The Astrophysical Journal Supplement Series, 159:277–281, 2005 August

LABORATORY EVIDENCE FOR SOLID-PHASE PROTONATION OF HNCO IN INTERSTELLAR ICES

R. L. Hudson,[1] R. K. Khanna,[2] and M. H. Moore[3]

Received 2005 February 28; accepted 2005 March 30

ABSTRACT

A recent study reported production of amino formate, $HC(O)ONH_2$ on warming a solid-phase $HNCO + HCl + H_2O$ mixture. Here we reinterpret those results and suggest that the synthesis of amino formate is unlikely and that what was actually observed was the production of $ClC(O)NH_2$ by a low-temperature, solid-phase acid-base reaction. The published infrared spectra are reexamined and are in full agreement with $ClC(O)NH_2$. This new interpretation also agrees with chemical expectations, previous laboratory work, and new density-functional calculations. A number of acid-base pairs are already known in the interstellar medium, and our new interpretation of $HNCO + HCl + H_2O$ chemistry suggests that the H_2NCO^+ cation is probably interstellar as well.

Subject headings: astrochemistry — infrared: ISM — ISM: clouds — ISM: molecules — methods: laboratory — molecular processes

1. INTRODUCTION

The HNCO molecule, isocyanic acid, is the simplest chemical species to possess the four main biogenic elements. This acid has been observed in cometary comae (Bockelée-Morvan et al. 2000), the interstellar medium (Buhl et al. 1973), and in external galaxies (Nguyen-Q-Rieu et al. 1991). As a likely parent of the OCN^- ion, associated with the 4.62 μm absorption feature in interstellar ices (Grim & Greenberg 1987; Hudson et al. 2001), HNCO has come under increased investigation by several laboratory groups. The solid-phase infrared (IR) spectrum of pure HNCO has been analyzed by Lowenthal et al. (2002), who reported assignments and band strengths for the fundamental vibrations. Raunier et al. (2004) studied the photochemistry of solid HNCO, with an eye toward making urea, and in an earlier paper examined the thermally promoted reactions of HNCO and H_2O (Raunier et al. 2003a). This same group also has studied the solid-phase reaction between HNCO and NH_3 (Raunier et al. 2003b), as have Novozamsky et al. (2001). Pettersson et al. (1999) investigated reactions of H atoms with HNCO and reported the formation of H_2NCO and $H_2NC(O)H$, while Fischer et al. (2002) examined possible dimerization of HNCO molecules.

A recent paper appearing here (Khanna et al. 2002) described a solid-phase reaction of HNCO and HCl in the presence of H_2O-ice. Warming a codeposited $HNCO + HCl + H_2O$ mixture from 20 to 200 K, under vacuum, produced a residue with the infrared spectrum shown in Figure 1. This residue was assigned to amino formate, $HC(O)ONH_2$, also known as *O*-formylhydroxylamine (CAS registry number 149150-78-7). Structures for both HNCO (I) and $HC(O)ONH_2$ (II) are shown in Figure 2.

There are two reasons to view this $HC(O)ONH_2$ assignment with caution. First, the IR spectrum of $HC(O)ONH_2$ is expected to show distinct absorbances from the aldehydic (H—C=O) group at $\sim$2850 cm^{-1} and at $\sim$1400 cm^{-1}, but the spectra of the alleged $HC(O)ONH_2$ in Khanna et al. (2002), reproduced in Figure 1*a*, have neither. Second, inspection of the structure of $HC(O)ONH_2$ in Figure 2 shows that to reach this product from HNCO requires considerable chemical change. The net effect would be rupture of both OH bonds of a water molecule, breakage of the N=C double bond in HNCO, insertion of the O atom there, and addition of the two remaining H atoms at the N and C atoms, a process not obvious for a reaction at temperatures under 200 K. For these reasons we have reexamined the chemistry of the $HNCO + HCl + H_2O$ system and offer an alternative assignment for the published IR spectra.

2. RESULTS

Figure 1 is based on the data of Khanna et al. (2002) and compares the IR spectrum of the reaction product, labeled "Residue," from warming $HNCO + HCl + H_2O$, with the spectrum of formamide, structure (III) in Figure 2. While formamide's IR spectrum has typical aldehydic features near 2850 and 1400 cm^{-1}, neither is obvious in Figure 1*a*, suggesting that the residue lacks the H—C=O functional group. Features from NH and NH_2 group vibrations (3500–3000 and $\sim$650 cm^{-1}) and a C=O group ($\sim$1700 cm^{-1}) are shared by both spectra. Finally, the upper spectrum has several distinct features below 1000 cm^{-1} that formamide lacks.

A clue to the identity of the residual material comes from the known chemistry of HCl. Since HCl is a strong acid, it dissociates to give H_3O^+ and Cl^- in H_2O-ice (Delzeit et al. 1993), and these ions can then react with other molecules present. For example, thermally induced proton transfer to C_3O_2 from $HCl + H_2O$ has been shown to give $ClC(O)—CH=C=O$ (Tamburelli et al. 1998). In the $HNCO + HCl + H_2O$ system, one thus expects that H^+ transfer will occur on warming from 20 K, so that the H_2NCO^+ cation will form, followed by association with the Cl^- counterion. In short, a consideration of the acid-base chemistry in this system leads to the predicted product being $ClC(O)NH_2$, structure (IV) in Figure 2 (CAS registry number 463-72-9). The relevant reaction is given in Figure 3.

Although $HC(O)NH_2$ and $ClC(O)NH_2$ share some structural features, the latter's spectrum will lack aldehydic bands ($\sim$2850, $\sim$1400 cm^{-1}), and indeed these are absent in the upper trace of Figure 1. Conversely, one or more features in the 500–400 cm^{-1} region, corresponding to a C—Cl stretch, are predicted for $ClC(O)NH_2$, based on IR spectra of $ClC(O)NH(CH_3)$ and $ClC(O)N(CH_3)_2$ (Kovács & Izvekov 1997; Rao & Rao 1977; Buder & Schmidt 1973). Figure 1*a* shows two such bands

---

[1] Corresponding author; Department of Chemistry, Eckerd College, St. Petersburg, FL 33711; hudsonrl@eckerd.edu.

[2] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742.

[3] Code 691, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

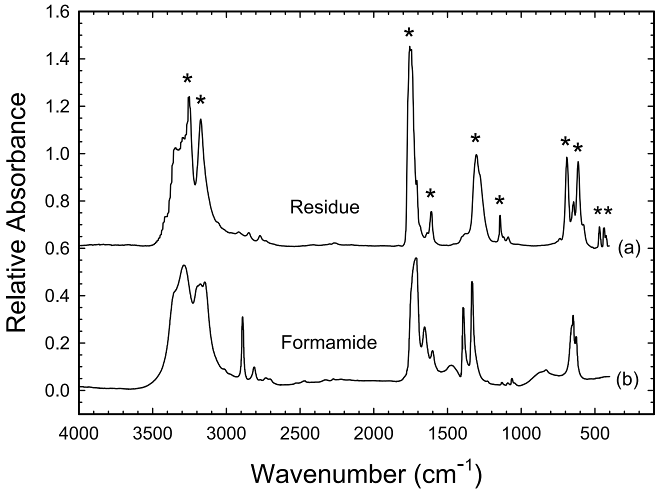


FIG. 1.—Mid-IR spectra of (*a*) the residue from warming a HNCO + HCl + H_2O mixture and (*b*) formamide. Spectra were recorded at 20 K after an annealing to about 200 K (residue) and 160 K (formamide). Note that these spectra were obtained by digitizing those of Fig. 4 from Khanna et al. (2002), flattening their baselines, and converting to absorbance values. This procedure involves some slight changes in relative intensities and resolution from the original data. Features marked with asterisks are listed in Table 1.

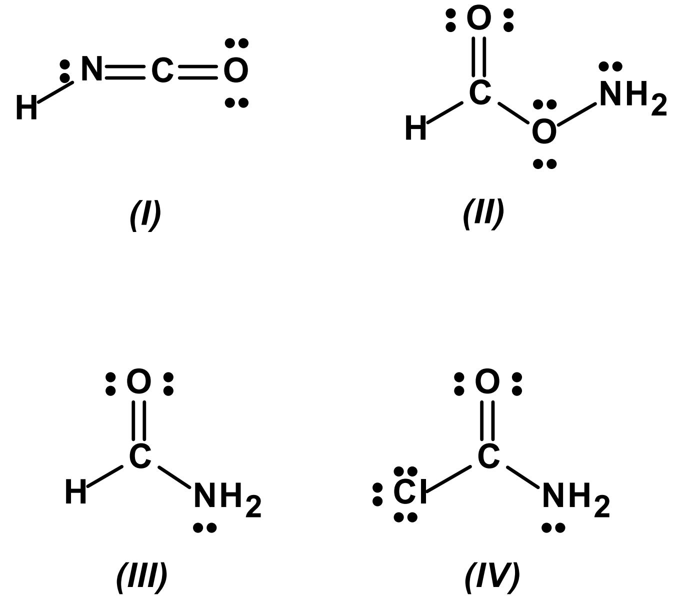


FIG. 2.—Structures for HNCO, $HC(O)ONH_2$, $HC(O)NH_2$, and $ClC(O)NH_2$.

between 500 and 400 cm^{-1}, while none are in Figure 1*b*. In all respects, the upper spectrum of Figure 1 agrees with expectations for the $ClC(O)NH_2$ molecule.

To support our spectral assignment, density-functional calculations have been undertaken for $HC(O)NH_2$ and $ClC(O)NH_2$ at the B3LYP/6-31G** level, the same as used by Khanna et al. (2002). The Spartan software package (Wavefunction, Inc., Irvine, California) has been used to compute vibrational band positions for optimized molecular geometries. At this level of theory the calculations do not include such complicating factors as anharmonicity, hydrogen bonding, crystallinity, and site splitting, and so insight, as opposed to numerical precision, is the goal.

Our density-functional results are summarized in Table 1, and no scaling factors have been applied to the calculated values. Formamide is included in Table 1 to demonstrate the general level of agreement that can be expected for these density-functional predictions. Ignoring the two absorptions above 3000 cm^{-1}, the calculated and observed IR band positions for formamide are in reasonable agreement, with an *average* deviation of about 4%. The C=O carbonyl feature shows the poorest agreement, probably due to perturbations cause by intermolecular hydrogen bonding.

Turning to $ClC(O)NH_2$, the calculations predict that for the 4000–2000, 2000–1500, 1500–1000, 1000–600, and 600–400 cm^{-1} regions, two IR bands will be seen in each case, for a total of 10 distinct features. That is exactly what the upper spectrum of Figure 1 shows. As with $HC(O)NH_2$, for the region below 3000 cm^{-1} there is again an average deviation of about 4% between the calculated IR band positions of $ClC(O)NH_2$ and the features in Figure 1. Once more, the worst offender is the C=O carbonyl feature, with a ~9% difference in predicted and observed positions. Repeating the calculations with the higher level B3LYP/6-311+G** and MP2/6-311+G** methodologies improved the agreement to ~7% for the C=O band, but the average variation from 3000–400 cm^{-1} only dropped from 4% to 3%. This variation in the C=O feature is reminiscent of that seen in similar calculations on the related molecule $ClC(O)N(CH_3)_2$ (Kovács & Izvekov 1997).

For completeness we repeated the calculations of Khanna et al. (2002) on the amino formate molecule, and verified that they indeed predict 10 bands from 4000 to 1000 cm^{-1}, and only two in the 1000–400 cm^{-1} region, at 854 and 823 cm^{-1}. This is very different from what is seen in the spectrum labeled "Residue" in Figure 1. Our conclusion is that the $ClC(O)NH_2$ assignment gives a better fit between theory and observation than the amino formate assignment.

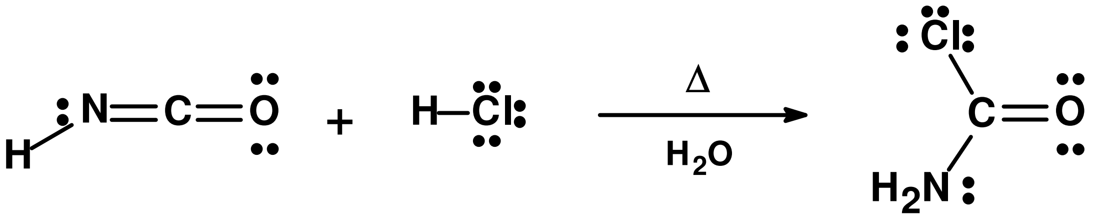
Given this agreement among chemical expectations from acid-base theory, spectral expectations supported by the IR data, and density-functional predictions, we assign the spectrum marked "Residue" in Figure 1 to $ClC(O)NH_2$. This molecule goes by several names, such as carbamic chloride, carbamyl chloride, carbamoyl chloride, and chloroformamide.

We also have made a preliminary exploration of reaction energies involving HNCO and other molecules. Table 2 gives results calculated at the B3LYP/6-31G** level for selected molecules and ions. Columns (2) and (3) give electronic (E_{el}) and zero-point vibrational energies (ZPE), as calculated by our software. All of these energies are for optimized structures with all vibrational frequencies being real numbers. Columns (4) and (5) of Table 2 convert these energies to a common set of units (eV), and the final column gives values of "corrected" energies, $E = E_{el} + \mathrm{ZPE}$. In § 3 we will use the *E*-values found in Table 2 to estimate reaction energies.

Results from calculations at the more sophisticated B3LYP/6-311+G** and MP2/6-311+G** levels were but slightly different from those in Table 2. Because of this, most of our computations were done with the B3LYP/6-31G* approach, as used in Khanna et al. (2002). Although there are points of interest regarding the structures of HNCO reaction products, our attention here is on energy differences.

3. DISCUSSION

Although we do not expect $ClC(O)NH_2$ to be an important interstellar species, the path to this molecule is of interest. The most likely mechanism for making $ClC(O)NH_2$ in the HNCO + HCl+ H_2O system is protonation of HNCO by HCl or $(H_3O^+)(Cl^-)$, to give H_2NCO^+, followed by combination with the Cl^- anion. Protonation of gas-phase HNCO has been studied experimentally, and the results show that the preferred site for H^+ addition is indeed the nitrogen atom (Wight & Beauchamp 1980; Hop et al.



(I) *(IV)*

Fig. 3.—Reaction of HNCO with HCl.

1989). Moreover, experiment and theory agree that HNCO has a positive proton affinity (DeKock & Jasperse 1983), meaning that the protonation step will be exothermic. From Table 2, we calculate $\Delta E = -0.35$ eV for the combination of HNCO and HCl to give $ClC(O)NH_2$.

Green (1981) has discussed the formation and stability of gas-phase H_2NCO^+ in the ISM. The most likely protonation sequence for HNCO is

$$H_2 \rightarrow H_2^+ + e^-, \qquad (1)$$

$$H_2^+ + H_2 \rightarrow H + H_3^+, \qquad (2)$$

$$H_3^+ + \mathrm{HNCO} \rightarrow H_2 + H_2NCO^+, \qquad (3)$$

with reaction (1) being initiated by cosmic radiation. Reactions (2) and (3) are ion-molecule processes, which generally are rapid, exothermic, and without activation barriers (Friedman 1968; Herbst & Klemperer 1973; Watson 1973). Our results in Table 2 give proton affinities of $(-31.793) - (-36.001) \approx 4.2$ eV for H_2 and $(-4589.479) - (-4597.049) \approx 7.6$ eV for HNCO, compared to experimental values of 4.4 eV (Aue & Bowers 1979) and 7.8 eV (Wight & Beauchamp 1980), respectively. This suggests that ion-molecule reaction (3). for converting HNCO into H_2NCO^+, is energetically feasible.

TABLE 1

Observed and Calculated Vibrational Band Positions

Approximate Description[a]	Calculated[b] (cm^{-1})	Observed[c] (cm^{-1})
$HC(O)NH_2$		
NH stretches	3740	3288
	3595	3165
CH stretch	2953	2890
CO stretch	1838	1720
HNH bend	1620	1655/1601
HNC bend + HCO wag	1434	1393
CN stretch	1274	1333
NH_2 rock (ip)[d]	1055	1129
HCNO def.[d] (op)[d]	1043	1063
C-NH_2 twist (op)	645	648
NCH bend (ip)	558	627
NH_2 wag (op)	131	...
$ClC(O)NH_2$		
NH stretches	3755	3254
	3609	3174
CO stretch	1919	1754
HNH bend	1612	1608
CN stretch	1272	1306
HNC bend (ip)[d]	1115	1146
ClCNO def.[d] (op)[d]	683	702
CCl stretch + NH_2 rock (ip)	629	658
C-NH_2 twist (op)	493	482
CCl stretch	429	450
NCCl bend (ip)	371	...
NH_2 wag (op)	180	...

[a] Based on Lundell et al. (1998).

[b] Gas-phase molecule; B3LYP/6-31G** calculation.

[c] Solid-phase sample at 20 K; spectra digitized from Khanna et al. (2002).

[d] (op) out-of-plane motion; (ip) in-plane motion; (def.) deformation.

Turning now to *solid-phase* HNCO, to our knowledge the present paper provides the first laboratory demonstration that condensed HNCO is also a proton acceptor. Frozen on the surface of interstellar grains, H_2O is the most abundant interstellar ice component, with HNCO being suggested by the presence of OCN^- (Hudson et al. 2001). Cosmic radiation in the ISM will ionize H_2O-ice and a reaction sequence similar to (1)–(3) will follow:

$$H_2O \rightarrow H_2O^+ + e^-, \qquad (4)$$

$$H_2O^+ + H_2O \rightarrow OH + H_3O^+, \qquad (5)$$

$$H_3O^+ + \mathrm{HNCO} \rightarrow H_2O + H_2NCO^+. \qquad (6)$$

These solid-phase reactions are driven by the energy of primary and secondary processes initiated by cosmic-ray bombardment, and so the lack of activation barriers is not as important as in the gas phase. Moreover, reactions (5) and (6) are ion-molecule reactions that, as already stated, are expected to have low or no activation energies. Reaction (5) occurs in the radiation chemistry of gas-phase and condensed-phase H_2O, where it is usually regarded as the earliest and fastest bimolecular reaction (Swallow 1973; Chatterjee 1987; Klassen 1987, Buxton 1987; Spinks & Woods 1990). Our results in Table 2 give $\Delta E = -1.2$ eV for reaction (5) along with $\Delta E = -0.15$ eV for reaction (6). Since both experiment and theory (DeKock & Jasperse 1983) show that HNCO has a greater proton affinity than H_2O, we expect reaction (6) will occur even with an expected dominance by H_2O in interstellar ices.

As already stated, the solid-phase chemistry of HNCO has been explored by several research groups. Photolysis of pure HNCO at 10 K is reported to produce NH_4^+, OCN^-, and urea (Raunier et al. 2004), and presumably ion irradiation of HNCO will give these same products. Codepositing room-temperature HNCO and NH_3 at ~10 K also has been shown to make NH_4^+ and OCN^- ions (Raunier et al. 2003b; Novozamsky et al. 2001). However, the efficiency of these HNCO reactions will be diminished in proportion to the abundance of H_2O in an interstellar ice. Conversely, any HNCO present in an H_2O-dominated ice will always be susceptible to reactions (4)–(6) since they begin with

TABLE 2

RESULTS OF B3LYP/6-31G** DENSITY FUNCTIONAL CALCULATIONS

Chemical Species (1)	Electronic Energy, E_{el}[a] (hartrees) (2)	Zero-Point Energy, ZPE[a,b] (kJ mol^{-1}) (3)	Electronic Energy, E_{el}[a] (eV) (4)	Zero-Point Energy, ZPE[a,b] (eV) (5)	$E = E_{el} + ZPE$[c] (eV) (6)
H_2	−1.17854130	26.7104	−32.069754	0.276834	−31.793
H_2^+	−0.605115637	27.8000	−16.466041	0.288127	−16.178
H_3^+	−1.34349338	53.7624	−36.558332	0.557208	−36.001
H_2O	−76.4197304	56.1108	−2079.4875	0.581548	−2078.906
H_2O^+	−75.9689817	48.8889	−2067.2220	0.506698	−2066.715
H_3O^+	−76.7056427	90.3954	−2087.2676	0.936883	−2086.331
OH	−75.7284735	22.0791	−2060.6775	0.228834	−2060.449
HNCO	−168.681492	55.9624	−4590.0589	0.580010	−4589.479
H_2NCO^+	−168.972256	88.9494	−4597.9710	0.921896	−4597.049
HCl	−460.800810	17.8949	−12539.033	0.185468	−12538.848
H_2NCOCl	−629.503928	96.6889	−17129.681	1.00211	−17128.679
H_2NCOOH	−245.143572	134.9917	−6670.6988	1.399091	−6669.300
NH_3	−56.5577290	90.3754	−1539.0148	0.936675	−1538.078
NH_4^+	−56.9059028	130.4344	−1548.4891	1.351858	−1547.137
OCN^-	−168.105104	28.3129	−4574.3745	0.293443	−4574.081

[a] 1 hartree = 27.211396 eV = 2625.5000 kJ mol^{-1} = 627.50956 kcal mol^{-1} = 219474.63 cm^{-1}.

[b] No scaling factors have been used.

[c] All values rounded to three decimal places.

an ionization of H_2O and are followed by H^+ transfers to make H_2NCO^+. Constraining the H_2NCO^+ abundance will be the amount of NH_3 present in an ice, since NH_3 can remove H^+ from both HNCO and H_2NCO^+ as shown in the following reactions:

$$HNCO + NH_3 \rightarrow NH_4^+ + OCN^-, \qquad (7)$$

$$H_2NCO^+ + NH_3 \rightarrow NH_4^+ + HNCO. \qquad (8)$$

Our results in Table 2 give $\Delta E = +6.3$ eV for reaction (7), so that a substantial matrix influence is needed if this reaction is to be important in an unannealed, unprocessed interstellar ice. However, for reaction (8), another ion-molecule process, we find $\Delta E = -1.5$ eV, suggesting more likely occurrence.

Beyond what has already been discussed, HNCO may play a role in the formation of another interesting molecule. Exposure of H_2O-ice to cosmic radiation generates not only H_2O^+ and H_3O^+ cations, but also OH^- anions. Combination of H_2NCO^+ and OH^- would yield the elusive carbamic acid molecule, H_2NCOOH, as shown in reaction (9):

$$H_2NCO^+ + OH^- \rightarrow H_2NCOOH. \qquad (9)$$

Alternatively, if H_2NCO^+ is a sufficiently strong acid, then it may react with H_2O molecules in the solid state according to

$$H_2NCO^+ + H_2O \rightarrow H_2NCOOH + H_3O^+, \qquad (10)$$

again producing H_2NCOOH. While the results in Table 2 give $\Delta E = -0.8$ eV for reaction (10), the mechanism may be so complex that the reaction is hindered. This is a case where a more extensive study of possible reaction pathways and barriers is clearly needed. For a discussion of carbamic acid, and the challenges in studying it, see Khanna & Moore (1999).

To summarize, we have shown that the solid-phase reaction between HNCO and HCl, in the presence of H_2O, leads to $ClC(O)NH_2$ and not $HC(O)ONH_2$. Previous work, the present results, and reactions (1)–(6) lead us to expect that HNCO will be a source of interstellar H_2NCO^+. This ion may be generated in either the gas phase, in an interstellar ice, or both.

A. Kovács (Budapest Technical University) is thanked for reprints of papers. NASA funding through the Planetary Atmospheres and SARA programs is acknowledged. R. L. H. also acknowledges the support of NASA for grant NAG-5-1843. This work was supported, in part, by a grant from the NASA Astrobiology Institute to the Goddard Space Flight Center.

REFERENCES

Aue, D. H., & Bowers, M. T. 1979, in Gas Phase Ion Chemistry, vol. 2, ed. M. T. Bowers (New York: Academic Press), 1

Bockelée-Morvan, D., et al. 2000, A&A, 353, 1101

Buder, W., & Schmidt, A. 1973, Spectrochim. Acta, 29A, 1419

Buhl, D., Snyder, L. E., Schwartz, P. R., & Edrich, J. 1973, Nature, 243, 513

Buxton, G. V. 1987, in Radiation Chemistry, ed. Farhataziz & M. T. Rodgers (New York: VCH), 323

Chatterjee, A. 1987, in Radiation Chemistry, ed. Farhataziz & M. T. Rodgers (New York: VCH), 26

DeKock, R. L., & Jasperse, C. P. 1983, Inorg. Chem., 22, 3839

Delzeit, L., Rowland, B., & Devlin, J. P. 1993, J. Phys. Chem., 97, 10312

Fischer, G., Geith, J., Klapötke, T. M., & Krumm, B. 2002, Zeit. für Natur., 57b, 19

Friedman, L. 1968, Annu. Rev. Phys. Chem., 19, 273

Green, S. 1981, J. Phys. Chem., 85, 1676

Grim, R. J. A., & Greenberg, J. M. 1987, ApJ, 321, L91

Herbst, E., & Klemperer, W. 1973, ApJ, 185, 505

Hop, C. E. C. A., Holmes, J. L., Ruttink, P. J. A., Schaftenaar, G., & Terlouw, J. K. 1989, Chem. Phys. Lett., 156, 251

Hudson, R. L., Moore, M. H., & Gerakines, P. A. 2001, ApJ, 550, 1140

Khanna, R. K., Lowenthal, M. S., Ammon, H. L., & Moore, M. H. 2002, ApJS, 140, 457

Khanna, R. K., & Moore, M. H. 1999, Spectrochim. Acta, 55, 961
Klassen, N. 1987, in Radiation Chemistry, ed. Farhataziz & M. T. Rodgers (New York: VCH), 30
Kovács, A., & Izvekov, V. 1997, J. Molec. Struct., 410, 403
Lowenthal, M. S., Khanna, R. K., & Moore, M. H. 2002, Spectrochim. Acta, 58, 73
Lundell, J., Krajewska, M., & Räsänen, M. 1998, J. Phys. Chem. A., 102, 6643
Nguyen-Q-Rieu, Henkel, C., Jackson, J. M., & Mauersberger, R. 1991, A&A, 241, L33
Novozamsky, J. H., Schutte, W. A., & Keane, J. V. 2001, A&A, 379, 588
Pettersson, M., Khriachtchev, L., Jolkkonen, S., & Räsänen, M. 1999, J. Phys. Chem. A, 103, 9154
Rao, L. S., & Rao, G. R. 1977, Indian J. Pure Appl. Phys., 15, 754
Raunier, S., Chiavassa, T., Allouche, A., Marinelli, F., & Aycard, J. P. 2003a, Chem. Phys., 288, 197
Raunier, S., Chiavassa, T., Duvernay, F., Borget, F., Aycard, J. P., Dartois, E., & d'Hendecourt, L. 2004, A&A, 416, 165
Raunier, S., Chiavassa, T., Marinelli, F., Allouche, A., & Aycard, J. P. 2003b, Chem. Phys. Lett., 368, 594
Spinks, J. W. T., & Woods, R. J. 1990, An Introduction to Radiation Chemistry (New York: Wiley), 255
Swallow, A. J. 1973, Radiation Chemistry (New York: Halsted), 133, 142
Tamburelli, I., Chiavassa, T., Borget, F., & Pourcin, J. 1998, J. Phys. Chem. A, 102, 422
Watson, W. D. 1973, ApJ, 185, 505
Wight, C. A., & Beauchamp, J. L. 1980, J. Phys. Chem., 84, 2503