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THE FORMATION OF CYANATE ION (OCN^-) IN INTERSTELLAR ICE ANALOGS

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ABSTRACT

Although the 2165 cm^{-1} (4.62 μm) "XCN" IR absorption in interstellar ices was first detected over 20 years ago, its assignment has remained controversial, and its mode of formation has seldom been studied. Here we report an extensive laboratory investigation of this band's formation in interstellar ice analogs. Ices with known or suspected interstellar molecules were proton-irradiated at 15–25 K to simulate interstellar energetic processing, and their IR spectra were recorded. Reactions for irradiated mixtures showing an XCN spectral band have been developed based on results with chemically related systems and with over 60 ices examined here. Combined with previous work, our new results leave no doubt that the band produced in the laboratory is due to OCN^-, the cyanate anion. Tests of the reactions leading to OCN^- are described, and independent methods of producing OCN^- are reported. The results of all of these new experiments help reveal the chemistry underlying this ion's formation and establish some of the conditions under which OCN^- might be found in interstellar ices. They also show that energetic processing is an efficient way to produce OCN^- in interstellar ices and that temperature increases to promote acid-base chemistry are unnecessary.

Subject headings: ISM: molecules — line: formation — line: identification — molecular processes

1. INTRODUCTION

The assignment of the prominent 2165 cm^{-1} (4.62 μm) feature in infrared spectra of protostars has remained controversial since the band's discovery by Soifer et al. (1979). Although the band was initially thought to be due to CO, perhaps because of the low resolution of the data, experiments by Moore et al. (1983) showed that proton irradiation of ices containing selected interstellar molecules (e.g., H_2O, NH_3, CO) produced a new feature in the 2165 cm^{-1} region distinct from CO. This suggested that the band might form when interstellar ices are processed by cosmic radiation. Lacy et al. (1984) observed a similar feature after vacuum-UV photolysis of a $CO + NH_3$ (3:1) mixture, and the carrier was dubbed "XCN." Other workers preferred an assignment to methylisocyanide, CH_3NC (Larson et al. 1985). After surveying the most likely carriers, Grim & Greenberg (1987) assigned the XCN feature to the intense asymmetric stretch (ν_3) of the cyanate anion, OCN^-. Their laboratory experiments, in which a $CO + NH_3$ (1:1) mixture was UV-photolyzed near 12 K, produced a band which matched the interstellar feature in shape, position, and width. Experiments with $^{13}CO + ^{14}NH_3$ and $^{12}CO + ^{15}NH_3$ ices gave isotopic shifts consistent with OCN^-. Schutte & Greenberg (1997) later detected additional bands in similar photolysis experiments, all in agreement with OCN^-, and also obtained ^{18}O isotopic shifts of the correct magnitude. Nevertheless, the OCN^- assignment in laboratory and interstellar ices has not achieved full acceptance as various organic residues, nitriles, and other materials have been considered for the 2165 cm^{-1} band (Strazzulla & Palumbo 1998; Bernstein, Sandford, & Allamandola 1997; Nuth & Moore 1988). This situation has led to the continuing designation of the laboratory and interstellar features and their carriers as "XCN." (See, for example, Gibb et al. 2000.)

Comparison of the interstellar 2165 cm^{-1} feature in W33A, an embedded protostar, to the band from irradiated or photolyzed ices containing CO and NH_3 indeed results in an excellent match, as seen in Figure 1. However, making a spectral assignment based on a single broad, featureless absorbance is difficult. Pendleton et al. (1999) recently surveyed possible XCN candidates and concluded that "a true identification of the carrier of the 4.62 μm band still cannot be made on spectroscopic arguments alone." Currently, there is not even agreement about the XCN carrier in laboratory ices, making the assignment of the interstellar feature all the more difficult.

As spectroscopy alone appears insufficient for an XCN assignment, we have reexamined the problem, with the added vantage point of reaction chemistry. Our approach differs from that of virtually all previous workers in three important ways. First we have sought to assign the laboratory XCN band and, by inference, the interstellar feature through a consideration of radiation and photochemical reaction pathways. Concomitantly, we have examined many different ices to determine those in which the 2165 cm^{-1} band can be produced by energetic processing. Finally, as a check on our work, we have generated OCN^- in H_2O ice independently by other radiation and photochemical methods. Despite a decade of debate since Grim & Greenberg (1987) proposed OCN^- for XCN, this appears to be the first publication of a reference spectrum of the cyanate anion generated in situ in H_2O ice at $\sim$15 K.

Taken as a whole, our work provides a self-consistent and chemically reasonable approach to the 2165 cm^{-1} band's assignment and can be used to understand essentially all previous laboratory work related to XCN. Despite the rather colorful XCN appellation, our new results leave no doubt that the laboratory band from energetically processed $CO + NH_3$ and more realistic mixtures of interstellar molecules is due to cyanate ion, OCN^-. Provided that our experiments and those of others incorporate the relevant details of interstellar ice chemistry, they also imply that

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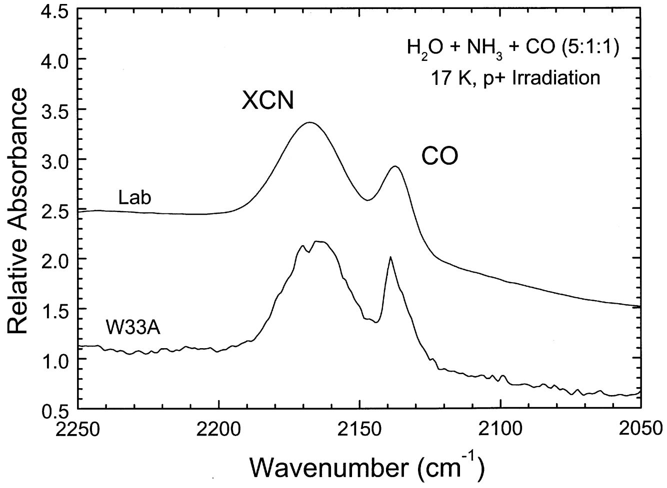

FIG. 1.—IR spectra of laboratory and interstellar ices. The upper trace is for an irradiated $H_2O + CO + NH_3$ (5:1:1) ice at 17 K. The lower trace is a spectrum of W33A from the *Infrared Space Observatory*. The radiation dose for the upper spectrum was about 19 eV molecule^{-1}.

OCN^- is a relatively common component of interstellar ices and that it can be made efficiently by energetic processing at low temperatures (∼15 K).

2. EXPERIMENTAL

Essentially all relevant experimental details are in print, including information on ice preparation, the IR spectrometer, the cryostat, and the proton radiation source (Moore & Hudson 2000; Moore & Hudson 1998; Hudson & Moore 1995). Chemical reagents were purchased largely from Aldrich, Matheson, and Cambridge Isotopes.

Ice samples typically were prepared by vapor-phase condensation onto a precooled (15–25 K) aluminum substrate (area ≈ 5 cm^2) in a high-vacuum chamber. Most ices were grown to thicknesses of several micrometers in ∼1 hour, with thicknesses being determined by a conventional laser interference system. In a few experiments, ices were made by injecting a room-temperature liquid-phase solution onto the precooled substrate (∼20 K) in the vacuum chamber. These experiments were with the following mixtures: $H_2O + H_2O_2$, $H_2O + CH_3CN$, $H_2O + C_2H_5NCO$, H_2O + formamide, H_2O + *N*-methylformamide, and H_2O + dimethylformamide. In all experiments, the amounts of the reagents used to make ices were measured carefully, but no attempt was made to obtain comparable proportions in the various experiments, which would be necessary to compare product yields.

To produce the 2165 cm^{-1} XCN spectral band, ices were exposed to a 0.8 MeV proton beam from a Van de Graaff accelerator to doses of 5–25 eV (18 amu molecule)$^{-1}$. The use of proton bombardment to mimic cosmic-ray bombardment and energetic processing has been discussed in other papers (e.g., Moore 1999; Moore et al. 1983). Since sample thicknesses were on the order of a few micrometers, the incident protons, having a range of 16 μm (Northcliffe & Shilling 1970), penetrated the ices and came to rest in the underlying metal substrate, not in the ice itself.

A few supporting far-UV photolysis experiments were done with a microwave-discharge hydrogen-flow lamp producing primarily Lyα photons (10.2 eV, 121.6 nm). Details can be found in Gerakines, Moore, & Hudson (2000), and references therein.

Mid-IR spectra were recorded as 60 scan accumulations for each ice before and after exposure to the proton beam (or photolysis lamp), typically from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}. Greater accumulations and higher resolution were occasionally employed. It was possible to measure the band strengths in all IR spectra recorded and thus determine yields of products in each experiment. In most cases this was not done as the purpose of our work was product identifications, not radiation yields. Finally, note that all IR band positions reported here supersede those made earlier on an older grating spectrometer (Moore et al. 1983).

3. RESULTS

For convenience in what follows, we often refer to the IR ice feature near 2165 cm^{-1} (4.62 μm) as the "XCN" band and the carrier as "XCN." To assign the band we follow several lines of argument, namely, reaction chemistry, band position, isotopic shifts, and thermal stability. Note again that essentially all earlier workers approached the "XCN problem" from the point of view of spectroscopy with relatively little work on the underlying chemical reactions. Our approach is to begin with the chemistry, test it, and then follow it to a spectroscopic assignment.

3.1. *Reaction Chemistry*

Most of our work on the XCN feature involves proton irradiation. Therefore, before presenting our new experimental results, it is appropriate to first consider the radiation products of two binary ices, namely $H_2O + CO$ and $CO + NH_3$. Essentially all of our experiments and interpretations were guided by these reactions.

To begin, since H_2O and NH_3 are isoelectronic molecules (eight valence electrons, one non-H atom), similar chemical properties are expected for them. Because we have previously investigated the radiation chemistry of $H_2O + CO$ ices (Hudson & Moore 1999), we can write the reactions expected for irradiated $CO + NH_3$. Irradiation of H_2O is known to yield, among other products, both H and OH radicals, and with CO present CO_2 readily forms as follows:

$$H_2O \rightarrow OH + H\ , \tag{1}$$

$$OH + CO \rightarrow H + CO_2\ . \tag{2}$$

An alternate path of formation for CO_2 involves the production of O atoms in irradiated H_2O ice and subsequent combination with CO:

$$O + CO \rightarrow CO_2\ . \tag{3}$$

Similar reactions will occur in UV-photolyzed ices although the mechanism for H and OH formation is somewhat different.

Ion irradiation of $H_2O + CO$ ice also generates HCOOH, formic acid (Hudson & Moore 1999), and $HCOO^-$, the formate anion (Hudson & Moore 2000a). When we irradiated $H_2O + CO + NH_3$, the HCOOH was removed, the $HCOO^-$ was enhanced, and NH_4^+ was seen, as expected from the following acid-base reaction:

$$HCOOH + NH_3 \rightarrow NH_4^+ + HCOO^-\ . \tag{4}$$

Figure 2 shows the appropriate spectra and identifications in the 1600–1100 cm^{-1} region.

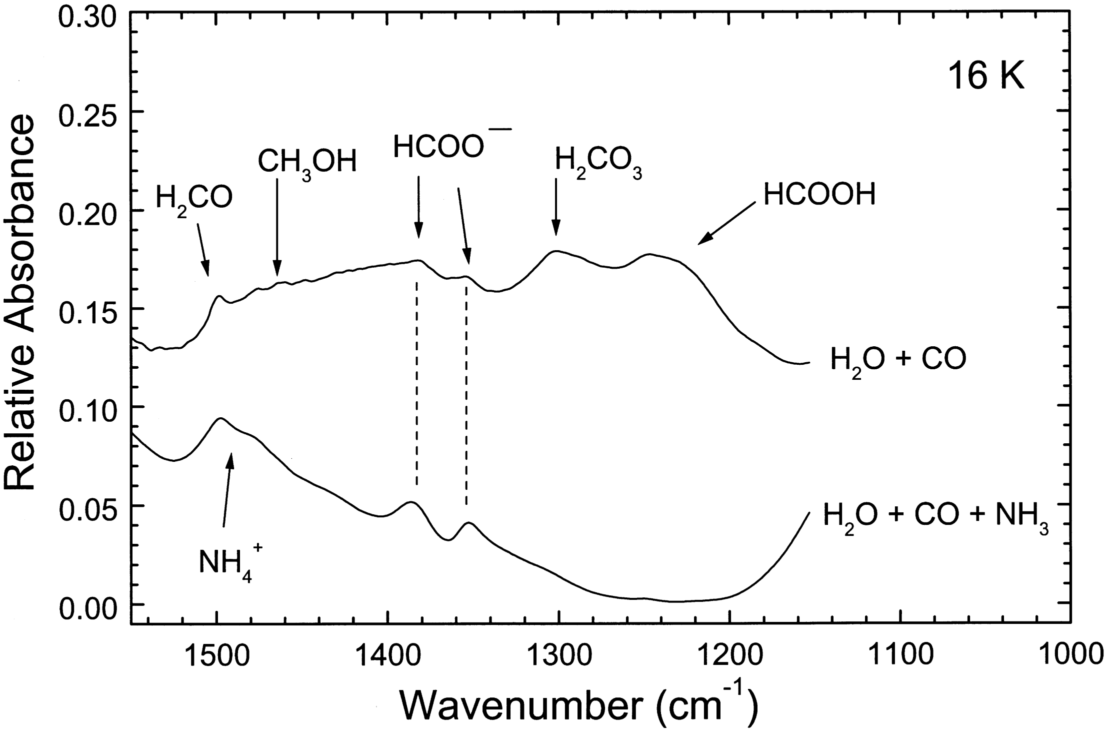

FIG. 2.—IR spectra of two irradiated laboratory ices at 16 K. The upper trace is an $H_2O + CO$ (5:1) ice and the lower trace is an $H_2O + CO + NH_3$ (5:1:1) ice. Both were irradiated to about 25 eV molecule cm^{-1}.

To a first approximation, the radiation products of a $CO + NH_3$ ice can be explained with four reactions similar to those above. Radiolysis generates NH_2radicals which lead to HNCO:

$$NH_3 \rightarrow NH_2 + H , \quad (5)$$

$$NH_2 + CO \rightarrow H + HNCO . \quad (6)$$

Alternatively, radiolysis will generate NH radicals which will combine with CO to form HNCO in a reaction analogous to reaction (3):

$$NH + CO \rightarrow HNCO . \quad (7)$$

In either case, after the acid HNCO forms, some fraction of it can be expected to react with the NH_3 present as follows:

$$HNCO + NH_3 \rightarrow NH_4^+ + OCN^- . \quad (8)$$

Seen this way, it would be remarkable were OCN^- *not* to form in a $CO + NH_3$ ice exposed to either ionizing radiation or far-UV photons. The path leading to cyanate involves, in essence, the same chemistry that produces CO_2 from CO in H_2O ice, an efficient, well-documented conversion (e.g., Allamandola, Sandford, & Valero 1988; Hudson & Moore 1999).

It is also possible to argue for reactions (5)–(8) using earlier work. The reaction of NH and CO to form HNCO, and other acids, has been established (Milligan & Jacox 1967; Jacox & Milligan 1964). The reaction between NH_3 and HNCO follows from elementary acid-base chemistry and has been considered by Grim et al. (1989a).

Like CO_2, OCN^- is a linear, 16 valence electron triatomic molecule, and so like CO_2 it is expected to form readily in radiolysis or photolysis experiments and to be stabilized at cryogenic temperatures. These facts, and the above analysis of the reaction chemistry, lead to certain expectations for both irradiated and photolyzed $CO + NH_3$ mixtures:

1. IR spectra of irradiated or photolyzed $CO + NH_3$ mixtures will show a strong band near 2165 cm^{-1}, the known position for the cyanate anion (Maki & Decius 1959).
2. This band will show ^{13}C and ^{15}N isotopic shifts of about 57 and 17 cm^{-1}, respectively (Maki & Decius 1959).
3. Since OCN^- is a reasonably stable anion, the 2165 cm^{-1} band will be present at temperatures at least up to where NH_3 sublimes, if not much higher.
4. The appearance of the 2165 cm^{-1} band of OCN^- will not be limited to $CO + NH_3$ mixtures. It is expected whenever radiolysis or photolysis generates reactants comparable to those in reactions (5)–(8).

We now turn to the first of these expectations, the detection of the 2165 cm^{-1} feature in radiation and photochemical experiments.

3.2. *The* XCN *Band in* $CO + NH_3$ *Ices*

Spectra of certain laboratory ices, both ion-irradiated and UV-photolyzed, have long been known to show an XCN feature, and an example is shown in Figure 3 with an enlargement in Figure 4.[4] In processed $CO + NH_3$ ices, a prominent feature is seen in the 2165 cm^{-1} region, exactly where OCN^- should be. As an aside, the question has been raised as to whether the bands seen in radiolysis and pho-

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[4] IR spectra of Figs. 3 and 4 for UV-photolyzed ices were taken from the Leiden database at http://www.strw.leidenuniv.nl/~ab. Independently, we have repeated the relevant experiments and verified the results.

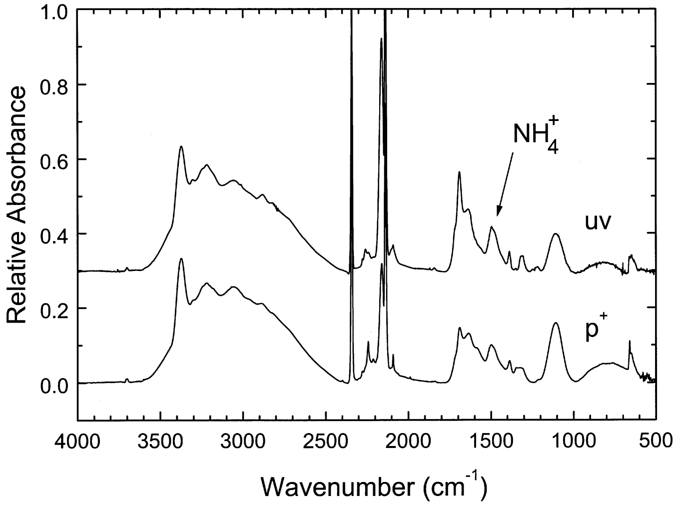

FIG. 3.—IR spectra of UV-photolyzed (*upper*) and proton-irradiated (*lower*) $CO + NH_3$ (1:1) ice at ~15 K. The upper spectrum was recorded after a UV exposure of 1 hour and the lower was recorded after a 0.8 MeV p^+ radiation dose of about 18 eV molecule^{-1}.

tolysis experiments are the same (Pendleton et al. 1999). Figures 3 and 4 shows that in all essentials the bands of the photolyzed and irradiated ices match.

We also have performed experiments with isotopically labeled molecules. Figure 5 compares the spectra from experiments beginning with (top to bottom) $^{12}CO + ^{14}NH_3$, $^{12}CO + ^{15}NH_3$, and $^{13}CO + ^{14}NH_3$. The spectra on the left are from photolysis experiments of Grim & Greenberg (1987), while those on the right are from our radiation experiments.[5] Again the agreement between the photolysis and radiation results is excellent. In a separate paper we have traced this agreement to common, and perhaps unrecognized, features in the underlying chemistry (Hudson & Moore 2000b). The ^{13}C and ^{15}N isotopic shifts shown in Figure 5 are precisely those expected for OCN^- (Maki & Decius 1959). In a $^{13}CO + ^{15}NH_3$ (1:1) radiation experiment we observed an isotopic shift of 75 cm^{-1} for the XCN band, the same as Maki & Decius (1959) measured for $O^{13}C^{15}N^-$. In yet another experiment, we ion-irradiated a $^{12}CO + ^{13}CO + ^{14}NH_3$ (1:1:1) mixture. The spectrum in the XCN region showed only two identical bands at 2164 and 2105 cm^{-1}, each about 27 cm^{-1} in width, with identical thermal behavior. In other words, the spectrum was a superposition of the ^{12}C and ^{13}C bands in Figure 5 with no hint of a new carrier with both ^{12}C and ^{13}C atoms. This observation is consistent with the carrier of the XCN band having one carbon atom.

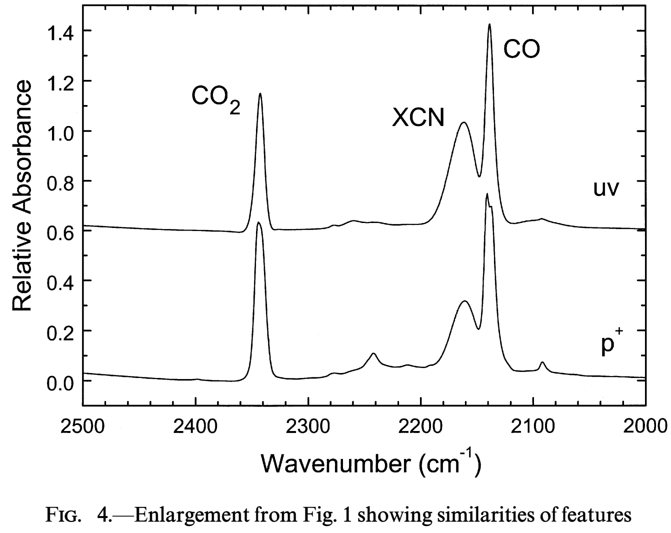

FIG. 4.—Enlargement from Fig. 1 showing similarities of features

We have found that the position of the XCN feature in ices is somewhat variable, ranging from about 2158 to 2170 cm^{-1} with a bandwidth (FWHM) of ~25 cm^{-1}. In $CO + NH_3$ mixtures at ~15 K, there is a slight increase (few cm^{-1}) with either photolysis time (Schutte & Greenberg 1997) or radiation dose, but in ices with H_2O as the dominant molecule, the band scarcely changes with processing. As with most condensed-phase bands, the position and width will depend somewhat on temperature and composition of the sample. Although the absolute intensity of the 2165 cm^{-1} band in Figure 4 has not been measured, its intensity relative to CO_2 is obviously high, and thus the carrier represents a major reaction product. In a separate paper we have estimated that about 14% of the initial CO in a $CO + NH_3$ (1:1) ice is converted into the "XCN" product after a dose of ~28 eV molecule^{-1} (Hudson & Moore 2000b).

There is general agreement between our work and that of others (Lacy et al. 1984; Grim & Greenberg 1987) regarding the XCN band's thermal stability. We have found that the carrier is stable under vacuum to temperatures well above 200 K, as would be expected for OCN^-. Although a complete investigation has yet to be reported, the upper limit to stability appears to depend on the accompanying residual molecules, the rate of warming, the sample thickness, and, of course, time.

3.3. *Assignment of the Laboratory* XCN *Band and Tests of the Assignment*

The expectations outlined at the end of § 3.1 and the results of § 3.2 are sufficient to assign the laboratory XCN band to OCN^- in $CO + NH_3$ ices. The cyanate ion is predicted by the reaction chemistry of § 3.1, and the spectroscopic data (band position, isotopic shifts, band's relatively high intensity) and the carrier's thermal stability are in complete accord with expectations for OCN^-. It might be possible to envision other products, such as isocyanide molecules, that could contribute to the 2165 cm^{-1} region. These can be ignored as being inconsistent with the measured isotopic shifts, being thermally unstable under vacuum compared to OCN^-, or possessing additional bands that are not observed. Furthermore, the chemical reactions leading to OCN^-, reactions (5)–(8), are so straightforward and efficient that it is reasonable to neglect minor contributors. The reactions in § 3.1 show that cyanate anion is a major reaction product.

Having written reactions for OCN^- formation, we tested them in several ways. Reactions (5)–(8) show that in $CO + NH_3$ mixtures an acid HNCO is formed by CO reacting with an intermediate possessing an N—H bond, such as NH_2 or NH. If a base, such as NH_3, is present, then HNCO reacts to make OCN^-. In short, the reactants needed to

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[5] Note that our spectra on the right in Fig. 5 have been scaled along the vertical axis to match the published (Grim & Greenberg 1987) spectra on the left.

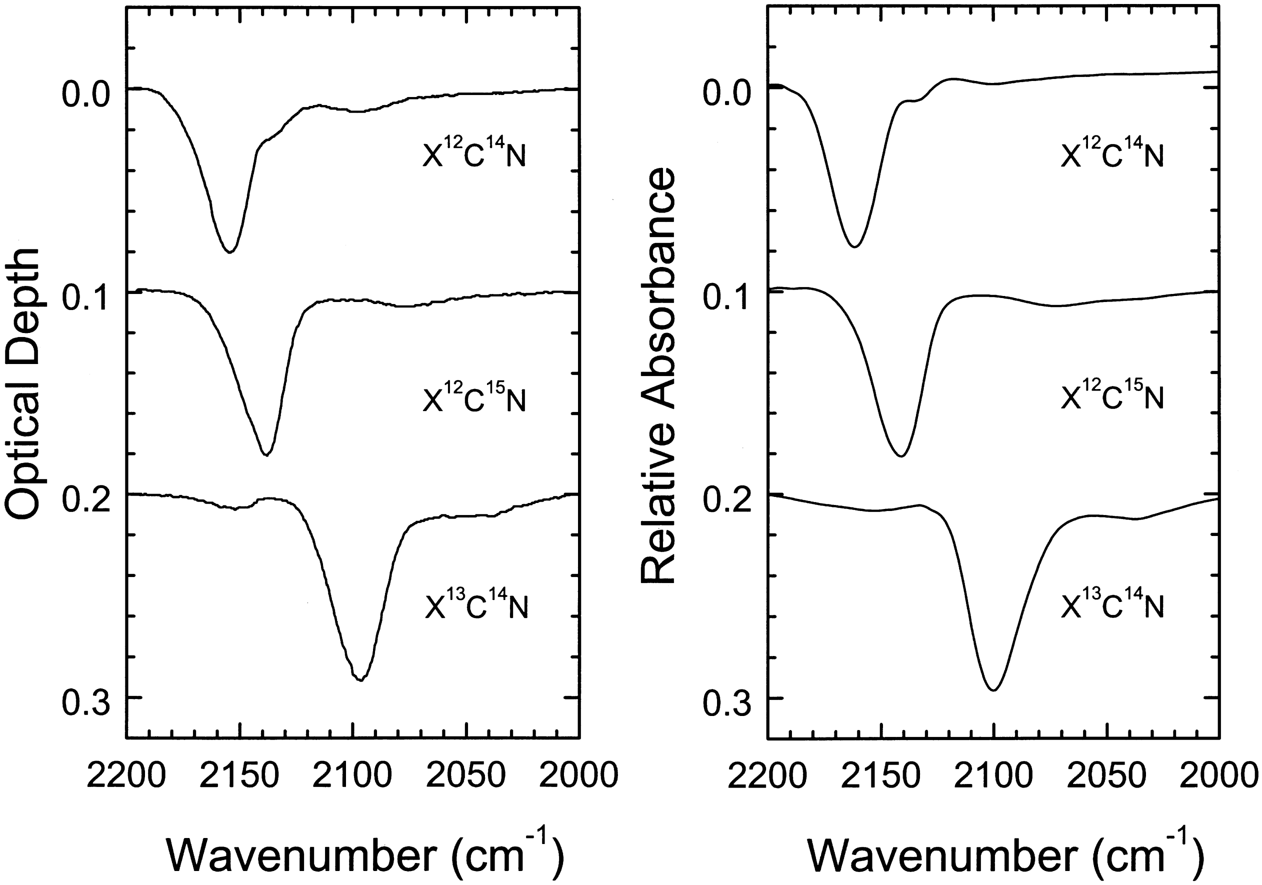

FIG. 5.—$CO + NH_3$ (1:1) ices after energetic processing. The spectra on the left are from Grim & Greenberg (1987) and were taken at 80 K after UV photolysis at 10 K. The spectra on the right were taken at 75 K after a proton irradiation at ~16 K. The ices were initially 1:1 mixtures of $^{12}CO + ^{14}NH_3$ (*top*), $^{12}CO + ^{15}NH_3$ (*middle*), and $^{13}CO + ^{14}NH_3$ (*bottom*).

make OCN^- are CO, some intermediate with an N—H bond, and a base. Also, the amount and type of base present will influence the relative amounts of HNCO and OCN^-.

These conclusions led us to irradiate the seven mixtures in Table 1 and search for OCN^- in each case. Our strategy was to begin with the $CO + NH_3$ mixture already studied and to change one reactant at a time. For example, in going from mixture 1 to mixture 2 in Table 1, we substituted CO_2 for CO, knowing that radiolysis of CO_2 produces CO (Palumbo & Strazzulla 1993). So the $CO_2 + NH_3$ ice was expected to, and did, produce OCN^-. Mixture 3 kept the CO and changed NH_3 to a different base, namely NH_2CH3, methylamine. Since irradiation of NH_2CH3 was expected to produce NH_2radicals, irradiation of the $CO + NH_2CH3$ mixture was expected to, and did, produce OCN^-. A more stringent test was mixture 4, $CO_2 + NH_2CH3$. On irradiation CO_2 and NH_2CH3 were expected to form CO and NH_2, respectively, reactants leading to HNCO. Since NH_2CH3 is a base, HNCO's conversion to OCN^- was predicted and observed.

TABLE 1

OCN^- IN IRRADIATED ICES

Ice Mixture	Ratio	OCN^- Seen?
1. $CO + NH_3$	1:1	Yes
2. $CO_2 + NH_3$	1:2	Yes
3. $CO + NH_2CH_3$	1:1	Yes
4. $CO_2 + NH_2CH_3$	~1:1	Yes
5. $CO + NH_3$	1:1	Yes
6. $CO + N_2 + H_2O$	1:1:5	Yes
7. $H_2O + CH_4 + NH_3$	~1:1:1	Yes
8. $H_2O + CH_4 + N_2$	~1:1:1	Yes

Table 1 also lists a second set of four mixtures to test our reactions, using the approach just described. From the CO $+ NH_3$ combination, we first varied the two reactants by substituting "$N_2 + H_2O$" in mixture 6 for NH_3. The following reactions were expected, starting with the radiolysis of N_2 to make N atoms:

$$N_2 \rightarrow N + N , \tag{9}$$

$$N + H_2O \rightarrow NH + OH , \tag{10}$$

$$NH + CO \rightarrow HNCO , \tag{11}$$

$$HNCO + H_2O \rightarrow H_3O^+ + OCN^- . \tag{12}$$

As expected, OCN^- was observed on irradiation of mixture 6. Results with mixtures 7 and 8 are already in the literature (Moore et al. 1983; Strazzulla & Palumbo 1998; Palumbo et al. 2000) and have been confirmed by us in the course of this work. OCN^- was observed after each mixture was irradiated.

To summarize, each of the seven mixtures in Table 1 constitutes a test of the chemistry leading to OCN^-. Each was expected to produce OCN^- on proton-irradiation, and in each case OCN^- was observed.

Our reactions (5)–(8) also predict that NH_4^+, ammonium ion, should form in irradiated or photolyzed $CO + NH_3$ mixtures. This ion is indicated in Figures 2 and 3 near 1500 cm^{-1}. Grim et al. (1989b) and Demyk et al. (1998) have studied this absorbance and made strong arguments for it as a contributor to the 6.8 μm feature in IR spectra of protostars, including W33A. There is also the possibility that H_3O^+ might form in interstellar ices, but it will be difficult to detect with IR spectroscopy owing to overlap of its features with those of H_2O. Ammonium is by far the most promising common cation for detection in H_2O ices.

3.4. *Acid-Base Tests*

Our results with an $H_2O + CO + N_2$ ice (Table 1, mixture 6) can be used for another test of our reactions. Since the only base present in this mixture is the relatively weak H_2O, the conversion of HNCO to OCN^- is expected to be less efficient than in $H_2O + CO + NH_3$. Figure 6 compares spectra for these two irradiated mixtures. The HNCO band at 2261 cm^{-1} (Crowley & Sodeau 1989 and references therein) is absent when the mixture includes NH_3, indicating efficient conversion due to reaction (13):

$$HNCO + NH_3 \rightarrow NH_4^+ + OCN^- . \qquad (13)$$

It is obvious from the figure that the OCN^--to-HNCO ratio is much greater when NH_3 is present.

Figure 7 shows another conversion of HNCO into OCN^-. Preliminary experiments demonstrated that proton irradiation of an $O_2 + CH_4$ mixture produced CO, presumably by hot-atom chemistry (Kaiser et al. 1997). Figure 7 shows that an initial mixture of $O_2 + CH_4 + N_2$ resulted in a band for HNCO (upper spectrum). Substituting NH_3 for N_2 in a new mixture and then irradiating gave the lower spectrum. Once more, NH_3 removed the acid and formed OCN^-, in accord with reaction (13).

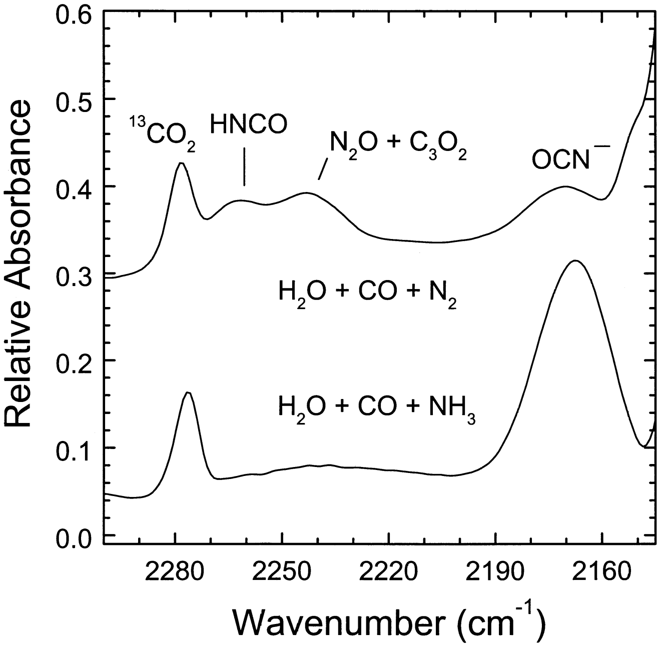

FIG. 6.—IR spectra of proton-irradiated polar ices near 16 K. The upper spectrum is of irradiated $H_2O + CO + N_2$ (5:1:1) and the lower spectrum is of irradiated $H_2O + CO + NH_3$ (5:1:1). Ices were irradiated and spectra were recorded at ~16 K.

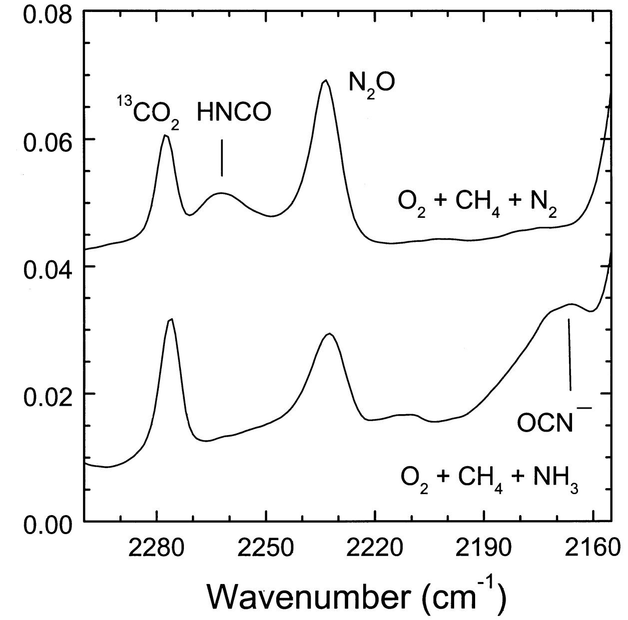

FIG. 7.—IR spectra of proton-irradiated ices near 16 K. The upper spectrum is of irradiated $O_2 + CH_4 + N_2$ (1:1:1), and the lower spectrum is of irradiated $O_2 + CH_4 + NH_3$ (1:1:1). Ices were irradiated and spectra were at ~16 K.

3.5. *Other Mixtures Examined with Interstellar Molecules*

We also irradiated selected two- and three-component mixtures composed of molecules either known or strongly suspected to be in interstellar ices. We considered the simplest carbon-bearing molecules ranging in oxidation state from CO and CO_2 to the fully reduced CH_4. The extremes for nitrogen were taken as N_2 and NH_3. Combined with H_2O, these gave the six mixtures listed in Table 2. Each mixture was proton-irradiated and its IR spectrum recorded. Figure 8 shows the OCN^- features, and Table 2 lists their positions. Only the $H_2O + CO_2 + N_2$ ice failed to show a clear feature from OCN^-. This same mixture did show an 1875 cm^{-1} band, apparently from NO, as well as features from H_2CO_3 (Gerakines et al. 2000).

In other experiments, we irradiated the binary mixtures in Table 3, which correspond to those of Table 2 but without H_2O. Of these mixtures, only $NH_3 + CO$ and $NH_3 + CO_2$ clearly showed OCN^- bands at 2164 and 2158 cm^{-1}, respectively. Irradiated $CO + N_2$ and $CO_2 + N_2$ ices displayed a band close to the position of OCN^-, but it did not match the OCN^- band's shape, position (2180 cm^{-1} vs. ~2165 cm^{-1}), width (5–10 cm^{-1} vs. ~25 cm^{-1}), ^{15}N isotopic shift (~4 cm^{-1} vs. ~18 cm^{-1}), or thermal behavior

TABLE 2

IRRADIATED THREE-COMPONENT ICE MIXTURES

Ice Mixture	Ratio	ν_3 (cm^{-1})	FWHM (cm^{-1})
1. $H_2O + CO + NH_3$	5:1:1	2167	26
2. $H_2O + CO_2 + NH_3$	1:1:2	2164	25
3. $H_2O + CH_4 + NH_3$	~1:1:1	2159	23
4. $H_2O + CO + N_2$	5:1:1	2170	25
5. $H_2O + CO_2 + N_2$	5:1:1		
6. $H_2O + CH_4 + N_2$	~1:1:1	2159	27

NOTE.—Irradiations done and spectra recorded at 15–18 K.

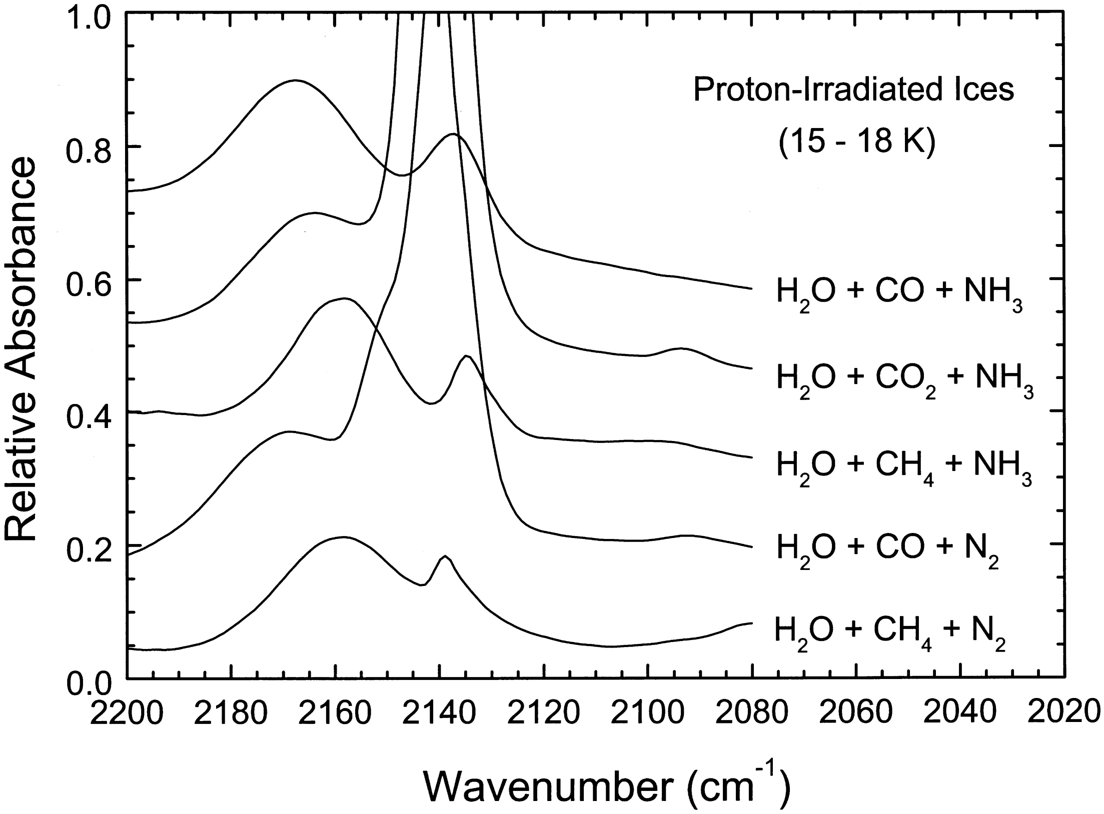

FIG. 8.—IR spectra of the ices listed in Table 2. Ices were irradiated and spectra were recorded at 15–18 K.

(stable to ~ 35 K vs. > 200 K). Furthermore, there is no obvious mechanism by which the ion OCN^- could be formed and stabilized in either $CO + N_2$ or $CO_2 + N_2$, both apolar matrices.

3.6. *Other Methods for the In Situ Generation of* OCN^-

Although the reactions in § 3.1 above led efficiently to OCN^-, we sought to generate this anion in H_2O at ~16 K by other in situ paths. Here we were not bound by the requirements that the ice molecules be astronomically relevant, although many were, or that the reactions follow from those in § 3.1 for $CO + NH_3$ mixtures. Our most straightforward synthesis of OCN^- was during radiolysis of an ice mixture made of H_2O and C_2H_5NCO, ethyl isocyanate. Alkyl halides such as C_2H_5Br are frequently used in radiation chemistry as scavengers of secondary electrons produced by an incident radiation, undergoing dissociative electron capture (Willard 1987) according to

$$e^- + C_2H_5Br \rightarrow C_2H_5 + Br^- \qquad (14)$$

to produce stable halide anions such as Br^-. A similar reaction occurs with alkyl cyanides:

$$e^- + C_2H_5CN \rightarrow C_2H_5 + CN^- . \qquad (15)$$

The high efficiency of reactions (14) and (15) derives from the halide and cyanide anions which are, in the language of organic chemistry, "good leaving groups" because of their considerable stability. As already explained, OCN^- is also quite stable, so a reaction similar to reactions (14) and (15) will occur on irradiation of $H_2O + C_2H_5NCO$, namely,

$$e^- + C_2H_5NCO \rightarrow C_2H_5 + OCN^- . \qquad (16)$$

After irradiating $H_2O + C_2H_5NCO$ (10:1) at 22 K we observed the OCN^- band at 2163 cm^{-1} (FWHM = 26 cm^{-1}) and found that it persisted to nearly 300 K. Figure 9 compares this OCN^- feature to spectra in the same region for the protostellar source W33A and for irradiated $H_2O + CO + NH_3$. To the best of our knowledge, the bottom trace of Figure 9 is the first publication of a reference spectrum of cyanate ion, produced in situ in an ice. Previous papers tended to rely on reference spectra of salts or mixtures made at room temperature (e.g., Grim & Greenberg 1987), in which the agreement with the ice spectrum was not as good as in Figure 9.

Five other methods were used for the generation of OCN^-. Proton irradiation of $H_2O + HCN$ gave OCN^-, probably via the mechanism of Crowley & Sodeau (1989) to make HNCO, followed by H^+ transfer to H_2O. Proton irradiation of $H_2O + CH_3CN$ (10:1) produced OCN^-, probably by a mechanism similar to that in $H_2O + HCN$.

TABLE 3

IRRADIATED TWO-COMPONENT ICE MIXTURES

Ice Mixture	Ratio	ν_3 (cm^{-1})	FWHM (cm^{-1})
1. $CO + NH_3$[a]	1:1	2164	27
2. $CO_2 + NH_3$[b]	1:2	2158	26
3. $CH_4 + NH_3$	5:1	...	...
4. $CO + N_2$[a]	1:1	...	...
5. $CO_2 + N_2$[c]	1:1	...	...
6. $CH_4 + N_2$	1:4	...	...

NOTE.—Irradiations done and spectra recorded at 15–18 K.

[a] Mixture also studied with ^{13}C and ^{15}N.

[b] Mixture also studied with ^{18}O.

[c] Mixture also studied with ^{15}N.

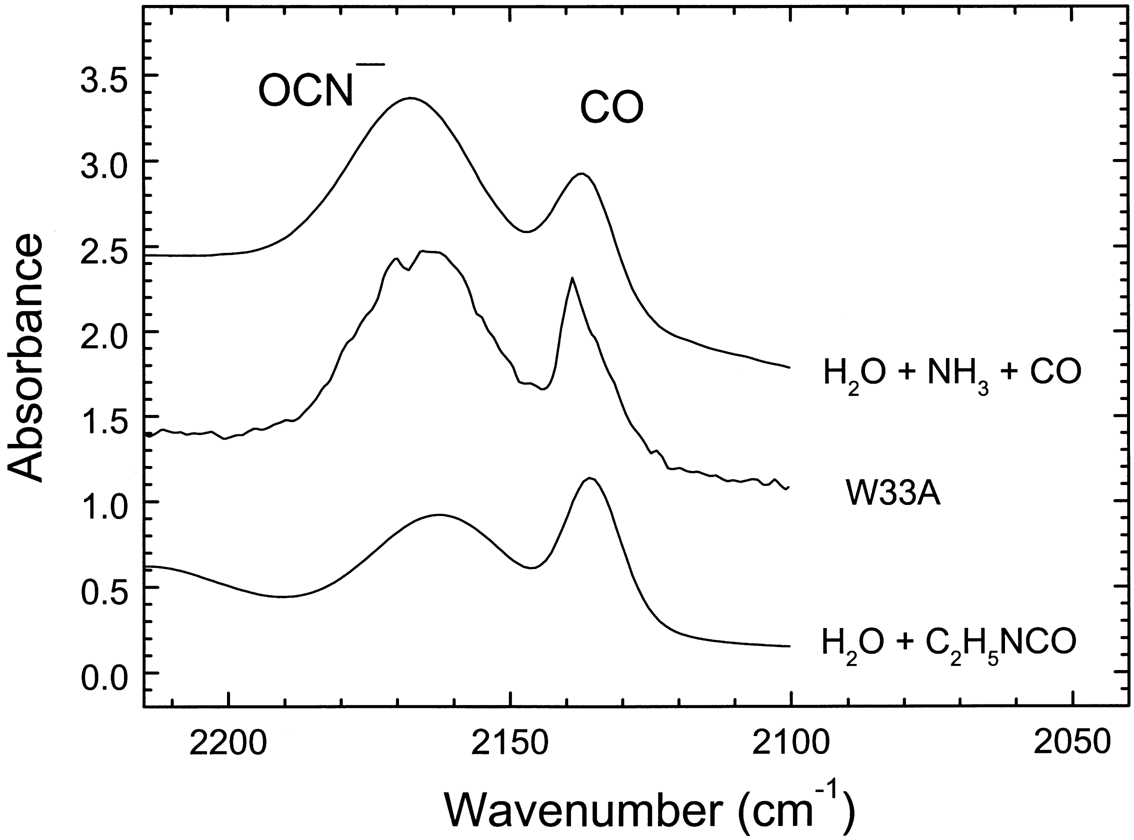

FIG. 9.—Comparison of laboratory and interstellar spectra. The spectrum of OCN$^-$ in irradiated $H_2O+C_2H_5NCO$ (10:1) compared to W33A and irradiated $H_2O+CO+NH_3$ (5:1:1). The two laboratory ices were irradiated and had their spectra recorded at ~16 K.

Far-UV photolyses of the following mixtures gave OCN$^-$: $H_2O+(CN)_2$ (5:1), H_2O+formamide (10:1), and H_2O + *N*-methylformamide (10:1). Far-UV photolysis of H_2O + dimethylformamide (10:1) did *not* produce OCN$^-$, which is interesting mechanistically. We list these experiments simply as additional ways to generate OCN$^-$, and we anticipate their description in a future paper. In all cases the spectral and thermal characteristics of the OCN$^-$ bands in these experiments matched those of the band in Figure 4.

These additional reactions for OCN$^-$ emphasize that this ion can be made by radiation and photochemical paths other than those already presented. Reactions such as (5)–(8) are reasonable from an astrochemical perspective but do not apply to mixtures such as the above.

3.7. "*Blank*" *Experiments*

IR spectra of many other proton-irradiated ices have been examined as "blanks." In none of these was a band near 2165 cm^{-1} expected, and in none was it found. These ices include irradiated binary mixtures of H_2O and the following: CO, CO_2, C_3O_2, CH_4, C_2H_6, C_2H_4, C_3H_6, C_2H_2, C_3H_4 (allene), C_3H_4 (propyne), CH_3OH, C_2H_5OH, H_2CO, CH_3COH, $(CH_3)_2CO$, HCOOH, CH_3COOH, $(CH_3)_2O$, *c*-C_2H_4O, $HCOOCH_3$, NH_3, O_2, N_2, N_2O, H_2O_2, OCS, SF_6, SiH_4, SO_2, and Kr. Many of these same molecules were also irradiated without H_2O, and in no case was a band seen that might possibly be confused with OCN$^-$. Also examined as blanks were irradiated HCN, CH_3CN, $CO+CH_4$, CO_2+CH_4, O_2+CH_4, N_2+O_2, N_2+O_2 +CO, O_2+NH_2, and N_2+NH_3. Again, these were not expected to show OCN$^-$, and none did.

The N_2+NH_3 mixture served not only as a blank, but as an important test for the reactions in § 3.1. Since CO and N_2 are both triply bonded 10 electron diatomic molecules, we expected their radiation chemistries to be similar. Writing reactions similar to (5)–(8), but with N_2 instead of CO, we could predict the following:

$$NH_3 \rightarrow NH_2 \text{ and/or } NH \ , \quad (17)$$

$$NH_2 + N_2 \rightarrow H + HN_3 \ , \quad (18)$$

$$NH + N_2 \rightarrow HN_3 \ , \quad (19)$$

$$HN_3 + NH_3 \rightarrow NH_4 + N_3^- \ . \quad (20)$$

The azide ion, N_3^-, was detected at 2025 cm^{-1} on irradiation of N_2+NH_3 (1:1) at 24 K. Similarly, irradiation of $^{14}N_2$ + $^{15}N_2$ + $^{15}NH_3$ (1:1:2) gave only two azide features at 2021 and 1960 cm^{-1}, acceptably close to the positions of, and the correct spacing for, $^{15}N^{14}N_2^-$ and $^{15}N_3^-$ (Theophanides & Turrell 1967). Since these were the only azide isotopomers predicted from reactions (17)–(20), their presence supports these reactions and, by inference, reactions (5)–(8) for $CO+NH_3 \rightarrow OCN^-$.

4. DISCUSSION

4.1. *Characteristics of the* OCN$^-$ *Band*

Our results show that OCN$^-$ can be recognized in laboratory spectra as a symmetrical band at 2158–2170 cm^{-1}, with a width (FWHM) of ~25 cm^{-1}. The band is thermally stable under vacuum to over 200 K. (These characteristics pertain to OCN$^-$ generated in situ near 16 K. Spectra taken of cyanate salts at room temperature or of cyanate-containing solutions may be slightly different.) Depending on the ice composition, the OCN^- feature may change slightly in position and intensity, as documented by Tegler et al. (1993), Grim & Greenberg (1987), and Lacy et al. (1984). A full study of this temperature dependence remains to be done. The OCN^- band also varies slightly with radiation and photochemical dose. This is understandable because the band depends somewhat on ice composition, which both radiolysis and photolysis will alter. All such spectral changes are minor in ices dominated by H_2O (Schutte & Greenberg 1997).

We have recently learned of a new OCN^- experiment in which IR spectra of UV-photolyzed $CO + NH_3$ and UV-photolyzed $CO + ND_3$ were compared (M. Bernstein 2000, private communication). The position of the OCN^- feature was lowered by several wavenumbers in the ND_3 experiment compared to the NH_3 experiment. This is as expected for two reasons. First, it is almost axiomatic that IR features of anions will shift as their cations change. Thus a small shift in OCN^- is expected on going from NH_4^+ to ND_4^+. Second, OCN^- undergoes hydrogen-bonding through both of its terminal atoms. This implies that a change from a protiated to a deuterated ice will be detected in the anion's vibrational bands. Such a change has been documented by Nelander & Nord (1982) for hydrogen bonding between H_2O and NH_3. Shifts of several wavenumbers were observed for water's symmetric stretch (ν_1) in going from H_2O-NH_3 pairs to H_2O-ND_3 pairs, and in going from D_2O-NH_3 pairs to D_2O-ND_3 pairs. Scheiner & Cuma (1996) have traced these shifts to differences in the zero-point vibrational energies of H and D bonds.

4.2. OCN^- *in Irradiated Mixtures*

We now consider the ices of Tables 2 and 3. Those containing NH_3 are treated first, and then those with N_2. Reactions (5)–(8) imply that formation of OCN^- occurs in the presence of CO, an "N-H" species, and some type of base to assist in the dissociation of HNCO. The key reactions can be summarized as follows:

$$NH_3 \rightarrow NH_2 \text{ and/or } NH\ , \quad (21)$$

$$NH_2 + CO \rightarrow H + HNCO\ , \quad (22)$$

$$NH + CO \rightarrow HNCO\ , \quad (23)$$

$$HNCO + \text{Base} \rightarrow \text{H(Base)} + OCN^-\ . \quad (24)$$

Given these reactions, it is not surprising that OCN^- was observed in experiments with both $CO + NH_3$ and $H_2O + CO + NH_3$. The H_2O does little beyond altering the matrix polarity and serving as a weak base, along with NH_3, for the H^+ transfer in reaction (24). Comparison of the OCN^- peaks in the $CO + NH_3$ and $H_2O + CO + NH_3$ ices shows that there is a matrix shift of about 3 cm^{-1} because of H_2O.

Turning to ices with CO_2 and NH_3, as already explained it was known that ion irradiation of CO_2 results in the formation of CO. Because CO is made during irradiation of both $CO_2 + NH_3$ and $H_2O + CO_2 + NH_3$, reactions similar to (21)–(24) will occur. This implies an OCN^- assignment for the features seen in these two ices at 2164 and 2158 cm^{-1}, respectively. Here a matrix shift of 6 cm^{-1} is seen for H_2O.

The two remaining NH_3-containing ices from Tables 2 and 3 are $CH_4 + NH_3$ and $H_2O + CH_4 + NH_3$. The former gives no IR band that might be assigned to OCN^-, and none is expected as no oxygen-bearing molecule was in the ice. But it is at first a puzzle that $H_2O + CH_4 + NH_3$ produces an "XCN" feature as neither CO nor CO_2 was initially present, implying that reactions (21)–(24) should be inapplicable. The solution to this puzzle is that radiolysis of a $H_2O + CH_4$ mixture is known to produce CO. Although the reaction pathway has not been determined, radiation synthesis of CO in $H_2O + CH_4$ ices has been observed both by us (Moore & Hudson 1998) and others (Strazzulla 1999). Because $H_2O + CH_4 + NH_3$ produces CO on radiolysis, reactions (21)–(24) will follow. Thus we confidently assigned the 2159 cm^{-1} band observed in irradiated $H_2O + CH_4 + NH_3$ to OCN^-.

The other six ices from Tables 2 and 3 include N_2 instead of NH_3. Radiolysis will break the N_2 bond to form N atoms and these, being very reactive radicals, will form NH and NH_2 if in an H_2O matrix. This implies that irradiating $H_2O + CO + N_2$ and $H_2O + CO_2 + N_2$ ices generates the reactants needed to make OCN^- according to reactions (21)–(24). The shape, position, and width of the band observed in our $H_2O + CO + N_2$ ice (Fig. 6) is reasonable for OCN^-.

The lack of any OCN^- feature in $H_2O + CO_2 + N_2$ was surprising. One explanation is that O atoms from CO_2 reacted with most of the N_2 to make N_2O, which we observed at 2236 cm^{-1} in both $CO_2 + N_2$ and $H_2O + CO_2 + N_2$. Another possibility is that N atoms were formed from N_2, followed by a competition between H-atom abstraction from H_2O to make NH and O-atom transfer from CO_2. The reactions are

$$N_2 \rightarrow N + N\ , \quad (25)$$

$$N + H_2O \rightarrow NH + OH\ , \quad (26)$$

$$N + CO_2 \rightarrow NO + CO\ . \quad (27)$$

No reaction analogous to (27) is expected with $H_2O + CO + N_2$ ices. As already mentioned, irradiated $H_2O + CO_2 + N_2$ ice did show an NO feature. Most likely, both sets of reactions sufficiently reduced the N_2 that little remained to make OCN^-.

From Table 2 we are left with just the $H_2O + CH_4 + N_2$ mixture. As already explained, CO will be produced on radiolysis of this mixture along with NH and possibly NH_2. These products will combine to make OCN^-. Note that the OCN^- positions in the N_2-containing three-component ices span a range of about 11 cm^{-1}.

Of the 12 mixtures in Tables 2 and 3, nine have been discussed so far. The remaining three are binary mixtures with N_2, all listed in Table 3. The $CH_4 + N_2$ mixture shows a number of interesting products, and these will be treated in a future paper. Bohn et al. (1994) examined the photochemistry of $CH_4 + N_2$ but neither they nor we find any feature in the "XCN" region, and none is expected from reactions (21)–(24). The final two ice mixtures are $CO + N_2$ and $CO_2 + N_2$. Negative results from both of these ices have already been presented. In the future we hope to write a full paper on the radiation chemistry of N_2 and CO, CO_2, and CH_4.

4.3. *Relationship to Work in Other Laboratories*

The reactions we have presented for OCN^- formation apply to essentially all published laboratory spectra in which an XCN band has been generated either photolytically or radiolytically. Photochemical work by Lacy et al. (1984) used mixtures of $CO + NH_3$ to generate an XCN feature through reactions (5)–(8). Subsequent photolysis experiments by Tegler et al. (1993) used mixtures of $H_2O + CH_3OH + CO + NH_3$ (100:50:10:10) to produce OCN^-. Under our interpretation, H_2O and CH_3OH simply served as very weak bases, and the CH_3OH was a second source of the CO needed for OCN^- formation.

The work that is most closely related to our own is that of the Catania group (Palumbo et al. 2000, and references therein). We know of no clear contradictions of their published results with what we present here. We have duplicated their work on $H_2O + CH_4 + NH_3$ and $H_2O + CH_4 + N_2$ ices and find that the ~ 2165 cm^{-1} band they report matches the characteristics of OCN^-. Their observation of OCN^- formation by N^+ implantation into a residue formed by irradiating an H_2O + hydrocarbon ice requires comment (Palumbo et al. 2000). Such residues have an ill-defined composition and have never been completely analyzed, and so it is impossible to write specific chemical reactions involving them. Nevertheless, it is true that virtually any organic material containing carbon, oxygen, and hydrogen will produce stable molecules, such as CO, on radiolysis (Spinks & Woods 1990). If a C/H/O-containing residue is bombarded with N^+, then CO and NH radicals are expected and thence OCN^-. We fully expect that irradiation of NH_3 mixed with most simple organic molecules containing carbon, hydrogen, and oxygen will produce OCN^-.

We briefly list three other experimental observations encompassed by our work.

1. Roessler (1991) shows a spectrum in his Figure 31 of irradiated NH_3 at 9 K. The sample clearly contains CO and CO_2, and so according to our work OCN^- should be present too. It does appear to be present and the feature is marked in Figure 31 at 2160 cm^{-1} but left unidentified.
2. Benit, Bibring, & Rocard (1988) reported radiation results on a $CO_2 + NH_3$ ice at 77 K. According to our Table 2, cyanate ion should have formed. A full spectrum was not published, but a feature at 2164 cm^{-1} was reported and left unidentified by Benit, Bibring, & Rocard (1988). We again suspect OCN^-.
3. The Leiden database[6] has an excellent collection of data on UV-photolyzed ices. The $CH_3OH + NH_3$ spectra there show an OCN^- feature growing in with photolysis time. Our interpretation is that the CH_3OH serves as the source of CO and then reactions (5)–(8) lead to OCN^-. It should be possible to alter the OCN^--to-HNCO ratio, as in our Figures 6 and 7, by beginning the experiment with $CH_3OH + N_2$ instead of $CH_3OH + NH_3$.

Finally, we wish to comment on the recent assignment (Palumbo et al. 2000) of the ~ 2165 cm^{-1} XCN feature in irradiated $H_2O + CH_4 + NH_3$ and $H_2O + CH_4 + N_2$ ices to "ROCN." The band was assigned to ROCN, described as a "nitrile compound containing O that is bonded to the organic residue," the residue being material generated during the irradiation. There are significant difficulties with this assignment, starting with the fact that organic nitriles typically show bands in the 2200–2300 cm^{-1} region (Bernstein et al. 1997), not at ~ 2165 cm^{-1}. Properly speaking, ROCN molecules are termed cyanates and are unstable with respect to molecules of the form RNCO, known as isocyanates, just as HOCN is unstable compared to HNCO (Jacox & Milligan 1964; Poppinger, Radom, & Pople 1987; Crowley & Sodeau 1989). Nevertheless, the vibrational spectra of several organic cyanates have been reported, and all show a strong CN absorption near 2250 cm^{-1} (Kauer & Henderson 1964; Groving & Holm 1965). This contradicts the assignment of a band in irradiated $H_2O + CH_4 + NH_3$ and $H_2O + CH_4 + N_2$ ices to a cyanate (Palumbo et al. 2000). There are a number of other difficulties with the ROCN assignment, so suffice it to say that we find no evidence for either an ROCN or RNCO contributor to the 2165 cm^{-1} band. Conversely, strong arguments (*vide supra*) based on reaction chemistry and the isoelectronic relationships of CO and N_2 on the one hand, and H_2O and NH_3 on the other, lead in a simple, direct way to the OCN^- assignment.

4.4. *Astrochemical Implications*

The molecules we used to generate OCN^- for Table 2 and Figure 8 are H_2O, CO, CO_2, CH_4, NH_3, and N_2. Since the first five are known interstellar ice molecules and N_2 is suspected, it is reasonable to expect interstellar ices to produce cyanate anion if exposed to UV photons, cosmic rays, or other sources of high-energy radiation. Nevertheless, since our mixtures contained no more than three components, one wonders if reactions in more complicated interstellar ices might prevent OCN^- formation. Along these lines we observe that UV photolysis produced OCN^- in experiments of Tegler et al. (1993) with a four-component ice, namely $H_2O + CH_3OH + CO + NH_3$ (100:50:1:1), and in the work of Allamandola, Sandford, & Valero (1988) on a five-component ice, $H_2O + CH_3OH + CO + NH_3 + C_3H_8$ (100:50:10:10:10). Thus, simply increasing the number of components is not sufficient to block OCN^- production.

Our reactions (21)–(24) show that NH and/or NH_2 radicals are needed for HNCO formation along with CO and a base, such as NH_3, to make OCN^-. NH_3 and CO are known interstellar ice components so that to prevent OCN^- production, a third molecule is needed to consume NH and/or NH_2radicals. The most reasonable candidate in interstellar ices is O_2, which has long been recognized by chemists as a free radical scavenger (Bauer & Daniels 1934). It should be possible to block OCN^- formation in ices made of, for example, $CO + NH_3 + O_2$, and experiments are needed to determine the amount of O_2 required. However, this line of thought may be irrelevant since O_2 is expected to reside mainly in the apolar outer parts of interstellar ice mantles and not in the H_2O-rich inner regions (Ehrenfreund et al. 1998).

The question also arises as to the amount of energetic processing needed for OCN^- formation in an interstellar ice. The doses we have used are on the order of 5–25 eV molecule^{-1} for radiation experiments. Estimates (Moore 1999; Moore, Hudson, & Gerakines 2000) show that ices in diffuse clouds could receive far more than this from UV photons alone. The estimate for dense interstellar clouds is that the dose will be in the lower-to-middle part of our range. Of course, all such doses will depend on cloud geometry.

We now return to Figures 1 and 9, comparing laboratory spectra of OCN^- with the *Infrared Space Observatory* spectra of W33A, a young stellar object embedded in a dense cloud. A recent analysis (Gibb et al. 2000)

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[6] See the Leiden University Department of Astronomy Web site at http://www.strw.leidenuniv.nl/~ab

gives the composition of the polar phase of W33A's ices as approximately $H_2O+CO_2+CO+CH_4+NH_3$ (100:13:6:1.5:15). Recognizing that these are the same molecules used in our experiments to make OCN^-, the striking similarity in shape, position, and width of the laboratory and interstellar bands, and the reasonable energetic processing needed to produce the laboratory spectrum, leads naturally to an assignment of OCN^- for the W33A feature. Our work shows that this band should be produced in W33A's polar ices, rich in H_2O, but not in the apolar phases, presumed rich in N_2, O_2, and CO. Both UV photons and cosmic radiation will promote OCN^- formation, and the contribution of each will perhaps be influenced by cloud morphology. We point out that this production of cyanate anion occurs without the need for temperature changes to drive acid-base chemistry. However, as temperature should rise with decreasing distance from W33A and other protostars, it is interesting to speculate that a conversion of NH_4^+ and OCN^- into urea might eventually occur, as in the classic experiment of Wöhler (1828).

We end with an interesting question recently proposed to us (M. Bernstein 2000, private communication): Is it possible to use the observed OCN^- abundance to constrain the NH_3 abundance in interstellar ices? Since each OCN^- ion observed is from a polar ice and presumably arises from a single NH_3, estimating a lower bound for an ammonia abundance should be possible. At present, however, more work needs to be done on the absolute strength of the OCN^- band at various temperatures and in the presence of various molecules. It would also be desirable to determine if NH_3 forms other N-containing products, such as N_2H_4 and NH_2OH.

5. SUMMARY AND CONCLUSIONS

By considering the reactions occurring in irradiated and photolyzed ices we have assigned the XCN band in proton irradiated interstellar ice analogs. The band's position, strength, width, thermal stability, and isotopic shifts are consistent with those of OCN^-, as reported earlier for photolyzed ices (Grim & Greenberg 1987). In addition, by studying the chemical reactions in ices we have found that OCN^- is as strongly expected in our experiments as is CO_2 in irradiated or photolyzed H_2O+CO. The reactions written have been tested in many ways, including systematic alterations of reactants, many blank experiments, comparisons with OCN^- generated by various in situ methods, and by alterations in the OCN^--to-HNCO ratio. The OCN^- assignment has been supported by every test undertaken.

Since our experiments involved reasonable radiation doses, representative interstellar temperatures, and known interstellar molecules, they imply that OCN^- will be formed in interstellar ices and trapped in polar ice mantles. Our work also suggests that energetic processing in the interstellar medium can produce sufficient OCN^- to account for the 2165 cm^{-1} (4.62 μm) band observed in interstellar ices. Temperature increases to promote acid-base chemistry are unnecessary. All things considered, OCN^- now appears to be as well established as other assignments that are based on a single band, such as CO. In fact, we know of no chemical evidence for any other contributor to the 2165 cm^{-1} (4.62 μm) feature.

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