied to explain how they form or are interrelated. Moreover the use of the expressions “electron donor” to describe MTHF and “electron acceptor” to describe CCl_4 and SF_6 implies that the chemical reactions of MTHF are somehow the opposite of those promoted by the other two molecules. Such is not the case. All of this unnecessarily weakens arguments for OCN^- in laboratory and interstellar ices by failing to reveal the underlying chemistry.

In this paper we suggest new interpretations for the results of Demyk et al. (1998) which are more in line with conventional reaction chemistry. It is *not* our purpose to detract from their experiments but rather to place them in a new context from where they may have greater implications for ice processing. We also present new experiments on proton-irradiated mixtures containing CO and NH_3 , both with and without H_2O . When combined with the photolysis experiments already published, our work offers a more comprehensive picture of energetic processing of interstellar ice analogues than heretofore available.

2. Experimental

Essentially all relevant experimental details have been published, including information on ice preparation, the IR spectrometer, and the 0.8 MeV proton radiation source (Moore & Hudson 1998; Hudson & Moore 1995). The hydrogen-discharge lamp we used for UV photolysis is similar to that described by others (Allamandola et al. 1988), giving energies largely centered around 6 and 10 eV. Although we can now perform both UV photolyses and proton irradiations within the same experi-

mental chamber, the only original experiments in this paper are proton irradiations.

3. Results

We begin by reviewing some experimental results already in print. To explain the observations, reactions will be written where possible. For the sake of clarity we use the words “photolysis” and “photolyze” in conjunction with all UV processing experiments. The corresponding terms for our proton-bombardment experiments are “irradiation” and “irradiate.”

3.1. Photolysis of solid CO + NH₃

Spectra published by Demyk et al. (1998) clearly show that four nitrogen-containing products are made on photolysis of CO + NH₃ (1:1) at 12 K. These products, with approximate band positions, are HNCO (2255 cm⁻¹), OCN⁻ (2160 cm⁻¹), NH₄⁺ (1460 cm⁻¹), and HC(O)NH₂ (1696 cm⁻¹). We have performed a similar UV-photolysis experiment, and concur with these spectral assignments. We believe that product formation can, to a *first* approximation, be explained on the basis of fairly simple reactions, beginning with the photochemical decomposition of NH₃, followed by reaction of NH₂ with CO, and then an acid-base reaction with NH₃:



Reactions (1) and (2) are analogous to those taking place in UV-photolyzed solid-phase mixtures of H₂O + CO:



Because NH₃ and H₂O are isoelectronic, showing similarities in chemical and physical properties, reactions (1) and (2) are fully expected from reactions (4) and (5). Seen this way, it would be rather remarkable were HNCO, and thus NH₄⁺ and OCN⁻, *not* to form in CO + NH₃ ice photolysis experiments. More complex reaction schemes can be devised, but reactions (1)–(3) serve as a first step in understanding the spectral observations.

Demyk et al. (1998) supported reaction (3) with an annealing experiment; see particularly their Figs. 3 and 4. In our own work we have observed a reaction similar to (3) involving formic acid, HCOOH, in proton-irradiated H₂O + CO ices. Proton irradiation of solid H₂O + CO produced both HCOOH and the formate ion, HCOO⁻. However when the reaction was repeated with NH₃ present, HCOOH was removed, HCOO⁻ was enhanced, and NH₄⁺ was seen, changes similar to those of reaction (3).

The last of the four nitrogen-containing photo-products reported by Demyk et al. (1998) is formamide, HC(O)NH₂. Radical-radical processes such as

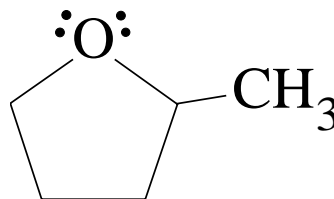
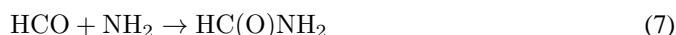


Fig. 1. Molecular structure of 2-methyltetrahydrofuran, MTHF

may explain formamide’s production, but alternative schemes exist. For example, if the order of radical addition to CO is reversed from reactions (6) and (7), then the first step will be



and then radical disproportionation gives both formamide and HNCO.



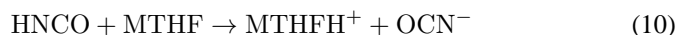
Additional experiments are needed to test this possibility. This paper will not treat formamide synthesis.

3.2. Photolysis of solid CO + NH₃ + added molecules

Other experiments of Demyk et al. (1998) were on three-component ices, each having CO:NH₃ = 1:1. The third component in one case was MTHF and, in other experiments, the third component was either CCl₄ or SF₆. We will comment on both types of experiments as they are fundamentally different from one another.

Radiation chemists have used MTHF, whose structure is shown in Fig. 1, for decades.¹ This compound is quite useful for the trapping and spectroscopic study of radiation products as it forms a clear, colorless, amorphous solid on freezing at 77 K. Being a base, MTHF is an electron *pair* donor. This does not mean that electrons are transferred from MTHF to another species to form anions, but rather that lone pair electrons associated with MTHF are available to complex with H⁺. This results in the stabilization of anions; in a sense, when MTHF is present, anions are protected from neutralization by H⁺. In fact, in radiation chemistry a common check for suspected anions is to carry out reactions in the presence of MTHF and other bases (Spinks & Woods 1990). Anions observed in the absence of MTHF will almost certainly be observed in its presence too.

In the case of CO + NH₃ + MTHF photolysis, reaction (2) will still form HNCO, but this acid’s decomposition will be altered. Protonation of MTHF will occur in competition with NH₃. The *two* relevant acid-base reactions are as follows:



In principle, this competition will reduce the amount of NH₄⁺ seen relative to OCN⁻. Although quantitative measurements

¹ Note that the formula for MTHF given by Demyk et al. (1998) is incorrect. The correct molecular formula is C₅H₁₀O.

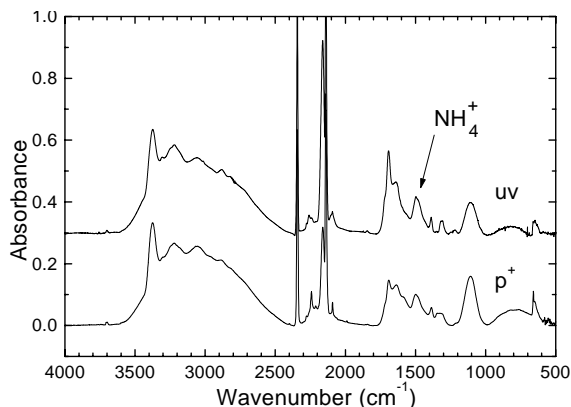


Fig. 2. IR spectra of UV-photolyzed (upper) and proton-irradiated CO + NH₃ (1:1) ice at ~ 15 K. The upper spectrum was recorded after a UV exposure of 1 hour and the lower was recorded after a 0.8 MeV p⁺ radiation dose of about 18 eV molecule⁻¹

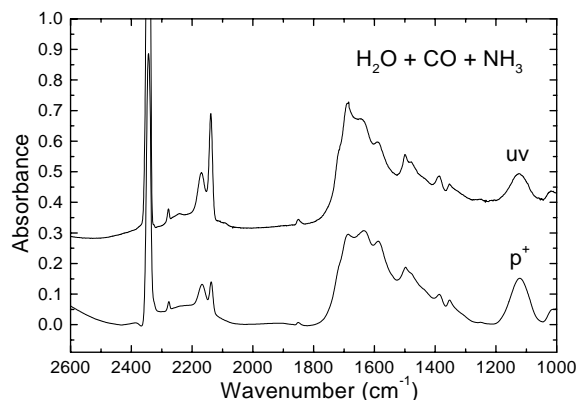


Fig. 4. IR spectra of UV-photolyzed (upper) and proton-irradiated H₂O + CO + NH₃ ices at ~ 15 K. The upper spectrum was recorded after a UV exposure of about 10 minutes and the lower was recorded after a 0.8 MeV p⁺ radiation dose of about 19 eV molecule⁻¹

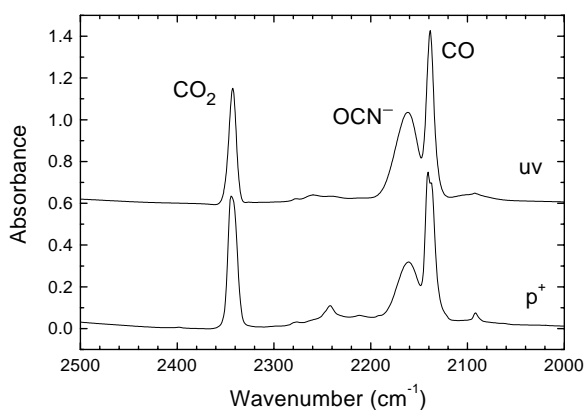


Fig. 3. Enlargement from Fig. 2 showing similarities of features

have not been reported, the published spectra do not show any enhancement of NH₄⁺ by MTHF. Furthermore, the presence of MTHF should *not* raise the amount of HNCO present. This too is consistent with the published experiments; essentially no HNCO is left unreacted in photolysis of either CO + NH₃ or CO + NH₃ + MTHF ices. See particularly Figs. 7–9 of Demyk et al. (1998). With reactions (3) and (10) in mind, note that it is incorrect to call MTHF simply an “electron donor” (Demyk et al. 1998) as that term can also imply a reducing agent participating in a one-electron transfer to form an ion or even a functional group bonded to an aromatic system. Two correct expressions are “electron pair donor” and “H⁺ acceptor”, both connoting the appropriate acid-base chemistry. A somewhat more vivid expression is H⁺ scavenger.

Turning now to the other three-component ices of Demyk et al. (1998), the molecule added to CO + NH₃ mixtures in these was either CCl₄ or SF₆. These molecules have found wide usage among radiation chemists as electron scavengers. A standard test for a radiation-induced reaction involving electron transfer is to repeat the reaction in the presence of SF₆ or a molecule possessing a carbon-halogen bond. In either case, electron capture occurs to form an intermediate radical which

dissociates to a second radical and a halide ion. By scavenging electrons, dopants such as CCl₄ and SF₆ reduce neutralization of cations, raising their abundances (Spinks & Woods 1990).

In the interstellar ice analogue experiments of Demyk et al. (1998), addition of either CCl₄ or SF₆ had several effects. The abundances of the NH₄⁺ and HNCO were raised relative to the abundance of OCN⁻. If only acid-base chemistry is operative then according to reaction (3), increases in OCN⁻ should accompany increases in NH₄⁺, the *opposite* of what the CCl₄ and SF₆ experiments showed. However, the relative increase in NH₄⁺ is exactly as expected if electron-transfer reactions take place (see previous paragraph). This possibility will be discussed later in this paper, and will be potentially quite important in understanding the ice photochemistry.

3.3. New radiation experiments

We now turn from the interpretation of UV-photolysis experiments to our own radiation experiments. Fig. 2 compares a photolyzed CO:NH₃ ice² and a proton-irradiated CO:NH₃ ice. The initial CO:NH₃ ratio was 1:1 in each case. The photolyzed ice’s spectrum agrees in all essentials with that published by Demyk et al. (1998). As far as we are aware, Fig. 2 is one of very few direct, published comparisons of spectra from UV-photolyzed and ion-irradiated samples. The 2400–2000 cm⁻¹ region from Fig. 2 is expanded in Fig. 3 to show the CO₂, OCN⁻, and CO features. Small features are due to ¹³CO₂ (2277 cm⁻¹), ¹³CO (2091 cm⁻¹), and various carbon oxides (Moore et al. 1991). HNCO shows a broad, weak band near 2260 cm⁻¹ in both spectra.

The similarities between the spectra of photolyzed and irradiated CO + NH₃ ices in Figs. 2 and 3 are obvious, with essentially every peak and inflection in one spectrum being matched in the other. Moreover, these similarities were preserved when

² The IR spectra shown in this paper for UV-photolyzed ices were taken from the Leiden database at <http://www.strw.leidenuniv.nl/~schutte/database.html>.

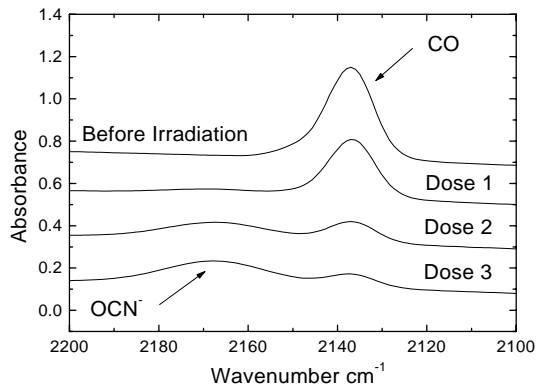
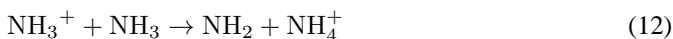


Fig. 5. Proton irradiation of a $\text{H}_2\text{O} + \text{CO} + \text{NH}_3$ mixture (5:1:1) at 17 K showing the conversion of CO into OCN^- (top to bottom). Doses 1, 2, 3 correspond to about 5.9, 17.8, and 28.4 eV molecule^{-1} , respectively

H_2O was initially present in the ice. Fig. 4 compares spectra of $\text{H}_2\text{O} + \text{CO} + \text{NH}_3$ mixtures which have been UV photolyzed and proton irradiated. Some differences exist in the 1600 cm^{-1} region, but they are far outweighed by the similarities across the two spectra. Finally, Fig. 5 demonstrates the smooth conversion of CO into OCN^- with increasing radiation dose. After $\sim 28 \text{ eV molecule}^{-1}$, 88 % of the CO has reacted (assuming an intrinsic band strength, $A(\text{CO}) = 1.1 \times 10^{-17} \text{ cm molecule}^{-1}$, Gerakines et al. 1995) and 14 % of that carbon forms OCN^- (assuming $A[\text{OCN}^-] = 4 \times 10^{-17} \text{ cm molecule}^{-1}$, d’Hendecourt & Allamandola 1986).

The primary action of the incident protons in our radiation experiments is to cause ionizations among the sample molecules. Ejected electrons travel through the ice sample leaving a trail of chemical change, including free radicals, ions, and neutral molecules. For the case of irradiated $\text{CO} + \text{NH}_3$, reactions can be written by analogy with irradiated $\text{H}_2\text{O} + \text{CO}$ (Hudson & Moore 1999):

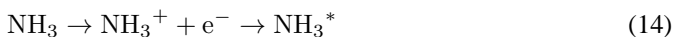


The formation of NH_4^+ in reaction (12) contributes to the broad NH_4^+ band in the 1480 cm^{-1} region of Fig. 2. Neutralization of NH_4^+ from reaction (12) by ejected electrons will prevent the NH_4^+ abundance from continuously rising:



NH_2 from reaction (12) will combine with CO, leading to HNCO , NH_4^+ , and OCN^- by reactions (2) and (3). The main reaction of CO not involving a nitrogen-containing species will be formation of CO_2 , presumably by a path similar to that in photolyzed neat CO (Gerakines et al. 1996).

Another mechanism operating in ion irradiations involves recombination of the original electron-cation pair followed by dissociation into NH_2 and H atoms. This is shown below:



Note that the final step, reaction (15), is essentially the same as reaction (1) for UV-photolyzed $\text{CO} + \text{NH}_3$ ices.

The balance between these two radiolysis pathways is unknown but, in the absence of other information, we assume that both contribute to product formation. It should be noted that the final NH_4^+ and OCN^- abundances in the ice will be equal only in the absence of electron trapping or scavenging by other molecules. This applies to both laboratory and interstellar ices.

To summarize, ion irradiation of $\text{CO} + \text{NH}_3$ ices involves two pathways to products, reactions (11)–(13) and reactions (14)–(15), both pathways involving ions and forming NH_2 . The second set of reactions ends with a step essentially identical to that seen in UV photolysis experiments. While both reaction pathways begin with formation of NH_3^+ , the second step in one path is H^+ -transfer while in the other it is e^- -transfer.

The above describes radiolysis in the absence of H_2O . When H_2O is present in irradiated $\text{CO} + \text{NH}_3$ ices, it will be a source of H^+ , e^- , H, and OH. Also, H_2O will compete as a base, probably weakly, with NH_3 . Reactions of CO will take place, and these have been described (Hudson & Moore 1999). However, the formation of NH_4^+ and OCN^- will proceed as already outlined.

4. Discussion

We first summarize the arguments for the OCN^- assignment and then address the implications of the experiments carried out and the reactions written. Finally we make a few general comments concerning interstellar ice chemistry.

4.1. Comments on the OCN^- assignment

Readers unfamiliar with interstellar ice analogue experiments may wonder how the broad, overlapping features in IR spectra of mixtures can be assigned to specific molecules. Admittedly tables of group frequencies provide little help. In general, however, four different approaches are available, and as many as possible ought to be employed when there are ambiguities. The four approaches are (i) comparison with reference spectra in ices, (ii) isotopic substitution, (iii) experiments to selectively alter reaction pathways, and (iv) arguments based on reaction chemistry. In assigning the 2160 cm^{-1} band in processed $\text{CO} + \text{NH}_3$ ices to OCN^- , all but the first approach have been used; preparing a solid-phase mixture of a salt and two gases at 15 K is non-trivial.

The first test applied to the OCN^- assignment was isotopic substitution. Experiments with ^{15}N and ^{13}C by Grim & Greenberg (1987) showed that the 2160 cm^{-1} band shifts as expected for OCN^- . Later, detection of weaker OCN^- bands, as well as ^{18}O experiments, were found to be consistent with this assignment (Schutte & Greenberg 1997). The scavenging experiments of Demyk et al. (1998) constitute a second test of the OCN^- assignment. They clearly demonstrated that the carrier of the 2160 cm^{-1} band is stable in MTHF, a reliable indication of anionic character. A third argument for the OCN^- assignment is the analysis of the reaction chemistry given in this present paper. As already mentioned, knowledge of reactions in processed

H₂O + CO ices leads to certain expectations for processed CO + NH₃ ices. The agreement between those chemical expectations and the experimental observations strongly implies that the underlying chemistry is understood and that the OCN⁻ assignment is correct.

4.2. New reactions and a suggestion

The similarities between the spectra of irradiated and photolyzed CO + NH₃ ices, as shown in Figs. 2 and 3, point to a common chemistry for the two types of processing, and indeed common reactions have already been noted. The major difference between the reaction networks written so far for photolysis and irradiation is electron-transfer reactions during radiolysis which leads to ions. To test the extent of this difference, scavenging experiments can be performed. Specifically, to test if electron transfer is occurring in a *photolysis* experiment with CO + NH₃ ice, an electron scavenger can be added. The primary effect will be to remove a certain fraction of electrons that would ordinarily neutralize NH₄⁺ in reaction (13), thus raising this cation’s abundance. If electron transfer plays no part in photolysis of CO + NH₃ ices then an electron scavenger should not influence the final products.

We suggest that the relevant experiments have already been done by Demyk et al. (1998) and that the results indicate that electron transfer occurs in UV-photolyzed CO + NH₃. Their experiments with both CCl₄ and SF₆ clearly showed that the NH₄⁺ abundance increased, relative to OCN⁻, as already described. These particular scavenging experiments imply that there are two sources for the products observed in the UV-photolysis experiments, one based on acid-base chemistry and the other on electron transfer, similar to what is seen in radiation experiments.

Although we have not identified the precise source of the electrons taking part in the photolysis experiments, we suspect NH₃. Its gas-phase ionization energy lies beyond the output of hydrogen-discharge lamps, but the more relevant physical property is the energy needed to photoeject an electron in the *condensed* amorphous phase. It is not unusual to find thresholds for photoemission of electrons in a condensed phase to lie below gas-phase values. One is reminded of the substantial difference between gas-phase ionization energies of some metals and the values of their work functions. In liquid H₂O, photoejection of electrons has been seen at energies down to about 6.5 eV, well within the range of hydrogen-discharge lamps, although the gas-phase ionization energy of H₂O is 12.6 eV (Boyle et al. 1969).

We have considered other electron sources in UV-photolyzed CO + NH₃ mixtures but they do not appear realistic. For example, an argument might be made for photoejection of an electron from OCN⁻, but considering the resistance of iso-electronic CO₂ to UV exposure, OCN⁻ is not expected to be an efficient source of electrons. Even if an electron were photoejected from OCN⁻, reaction (3) should be drawn to the right to produce yet more NH₄⁺ and OCN⁻ at the expense of HNCO, so that the acid will be completely consumed. However this

contradicts the electron scavenging experiments. HNCO was at its *greatest* abundance when either CCl₄ or SF₆ was present to remove electrons. Two-photon processes also appear rather unlikely.

In our experience chemical changes in UV-photolyzed ices are nearly always interpreted in terms of neutral free radicals and acid-base chemistry. Our suggestion of electron transfer is somewhat novel, and additional work is needed to test it, such as scavenging experiments with other photolyzed mixtures. If substantiated, our suggestion will help explain similarities in the chemistries of irradiated and photolyzed interstellar ice analogues, and may even suggest new interpretations of published experiments. For example, H₂O, the most abundant interstellar ice molecule, may undergo photoejection in the same way as we suspect for isoelectronic NH₃. Another common interstellar ice component, CO₂, is an e⁻ scavenger. The importance of this property in understanding CO₂ ice experiments and interstellar ice observations remains to be investigated.

In our opening paragraph we said that the “XCN” band at 4.62 μm is one of two major unidentified features in ISO spectra of interstellar ices, the other being a prominent absorption at 6.85 μm. Although this paper is concerned primarily with the laboratory assignment and formation of OCN⁻, the results may impact interpretations of the 6.85 μm interstellar ice feature. One consideration for any interpretation of that band, and for laboratory ice chemistry, is the balance of electrical charges. Our work shows that there may be multiple contributions to the positive and negative ion inventory in ices, depending on ice composition and the reaction mechanisms at work. Although some of the contributing ions may be observed, others may be difficult to detect. IR bands of NH₄⁺, OCN⁻, and HCOO⁻ are known, reasonably strong, and characteristic of these ions. Much less is known about potential contributors from CO₂, such as HCO₃⁻ and CO₃²⁻, protonated forms of alcohols and ethers, and even the ionic contributors from H₂O radiolysis, OH⁻ and H₃O⁺.

5. Conclusions

Through an examination of published data and new experiments, we have determined that electron-transfer reactions can take place in UV-photolyzed ices. This conclusion helps to explain why the UV- and ion-induced chemistries of these ices appear to be similar (Figs. 2–4). Depending on the importance of electron transfer, realistic UV processing schemes may need to include both H⁺ transfer (conventional acid-base) and e⁻ transfer (oxidation-reduction) along with reactions of neutral free radicals. Such schemes may not have the virtue of simplicity but they will have the benefit of explaining the observed chemistry, which is of greater importance. The experiments published by Demyk et al. (1998) are an excellent beginning.

Acknowledgements. NASA funding through NRA 344-33-01 and 344-02-57 is acknowledged by both authors. RLH acknowledges support through NASA Grant NAG-5-1843 and the NASA/ASEE Summer Faculty Fellowship Program (1996, 1997). Eckerd College is acknowledged for a research leave to RLH to complete this work. Claude

Smith and Steve Brown of the NASA/Goddard Radiation Facility are thanked for assistance with the proton irradiations. Perry Gerakines is thanked for assistance with photolysis experiments, preparation of this manuscript, and helpful discussions.

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