

## THE INFRARED SPECTRUM OF A LABORATORY-SYNTHESIZED RESIDUE: IMPLICATIONS FOR THE 3.4 MICRON INTERSTELLAR ABSORPTION FEATURE

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### ABSTRACT

Proton irradiation of low-temperature ice mixtures of water, ammonia, and methane or propane results in the synthesis of an organic, room temperature residue whose dominant infrared signatures occur near 3.4  $\mu\text{m}$  and 9.9  $\mu\text{m}$ . The 3.4  $\mu\text{m}$  laboratory-produced feature is compared with the interstellar 3.4  $\mu\text{m}$  absorption feature in IRS 7 and OH 01-477.

*Subject headings:* infrared: spectra — interstellar: molecules — laboratory spectra

The presence of a possible absorption feature near 3.4  $\mu\text{m}$  is evident in the spectrum of several infrared sources associated with molecular clouds. These sources include the galactic center source IRS 7 (Allen and Wickramasinghe 1981; Wickramasinghe and Allen 1980; Soifer, Russell, and Merrill 1976), OH 01-477 (Wickramasinghe and Allen 1980), NGC 2264IR and CRL 490 (Merrill, Russell, and Soifer 1976), CRL 2591 (Merrill and Soifer 1974), and the BN Nebula (Gillett and Forrest 1973). A variety of theories has been proposed concerning the materials responsible for this absorption and other unidentified absorptions at 6.2, 7.8, 8.6, and 11.3  $\mu\text{m}$  in many sources. Since the stretching vibration of CH occurs near 3.4  $\mu\text{m}$ , speculations concerning the nature of the material have included carbonaceous compounds (Knacke 1977), polysaccharides (Hoyle and Wickramasinghe 1977), biological compounds (Hoyle *et al.* 1982), and various chemical functional groups bound at reactive sites on carbon grains (Duley and Williams 1981).

This *Letter* discusses the infrared spectrum of a non-volatile residue produced by proton irradiation of a low-temperature ice mixture of water, ammonia, and methane or propane. The dominant infrared absorption features of the synthesized residue occur at approximately 3.4  $\mu\text{m}$  and 9.9  $\mu\text{m}$ .

A gaseous mixture of  $\text{H}_2\text{O} + \text{NH}_3 + \text{CH}_4$  ( $\sim 0.4:1.0:0.8$ ) was deposited onto a 20 K aluminum mirror to form a thin ice film (thickness  $\leq 5 \mu\text{m}$ ). The ice was irradiated with 1 MeV protons from a Van de Graaff generator with an incident beam current of  $\sim 10^{-8}$  amp. The estimated total absorbed energy density in the film was  $1.7 \times 10^{17}$  MeV  $\text{cm}^{-3}$ , a value estimated to be equivalent to that absorbed by the outer layers of a comet in the Oort cloud in  $\sim 2 \times 10^9$  yr

due to galactic cosmic-ray protons (e.g., Donn 1976; Whipple 1977). In a series of experiments, Brown *et al.* (e.g., Brown *et al.* 1980) have measured the erosion rate of water ice films during proton irradiation. These rates indicate a fraction of about  $3 \times 10^{-5}$  of our film would have been lost due to sputtering, thus sputtering effects can be neglected.

Figure 1 shows the infrared spectrum from 2.5  $\mu\text{m}$  to 15  $\mu\text{m}$  of an  $\text{H}_2\text{O} + \text{NH}_3 + \text{CH}_4$  ice mixture at 20 K before and after irradiation. After irradiation, the ice sample was warmed to 300 K and the infrared spectrum of the synthesized residue on the aluminum mirror sample holder (unextracted) was measured (see Fig. 2). The spectrum of the residue after it was extracted using an organic solvent and deposited onto a transmitting KBr crystal is also shown. Three samples are plotted in Figure 2. Samples B and C contained  $\text{CH}_4$  and sample A contained  $\text{C}_3\text{H}_8$  as a source of carbon.

The laboratory absorption band near 3.4  $\mu\text{m}$  has features at 3.39  $\mu\text{m}$ , 3.43  $\mu\text{m}$ , and 3.51  $\mu\text{m}$ . A second absorption band is observed in most samples at 9.9  $\mu\text{m}$ . One residue also showed a small signature near 6.7  $\mu\text{m}$ .

An effort was made to analyze the residue composition. Hundreds of peaks were present in gas chromatographic recordings which were not present when similarly treated blank samples were observed. Mass spectrometric analysis showed a great variety of organic species with the highest molecular weight greater than 300 for singly ionized molecules.

A comparison of the laboratory spectrum of the residue from sample B and two sources, IRS 7 (Allen and Wickramasinghe 1981) and OH 01-477 (Wickramasinghe and Allen 1980) is given in Figure 3. Features at 3.43  $\mu\text{m}$  and 3.51  $\mu\text{m}$  in the laboratory spectrum would just be resolvable in the OH 01-477 data ( $\tau$  vs.  $\lambda$ ) which had been smoothed to a resolution of 0.08  $\mu\text{m}$ . Wickramasinghe and Allen's spectrum for OH 01-477 shows peaks at 3.38  $\mu\text{m}$  and 3.45  $\mu\text{m}$  (Fig.

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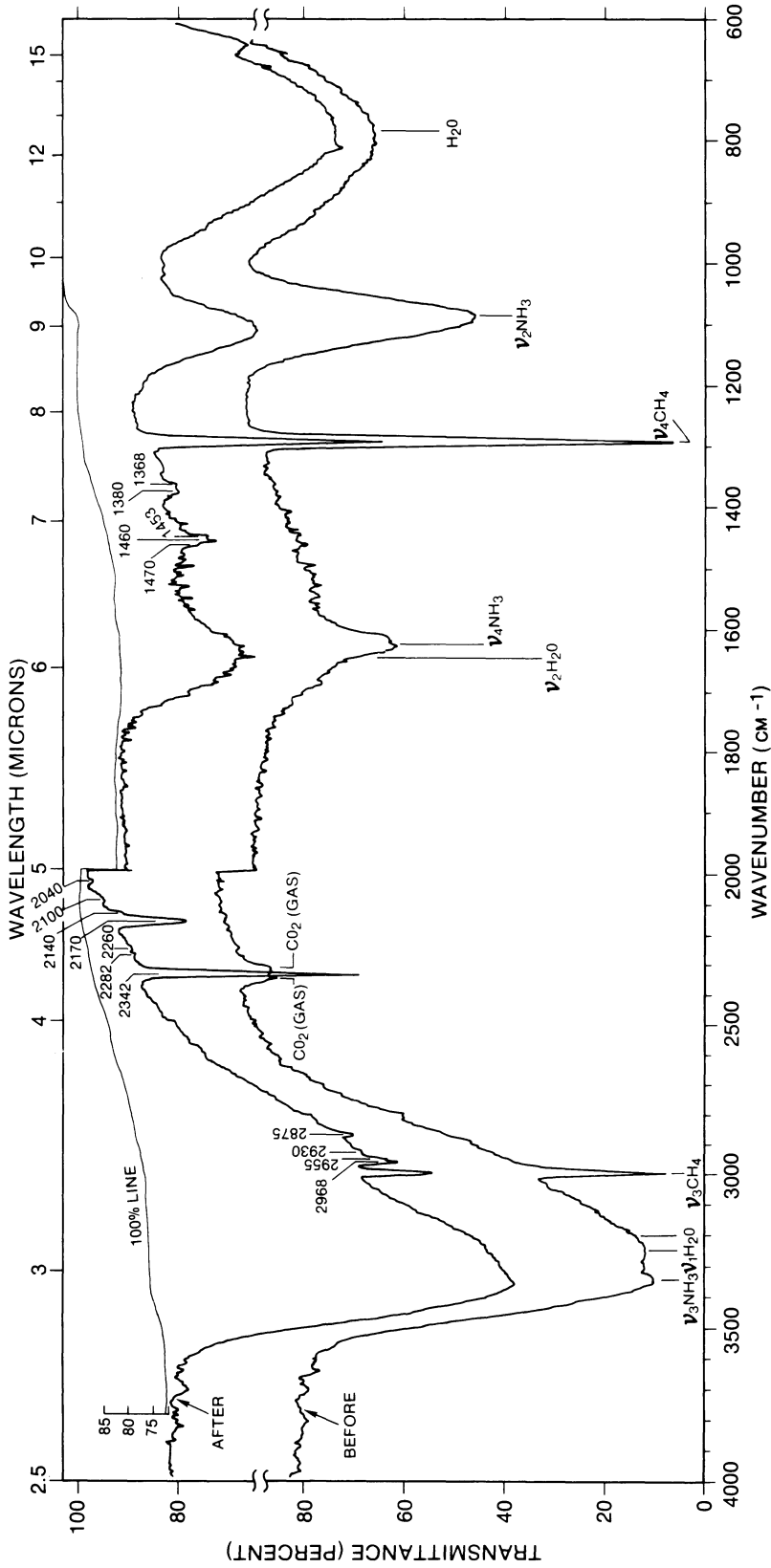


FIG. 1.—Infrared spectrum of an  $\text{H}_2\text{O} + \text{NH}_3 + \text{CH}_4$  ( $\sim 1:3:2$ ) ice mixture at 20 K before and after irradiation with 1 MeV protons. Total absorbed fluence was  $1.98 \times 10^{14}$   $\text{MeV cm}^{-2}$  in the  $2.8 \mu\text{m}$  thick film.

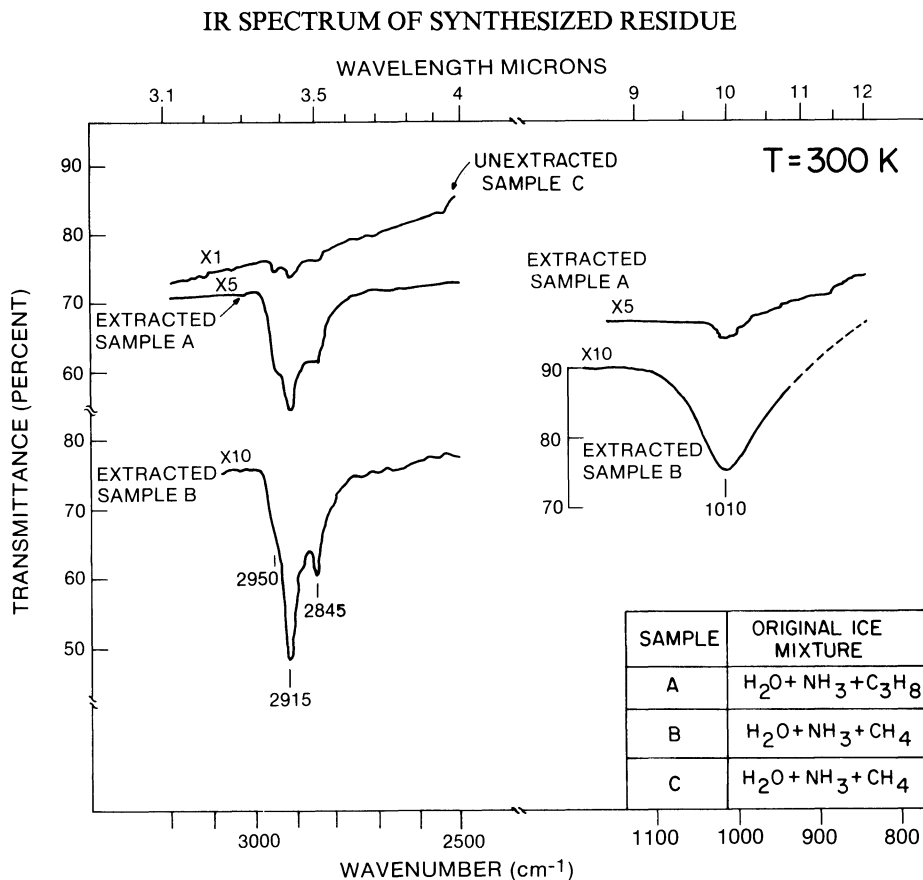


FIG. 2.—Infrared spectrum of residues near  $3.4 \mu\text{m}$  and  $9.9 \mu\text{m}$ . Extracted residues A and B were measured on KBr crystals. Spectrum C was obtained by reflection of the unextracted residue on the aluminum mirror.

3a). Observations of IRS 7 (Allen and Wickramasinghe 1981) extend over a wider wavelength region with a resolution of  $\sim 0.03 \mu\text{m}$  and show corresponding absorption features at  $3.40 \mu\text{m}$  and  $3.48 \mu\text{m}$  (Fig. 3b). Our laboratory residue looks quantitatively similar to both the OH 01 – 477 and the IRS 7 data in the  $3.4 \mu\text{m}$  region. In particular, the  $0.08 \mu\text{m}$  separation between the main peak and the shoulder in IRS 7, Figure 3b, is very similar to the laboratory spectrum.

Figure 4 compares the  $3.4 \mu\text{m}$  and  $9.9 \mu\text{m}$  absorption features of the residue with the data of IRS 7 from  $2 \mu\text{m}$  to  $15 \mu\text{m}$  (e.g., Willner *et al.* 1979). The  $9.9 \mu\text{m}$  feature is less intense than the  $3.4 \mu\text{m}$  feature and, although it occurs within the  $9.7 \mu\text{m}$  interstellar feature, it would make only a small contribution. The  $9.7 \mu\text{m}$  interstellar feature is commonly thought to be due to the stretching vibration of the Si-O bond, although it can also be fit by other materials, such as a mixture of the diatomic oxides of Si-O and Mg-O (Duley, Millar, and Williams 1979), and high molecular weight organic compounds (Hoyle and Wickramasinghe 1980; Khare and Sagan 1979). The latter will also produce features of comparable strength in the  $2 \mu\text{m}$  to  $15 \mu\text{m}$  region (Szymanski 1964) which are generally not seen in the interstellar infrared sources.

This laboratory simulation demonstrates the synthesis of complex organic molecules from simple interstellar type molecules at low temperatures by 1 MeV proton irradiation. The composition and proportions of the initial laboratory ice are consistent with models of interstellar molecular clouds. The good match of the  $3.4 \mu\text{m}$  interstellar and laboratory-residue absorption peaks suggests the presence of complex, not well-defined carbonaceous material in interstellar space. Donn and Jackson (1970) and Greenberg (1982) have indicated that interstellar irradiation of simple ice mixtures in or on grains would synthesize such material.

The photochemical synthesis of complex organic molecules in ice mixtures at low temperatures has been studied at Leiden (Greenberg 1982). Their infrared spectrum of the room temperature residue is different from the one reported in this *Letter*, although it does show weak features in the  $3.4 \mu\text{m}$  region. The combined effects of ultraviolet photons and particle radiation (characteristic of interstellar space) on the synthesis of organic compounds from ice mixtures need to be studied.

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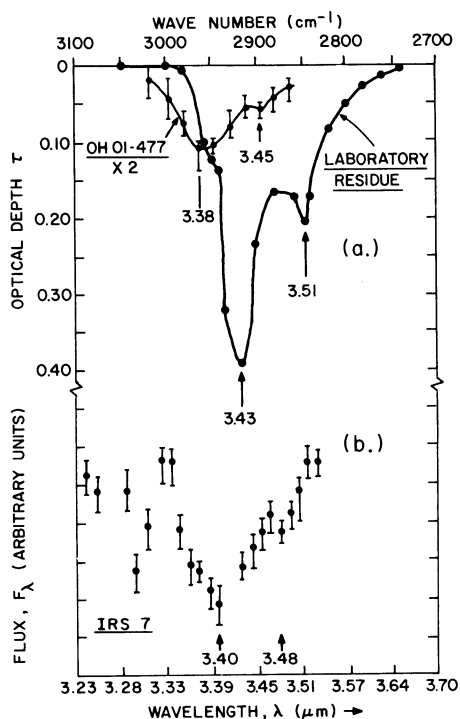


FIG. 3.—(a) Infrared spectrum of the laboratory residue at 300 K is compared with the 3.4  $\mu\text{m}$  feature in the source OH 01-477. OH 01-477 data are from Wickramasinghe and Allen (1980) where the spectrum had been smoothed to a resolution of 0.08  $\mu\text{m}$ . (b) Spectrum of the laboratory residue can be compared with the spectrum of the 3.4  $\mu\text{m}$  feature in the source IRS 7. The IRS 7 data are redrawn from Allen and Wickramasinghe (1981). Resolution is  $\sim 0.03 \mu\text{m}$ .

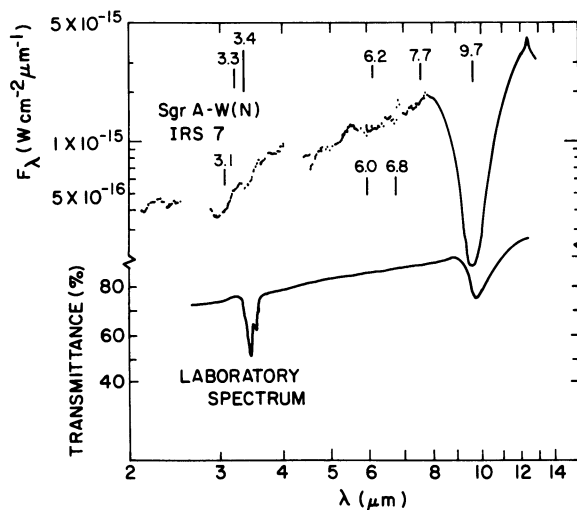


FIG. 4.—Infrared spectrum of the laboratory residue compared with the spectrum of IRS 7 from 2  $\mu\text{m}$  to 15  $\mu\text{m}$  (Willner *et al.* 1979). Wavelengths of peak absorption of the laboratory spectrum are 3.43  $\mu\text{m}$  and 9.9  $\mu\text{m}$ .

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*Note added in proof.*—The similarity between the spectrum of dry *E. coli* and the observed absorption of interstellar material in the 3.4  $\mu\text{m}$  region is discussed by Hoyle *et al.* (1982). In the 3.4  $\mu\text{m}$  region, the spectrum of our laboratory-synthesized residue (Fig. 2) matches closely that of *E. coli* as well as the interstellar feature. We have recorded the infrared absorption spectrum of *E. coli* mixed in oil and also in a CsI pellet prepared at a pressure of  $1.7 \times 10^4 \text{ kg cm}^{-2}$  ( $5 \times 10^4 \text{ p.s.i.}$ ). Both samples showed a similar 3.4  $\mu\text{m}$  feature, in addition to stronger absorptions near 6.56  $\mu\text{m}$ , 8.2  $\mu\text{m}$ , and 9.45  $\mu\text{m}$  which do not occur in the laboratory-synthesized residue. Material of the type produced by irradiation of ice mixtures is a much more plausible candidate for the source of the 3.4  $\mu\text{m}$  absorption in interstellar space than dried microorganisms.

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