IONS IN GRAIN MANTLES: THE 4.62 MICRON ABSORPTION BY OCN$^-$ IN W33A

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Received 1987 May 21; accepted 1987 July 13

ABSTRACT

The 4.62 μm absorption feature in W33A has been uniquely identified with the presence of OCN$^-$ ions in grain mantles. An extensive experimental study of the peak position and absorption strength of this band produced by ultraviolet photolysis of various isotopically labeled ices provided the strict criteria needed to eliminate all conceivable molecular candidates other than the cyanate ion OCN$^-$. The experiments provide further proof for the ultraviolet photoprocessing of interstellar mantles leading not only to the formation of radicals and more complex molecules but to molecular ions and salts as well. The presence of ions in the solid phase has significant implications for chemical reaction schemes in low-temperature solids and interpretations of interstellar absorption spectra.

Subject headings: infrared: spectra — interstellar: grains — interstellar: molecules

I. INTRODUCTION

The spectral features shown in the first infrared observations toward the protostellar object W33A by Soifer et al. (1979) provided an incentive to obtain higher resolution spectra in the region of the CO stretching mode (2200–2000 cm$^{-1}$). It was shown by Lacy et al. (1984) that the 4.61 μm band is in fact a superposition of two absorption features, one peaking at 4.67 μm (2140 cm$^{-1}$) and assigned to solid CO, and the other peaking at 4.62 μm (2165 cm$^{-1}$). Laboratory experiments carried out in the Leiden Laboratory led to the tentative identification of the 2165 cm$^{-1}$ absorption as probably due to a molecule containing a triple bonded CN fundamental group suggestively labeled “XCN.” Surprisingly, however, it appeared that a CO/NH$_3$ mixture was more efficient in producing the “XCN” band than a CH$_4$/NH$_3$ mixture, suggesting that oxygen atoms might be involved. High-resolution spectra ($\lambda/\Delta \lambda = 2000$) by Larson et al. (1985) determined the peak location to be 2165.5 ± 0.1 cm$^{-1}$ and definitely excluded the possibility of gaseous CO giving rise to the 4.62 μm band. On the basis of wavelength correlations, Larson et al. (1985) suggested that the 2166 cm$^{-1}$ interstellar band was due to CH$_3$NC and that the newly reported absorption feature at 2042 cm$^{-1}$ could be assigned to either CN, C$_3$, or CH$_3$OH. However, since the 2042 cm$^{-1}$ feature appeared only in irradiated ices containing sulfur, Geballe et al. (1985) were led to suggest carbonylsulfide, OCS. For “XCN” d’Hendecourt et al. (1986) suggested other candidates such as cyanogen (C$_2$N$_2$) and pyruvoisonitrile (CH$_3$CONC). From the experiments a lower limit of 2 × 10$^{-17}$ cm molecule$^{-1}$ was deduced for the integrated absorbance value of the CN stretch of “XCN” (hereafter without the quotes).

Laboratory experiments play an important role in the identification of the interstellar features not only because they may be reproduced but also, as we shall show in this Letter, because we may arbitrarily vary isotopic species in the irradiated grain mantle analogs to provide unambiguous identifications.

II. POSSIBLE CANDIDATES

All candidates proposed so far are listed in Table 1 together with other likely candidates found by a systematic literature search. As can be seen in standard books on infrared spectroscopy, simple cyanides (R—C≡N) generally absorb near 2280–2240 cm$^{-1}$ (Bellamy 1968) and can therefore be rejected as possible carriers of XCN. On the other hand, isocyanoacids (R—N≡C) are better candidates because they generally show absorptions about 100 cm$^{-1}$ lower in frequency compared to their cyanide isomers (Bellamy 1968). Methylosicyanide comes to mind because its absorption frequency at 2161 cm$^{-1}$ in argon (Freedman and Nixon 1972) or 2166 cm$^{-1}$ in vapor (Williams 1956) is so close to that observed. Furthermore, it is a relatively simple molecule. However, why methylosicyanide should be made more efficiently in a CO/NH$_3$ ice than in a CH$_3$/NH$_3$ ice (Lacy et al. 1984) is difficult to understand.

Cyanogen (C$_2$N$_2$) is immediately rejected for two reasons: first, because the CN fundamental both in the gas phase (Kim and King 1984) and in a solid (Nixon and Cross 1950) has a weak integrated absorption coefficient of only 8 × 10$^{-19}$ cm molecule$^{-1}$, which is too low to satisfy the experimental criteria for the absorbance value of XCN; second, because of the absence in the laboratory spectra of the expected very strong infrared absorption near 750 cm$^{-1}$ (Verderame, Nebgen, and Nixon 1963).

Three isomers of diazomethane (H$_2$C≡N=N=N) which may be generated by ultraviolet photolysis (Ogilvie 1969a) absorb near 2170–2160 cm$^{-1}$ (Ogilvie 1969b; King and Strope 1971). These species include isodiazomethane (HC=N=NH), isocyamid (C≡N=NH$_2$) and carbodiimide (HN=NC=NH). The reaction scheme leading to, e.g., carbodiimide would be
TABLE 1
POSSIBLE CARRIERS OF THE 4.62 MICRON XCN ABSORPTION

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Frequency (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃N₂</td>
<td>2165</td>
<td>1</td>
</tr>
<tr>
<td>CH₃NC</td>
<td>2161, 2166</td>
<td>2, 3</td>
</tr>
<tr>
<td>NH₂NC</td>
<td>2159</td>
<td>4, 5</td>
</tr>
<tr>
<td>HNCNH</td>
<td>2169</td>
<td>4, 5</td>
</tr>
<tr>
<td>HCNCH</td>
<td>2169</td>
<td>4, 5</td>
</tr>
<tr>
<td>OCN⁻ (in KI)</td>
<td>2156</td>
<td>6</td>
</tr>
</tbody>
</table>


complicated starting from a CO/NH₃ mixture, since quite a few steps are needed to generate this molecule. The fact that the XCN band shows up immediately in the photolysis experiments argues against this possibility. Another problem that arises in the identification of XCN with a compound such as carbodimide is the absence in the laboratory spectra of the strong absorption band near 900 cm⁻¹ (King and Strope 1971).

The molecules discussed so far do not involve an oxygen atom. Isocyanates (R—N=C=O) which do have an oxygen containing fundamental group exhibit characteristic absorption frequencies near 2260 cm⁻¹ (Bellamy 1968), 100 cm⁻¹ too high, and are therefore rejected too. A similar group of molecules, thiocyanates (R—S=C≡N), may be candidates for the interstellar band because they show strong absorption in the 2170–2130 cm⁻¹ region (Bellamy 1968). However, because of the low cosmic abundance of sulfur relative to oxygen, carbon and nitrogen and, most of all, because of the fact that in the laboratory the 2165 cm⁻¹ absorption is efficiently made by photolysis in samples containing no sulfur atoms, sulfur-bearing species are counterindicated as giving rise to the XCN band.

The cyanate ion (OCN⁻) is known to show extremely strong absorptions in the 2200–2100 cm⁻¹ region depending on the crystal structure (Maki and Decius 1959; Nakamoto 1963). At the start of our investigations no ions were considered, because the photolysis of molecular ices was believed to be based on reaction schemes involving only radicals and neutral species. This appears not to have been correct even though the photon energies are not likely to produce ions directly, although some earlier suggestions were made in this direction (Hagen 1982). Thus as a last candidate we have been led to propose OCN⁻.

The experiments described in the next section were designed to either rule out or discriminate between the two remaining XCN candidates, CH₃NC and OCN⁻.

III. EXPERIMENTS

The study described in this section uses infrared spectroscopy to study the effect of isotopic differences on the molecular vibrations of possible interstellar grain mantle components. For example, in the simple diatomic case where the frequency ν of a vibrational mode depends on the reduced mass, \( \mu = m_1 m_2/(m_1 + m_2) \), according to \( \nu \approx \mu^{-1/2} \), isotopic substitutions for either \( m_1 \) or \( m_2 \) will lead to a rather well-defined frequency shift of the absorption band. For a review of the spectra of labeled compounds see Pinchas and Lauflicht (1971). The basic experimental technique involves deposition of gas mixtures on a cold (7 = 12 K) surface in a cryostat and subsequent ultraviolet irradiation analogous to photoprocessing of interstellar grain mantles (see Hagen, Alamandola, and Greenberg 1979 for experimental details).

We have studied the infrared absorption spectra, after ultraviolet photolysis, of the following dirty ices: CO/NH₃ = 1/1, CO/NH₃ = 1/1, and CO/NH₃ = 1/1, for equal amounts of time (15 minutes, 30 minutes, 1 hr, 2 hr, and 4 hr). After photolysis the samples were warmed up stepwise at intervals of 20 K to room temperature and an infrared absorption spectrum was taken with 4 cm⁻¹ resolution at each temperature. The full photolysis time (4 hr) for all the mixtures led typically to disappearance of 10% of the initially deposited molecules. Several new bands appeared due to the formation of photoproducts but we limit ourselves to a discussion of the XCN feature.

a) Peak Frequencies and Isotope Shifts in CO/NH₃ Mixtures

Figure 1 shows the infrared spectra of the CO/NH₃, CO/CH₃NC, and CO/NH₃ mixtures after 4 hr ultraviolet irradiation and subsequent heating to approximately 80 K. The heating eliminates the CO which dominates the XCN feature at 12 K. Table 2 summarizes the peak positions of the XCN absorptions in the various photolyzed mixtures, together with the positions known for OCN⁻ and CH₃NC. The observed laboratory features are shifted with respect to the non-isotopically enriched photolyzed mixtures by 17 cm⁻¹ for X¹³C¹⁵N (2140 cm⁻¹) and 57 cm⁻¹ for X¹³C¹⁴N (2100 cm⁻¹), respectively. Clearly the 41 cm⁻¹ shift reported for X¹³C in methylisocyanide (Freedman and Nixon 1971) is too disrepannt to be explained in terms of different molecular interactions in the ices. On the other hand, the ~ 17 cm⁻¹ (¹⁵N) and ~ 57 cm⁻¹ (¹³C) isotopic shifts for OCN⁻ appear to be essentially independent of the different crystal fields, e.g., KI, KBr (Maki and Decius 1959), and agree extremely well with the shifts of 57 cm⁻¹ for X¹³C¹⁴N and 17 cm⁻¹ for X¹³C¹⁵N in the photolyzed CO/NH₃ mixtures. Thus the isotopic shifts not only definitely exclude CH₃NC as a possible carrier of the XCN band, but moreover they confirm OCN⁻. We conclude that the 4.62 μm feature can be assigned to this last species exclusively.

b) The Integrated Absorbance Value

The minimum absorbance value for the CN fundamental stretch of OCN⁻ may be estimated assuming that either all photolyzed CO or all photolyzed NH₃ is converted into OCN⁻. Both assumptions lead to an integrated absorbance value for OCN⁻ of 2 × 10⁻¹⁷ cm molecule⁻¹ which is in agreement with the value reported for XCN by d'Hendecourt et al. (1986). This number is a lower limit since photodissociation of CO and NH₃ must lead to more products than just OCN⁻. The cyanate ion shows "an exceptionally strong anti-symmetric vibration absorption" (Maki and Decius 1959). Integrated absorbance values between 6 and 8.5 × 10⁻¹⁷ cm

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molecule$^{-1}$ have been obtained by Schetting and Hisatune (1970). The same vibration in methylisocyanide has an integrated absorbance value greater than $1 \times 10^{-10}$ cm molecule$^{-1}$ (d'Hendecourt and Allamandola 1986).

c) Search for a Positive Counterion

Since the 4.62 $\mu$m feature has been identified with a negative ion, positive ions must also exist in the photolyzed ices. A likely counterion in the experiments is the ammonium ion, NH$_{4}^{+}$. This molecule is known to absorb near 1400 cm$^{-1}$ (Nakamoto 1963 and references therein). In our samples we see an absorption near 1390 cm$^{-1}$, which is in reasonable agreement with this value. Furthermore the CO/$^{15}$NH$_{3}$ experiment did not show a shift of this band, which is consistent with the fact that the frequency shift of $^{15}$NH$_{4}^{+}$ with respect to $^{14}$NH$_{4}^{+}$ is only 1 cm$^{-1}$ (Nakamoto 1963).
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TABLE 3
OCN⁻ BAND POSITIONS IN VARIOUS PHOTOLYZED DIRTY ICES

<table>
<thead>
<tr>
<th>Composition</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/NH₃ = 1/1²</td>
<td>2157</td>
</tr>
<tr>
<td>H₂O/CO/NH₃ = 1/1/1²</td>
<td>2160</td>
</tr>
<tr>
<td>H₂O/CO/NH₃ = 2/1/1²</td>
<td>2163</td>
</tr>
<tr>
<td>H₂O/CO/NH₃ = 3/1/1*</td>
<td>2166</td>
</tr>
<tr>
<td>H₂O/CO/NH₃ = 5/2/1*</td>
<td>2166</td>
</tr>
<tr>
<td>H₂O/CO/CH₄/NH₃ = 6/2/1/1*</td>
<td>2167</td>
</tr>
</tbody>
</table>

*This Letter.
*²d'Hendecourt et al. 1986.

IV. OCN⁻ FORMATION

Strong OCN⁻ absorptions appear after only 15 minute photolysis of the CO/NH₃ mixtures. It is certainly not easy to picture how formation of the CH₃NC candidate could be so rapid because it not only requires first stripping all the hydrogen atoms from ammonia and successive bonding to a carbon atom, but also the breaking of the strong CO bond. On the other hand the formation of OCN⁻ is straightforward. The fact that the band is made more efficiently in a CO/NH₃ mixture than in other mixtures is now not surprising. If the 4.62 μm absorption also appears in experiments without oxygen being “officially” present in the initial mixtures (e.g., CH₄/NH₃), we are convinced that this occurs because of oxygen impurities leaking in slowly during the experiment or being already present in the gas bulb.

The reaction scheme starting with NH₃ and CO in the gas phase and leading ultimately to the formation of ammoniumcyanate involves the intermediate OCN⁻ ion (Hubbard et al. 1975). In a solid this process will be more efficient because the reacting molecules may be direct neighbors permitting charge transfer reactions to occur readily. Because the reactions take place at low temperature the ions are not allowed to form a crystalline structure, explaining why we are able to see isolated OCN⁻ and NH₃⁺ ions. Upon warmup, when most volatile products have been evaporated, crystallization takes place and the ammonium salt, NH₄NCO, forms. The infrared spectra clearly show this.

As pointed out by Hubbard et al. (1975) NH₄NCO transforms at room temperature into urea (NH₂CONH₂), a product that has been identified as a substantial component in the organic residues that remain after the ultravioletphotolyis of dirty ices (Agarwal et al. 1985; Schutte 1987). This could explain the disappearance of the 2217 cm⁻¹ NH₄NCO band in the final stage of the warmup sequence.

V. ASTROPHYSICAL IMPLICATIONS

One of the major implications of our results is that they firmly establish the presence of ionized species in interstellar...
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grain mantles. The definitive identification of the 4.62 μm absorption feature with OCN− also provides evidence for the presence of a positive ion, NH4+, absorbing near 1390 cm−1. Since both species are expected to appear simultaneously in the processed ices it is worthwhile to search for the NH4+ ion in the interstellar spectra. A preliminary inspection of the 5–8 μm region of protostars (Tielens et al. 1984) for an absorption in the 7.0–7.4 μm (1430–1350 cm−1) region shows two features, one centered at 7.08 μm (1413 cm−1) and another at 7.29 μm (1372 cm−1). Although these features may be interpreted as resulting from methyl and methylene deformation modes of saturated hydrocarbons, the correlation between the 2165 and 1390 cm−1 laboratory bands could as well show that one of the observed bands near 7.2 μm is due to NH4+. The need for high-resolution spectra with a better signal-to-noise ratio of the protostellar sources in the 5–8 μm region is clearly indicated.

The assumption made by Lacy et al. (1984) that the integrated absorbance value for “XCN” is less than or equal to that of CO leads to an overestimate of the OCN− column density. The lower limit of 2 × 1017 cm molecule−1 for OCN− leads to an upper limit for the OCN− column density toward W33A of 1.9 × 1018 cm−2. This is about 4% of the minimum H2O column density of about 4.7 × 1019 cm−2 (Tielens et al. 1984). Using a mean OCN− absorbance value of 7 × 10−17 cm molecule−1 (Schettino and Hisatune 1970), the OCN− column density is about 5 × 1017 cm−2. This implies a 1% concentration of OCN− relative to H2O.

Since it appears that ions as well as radicals are generated in the ultraviolet photolysis, it is important to consider their influence on the solid state reactions schemes in interstellar dust. Furthermore it is possible that a number of other ions, such as CN− or CO2−, are generated which has implications for the interpretation of interstellar spectra. Since we do not observe any absorption appearing in our spectra near 2040 cm−1, we believe the identification of this band as resulting from the CN radical (Larson et al. 1985) cannot be correct. The CO/NH3 infrared spectra do however show a weak broad feature centered at 2100 cm−1, which may result from a CN bearing molecule or ion, such as HCN or CN−. Having clearly established the presence of ions we intend to investigate the possibility that the 6.8 μm feature arises from the isolated carbonate ion, CO2−. The fact that the ratio of the 6.8 μm to 4.62 μm absorption in W33A is about the same as in our photoprocessed and annealed grain mantle analog samples supports this hypothesis. Although we cannot exclude the metal carbonate (CaCO3, MgCO3) candidates as proposed by Knacke and Krätgtscher (1980), Sandford and Walker (1985), or Hecht et al. (1986), the appearance of the 6.8 μm feature as due to isolated CO2− in a photoprocessed grain mantle seems to fit better with the OCN− ion identification of the 4.62 μm absorption. At this stage we are not able to distinguish between the carbonate ion and the tentative identification of the 6.8 μm feature with methyl(ene) deformation modes of saturated hydrocarbons (Tielens et al. 1984; d’Hendecourt et al. 1986). But, by an investigation of the laboratory-produced 6.8 μm feature with deuterated ammonia, as well as isotopically labeled oxygen and nitrogen molecules, we hope to test all possibilities. We will report on the 6.8 μm feature in a future publication.

The appearance of an absorption near 2215 cm−1 at high temperature in the laboratory points to the formation of a nonvolatile salt. It would be worthwhile to search for such a feature in objects showing the 3.4 μm features. This would then indicate the presence of such nonvolatile products as salts along with the CH fundamental groups in organic refractory grain mantles.

Since the OCN− appears to persist in an interstellar ices rather high temperatures (OCN− is less volatile than H2O) the ion must be a parent molecule in the cometary ices. When a comet enters the solar system, sublimation of the ices and photodissociation of the released OCN− may be one of the sources for the CN emission since the estimated concentration of CN parent molecules in comets relative to H2O is in the order of 0.1%.

VI. CONCLUSIONS

Ultraviolet photolysis of isotopically enriched molecular mixtures has finally led to the unambiguous identification of the 4.62 μm interstellar absorption feature as OCN−. The formation of this species implies the presence of a positive counterion, NH4+, and a search for this species in the interstellar absorption spectra is warranted. Iodion formation in interstellar ices may have implications for the solid state chemical reaction schemes. A search for absorptions near 2200 cm−1 toward diffuse medium objects, such as IRS 7, might reveal additional information on organic refractory grain mantle composition containing, for example, such nonvolatile salts as NH4NCO.

We have shown the power of experiments using isotopically labeled samples to provide unambiguous identification of interstellar absorption features, where a simple comparison between the interstellar peak locations and literature data may be inadequate.

We wish to thank Martien de Jong for his assistance in performing the experiments. We thank Willem Schutte for the many discussions and Gerard van der Zvet for a critical reading of the manuscript.

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