LABORATORY SPECTRA OF 10 K ICES: A COMPARISON WITH SOME ASTRONOMICAL SPECTRA

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ABSTRACT. A series of experiments in which mixtures of ices are irradiated with ultraviolet light have been performed. The evolution of these simulated interstellar grain mantles is followed by infrared spectroscopy. The appearance of new bands is observed and possible identifications of these bands are discussed.

1. INTRODUCTION

The time dependent behavior of the composition, abundance and distribution of molecules in both the gas and solid phases in dense molecular clouds has been calculated in a previous paper (d'Hendecourt et al., 1985, paper 1). A limited set of grain surface reactions was taken into account: only low temperature (10-20 K), diffusion controlled reactions have been considered and only reactions with a negligible activation energy have been included. Infrared spectroscopy is a powerful tool for the study of molecular grain mantles in dense interstellar clouds (Allamandola, 1984) because the characteristic frequencies of molecular vibrations lie in the mid infrared region of the spectrum (2-25 microns). Accretion mantles have been observed in many objects (Soifer et al., 1979; Aitken, 1981; Willner et al., 1982; Knacke et al., 1982) and various molecules such as water and ammonia firmly identified. More recently, solid CO has been discovered (Lacy et al., 1984). Such accretion mantles can be easily simulated in the laboratory by condensing gases of different cosmically abundant molecules, onto a cold (10 K) substrate and measuring their IR absorption spectrum. These simple ices can then be irradiated with ultraviolet light so that complex chemistry occurs. IR spectroscopy is again used to identify the new molecules formed. This semi-empirical approach allows a direct comparison with observed astronomical spectra.

2. EXPERIMENTAL "MANTLE" COMPOSITION

The experimental mantle composition has been chosen from the calculations

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described in paper 1. A classical gas phase ion-molecule reaction scheme describes the evolution of the gas phase molecular species which are able to stick onto the grains where they can react (Tielens and Hagen, 1982; paper 1) and evaporate back to the gas phase under certain circumstances (d'Hendecourt et al., 1982). Naturally, mantle composition will differ according to various physical conditions in the cloud considered but basically, two different classes of mantles do arise: those in which water is dominant (60%) and those in which CO or CO_2 and O_2 are dominant. For the photolysis experiments, two mixtures were selected: mixture 1: $H_2O/CO/CH_4/NH_3/6/2/1/1$ and mixture 2: $H_2O/CO/CH_4/NH_3/O_2/N_2/1/1/0.4/0.4/1/0.04$ as representative of interstellar grain mantles at a time of their evolution (paper 1 and d'Hendecourt et al., 1986, paper 2).

3. MANTLE MODIFICATION BY U.V. PHOTOPROCESSING

The IR spectra of the initial and irradiated mixtures are displayed in figures 1 and 2 for direct comparison
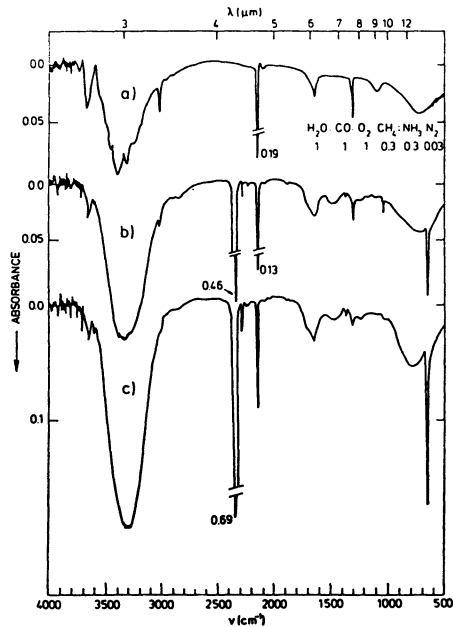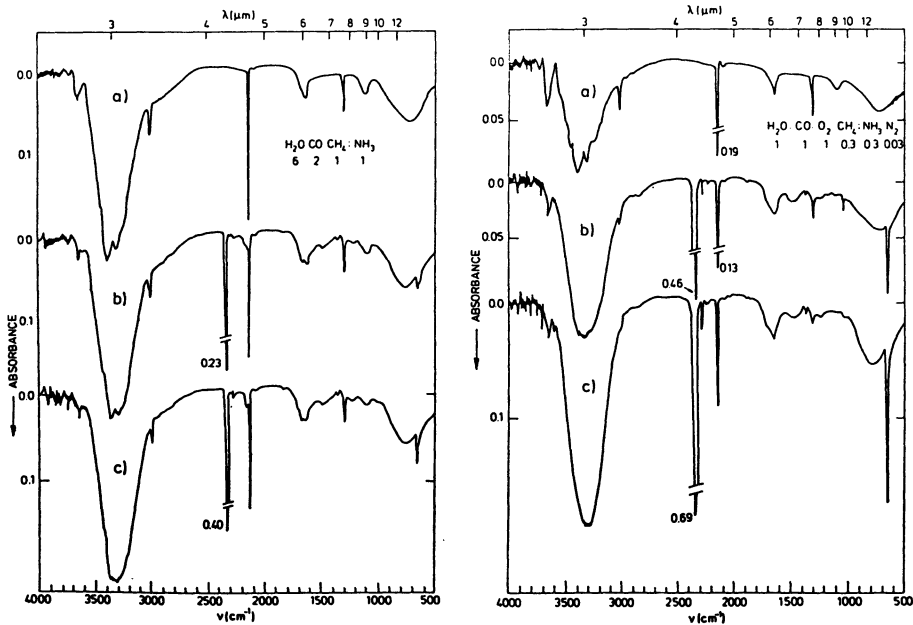
Figures 1 and 2 : Infrared spectra of mixtures 1 and 2: (a) no irradiation, (b) and (c) after 4 hours irradiation respectively.

On these spectra we note that: the bands characterizing methane, ammonia and, to a lesser extent, carbon monoxide show a steady decrease due to photolysis and subsequent reactions. The most intense new bands appear at 2343 cm^{-1} (4.27 μm; FWHM = 12 cm^{-1}), 1470 cm^{-1} (6.8 μm; FWHM $\approx$ 100 cm^{-1}), 2167 cm^{-1} (4.61 μm; FWHM $\approx$ 25 cm^{-1}), 1850 cm^{-1} (5.41 μm;

FWHM $\approx$ 15 cm^{-1}), 1370 cm^{-1} (7.3 μm; FWHM = 20 cm^{-1}), 1220 cm^{-1} (8.2 μm; FWHM $\approx$ 50 cm^{-1}) and finally 660 cm^{-1} (15.2 μm; FWHM = 22 cm^{-1}), in the shoulder of the so called "12 micron" ice band. The region 1800–1400 cm^{-1} shows many changes: one can note new strong absorption bands, not mentionned above, at 1770 cm^{-1} (5.81 μm), 1695 cm^{-1} (5.90 μm, a very strong and broad absorption, FWHM = 45 cm^{-1}), and 1585 cm^{-1} (6.31 μm, a weak, broad and shallow absorption). Weaker bands are observed around 2960 cm^{-1} (3.38 μm), 2900 cm^{-1} (3.53 μm), 1090 cm^{-1} (9.2 μm; FWHM = 15 cm^{-1}) and 1020 cm^{-1} (9.8 μm; FWHM = 20 cm^{-1}). The ratio and position of the strongest new lines at 2347 cm^{-1} (4.26 μm) and 660 cm^{-1} (15.2 μm), permit the unequivocal identification of the CO_2 molecule (Schimanouchi, 1972). The next molecule which can be readily assigned with confidence is formaldehyde (H_2CO), with the lines situated at 1720 and 1500 cm^{-1}, corresponding to the CO stretch and the CH_2 scissoring modes respectively (Schimanouchi, 1972). This positive identification was made on the basis of the IR spectrum of H_2CO in a complex matrix obtained by van der Zwet et al., 1985. This identification is further supported by the presence of absorptions at 1850 cm^{-1} and 1090 cm^{-1} due to the HCO radical (Mulligan and Jacox, 1964, 1971), the intermediate in H_2CO production.

In addition to the new bands attributable to specific molecules, others appear which do indicate the presence of a particular molecular subgroup: (i) a band, located at 2167 cm^{-1}, adjacent to the CO absorption band at 2143 cm^{-1}, grows steadily upon photolysis at 10 K. This band has been observed in W33A by Lacy et al. (1984). It has been attributed to the absorption of a CN stretching vibration in an unknown molecule. Because this vibration absorbs at 2265 cm^{-1} in normal nitriles (Bellamy, 1956) and because, in these experiments, this band seems to be correlated with an absorption around 1695 cm^{-1}, a classical position for a carbonyl absorption, d'Hendecourt et al. (1986) have tentatively attributed the 2165 cm^{-1} absorption to a molecule like CH_3CONC. We emphasize that the integrated intensity of this band is large and a deduction of the column density of this molecule to W33A is given in paper 2. (ii) the appearance of a broad absorption band around 1500–1400 cm^{-1} ("6.8" μm) is also quite significant because of the occurrence of the same absorption in the spectrum of W33A and in other protostellar objects (Willner et al., 1982). In this region, the number of candidates is very large so that a precise identification of the molecule is meaningless. This band occurs at the correct frequency for identification with the deformation modes of saturated hydrocarbons, as pointed out by Hagen et al. (1980). A more precise discussion of this identification is given in paper 2, and comparison with observations can be found in Tielens et al. (1984). The fact that, in these experiments, this strong absorption at 6.8 micron is correlated with a relatively weak absorption in the 3.4 micron region (CH stretch in hydrocarbons), points to the formation of saturated aliphatic hydrocarbons in which the methyl and methylene groups are adjacent to unsaturated groups such as alkoxy and carbonyl groups (d'Hendecourt and Allamandola, 1986).

In mixture 2, the evolution is rather similar and is fully described in d'Hendecourt et al. (1986).

4. ASTROPHYSICAL CONDITIONS

These implications are discussed extensively in paper 1 and 2 in terms of the role of the grains in interstellar molecule formation and in terms of low temperature chemistry on the grains surface versus "hot" atom chemistry initiated by UV radiation. Here, we focus on the 5-8 micron region observed in W33A as compared with various mixtures. Figure 3 shows this comparison.

From this kind of comparison and the deductions made from the experiments, it is possible to estimate the amount of material in the line of sight to this object: about 3 to 11% of the available cosmic carbon is present in the line of sight of W33A in the form of solid aliphatic hydrocarbons. This value is slightly lower than the one derived by Tielens et al. (1984) but this is due to the fact that the aliphatic hydrocarbons have larger IR cross-sections at 6.8 μm than the saturated hydrocarbons.
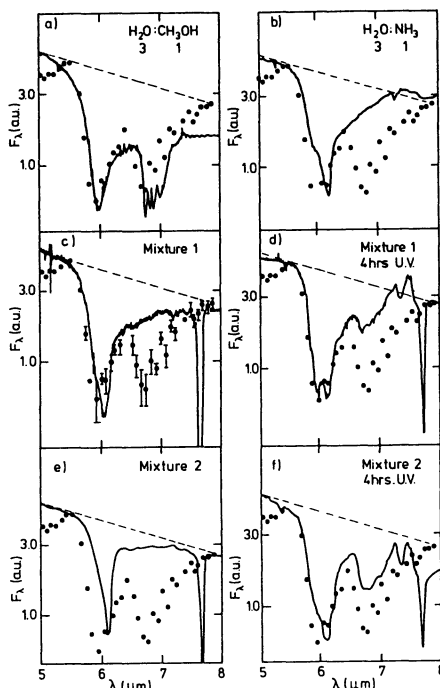

Figure 3: Comparison of the spectrum of W33A (dots) and various laboratory mixtures (observations from Soifer et al., 1979).

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DISCUSSION

S. FEDERMAN: Because of abundance and kinetic arguments, all grain
surface chemistry should be taking place in a sea of hydrogen. How
does this affect your models? Several layers of hydrogen may also
lessen the amount of condensation.
D'HENDECOURT: That is an interesting point: the binding energy of H_2
on H_2O ice is ~ 900K (this is equivalent to the binding energy of CO on
CO). So there will be some H_2 on the surface of the grains. However,
H_2O ice is indeed observed as a solid so that molecules (including CO)
do stick on the grains.

WILLIAMS: I note that you assume a high mobility of H-atoms, which I
also find. How is it that you have a high population of radicals in
the grain when the H-atoms will readily saturate them?
D'HENDECOURT: The binding energy of H on H_2O surface is about 300-500K
so that this H atom is mobile on an H_2O surface at 10K. Roughly
speaking, the binding energy inside the H_2O lattice of the same H atom
is about double of that. As a consequence, H atoms will diffuse (slowly
even at 10K) from the inside towards the outside. For an H atom
landing on the surface, it is far more likely to diffuse on the surface
than to move inwards.

PIRRONELLO: How your results would change if the hypothesis of a very
low mobility of H atoms on amorphous grain surfaces, supported by
Smoluchowski calculations is correct?
D'HENDECOURT: I am aware of the hypothesis of Smoluchowski. I must
say that it contradicts laboratory measurements of binding energies of
H and H_2 on H_2O ice. Nevertheless, if this hypothesis is true, I
think that it is rather difficult to form as much H_2O ice on the grains
as is observed. My model predicts a lot of water ice on grains.

GREENBERG: I like to reinforce d'Hendecourt's comment to Pirronello's
question about Smoluchowski's H atoms sticking. It is true, if H
atoms come and they sit locally, then the cross section for reaction of
H and O becomes roughly their area and no more, and it has to be grain
area, if you ever have to make water molecule which are seen. So
obviously the answer is that proof is in the pudding. You see water
molecules on the mantles and therefore they must have been made there.
What you might say now is that Smoluchowski is partly right. May be
they do not go swinging all the way around, they have to go a little
tubular way around and they can sort of wander around through 50% or
75% of the surface but not the 100%, and that will not make much dif-
ference in the calculations that he was talking about.

LEGER: Your model and your laboratory data predict significant amount
of frozen CO_2 on grains. Unfortunately the 4.27 μm band of CO_2 is not
observable from the ground. Is this band a good target for ISO?
D'HENDECOURT: Yes, it is. Although CO_2 can be detected by a weaker

band at 15.2 μm - IRAS LRS Spectra could eventually be interesting although the resolution of LRS instrument is probably too low to really detect CO_2.