

Laboratory identification of the emission features near 3.5 μm in the pre-main-sequence star HD 97048

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Summary. This paper presents the results of a laboratory study of formaldehyde (H_2CO) suspended in low temperature molecular matrices with compositions similar to what may be found in the “dirty ice” mantles of grains. It is shown that the emission features near 3.5 μm in the pre-main-sequence star HD 97048 can be matched by a mixture of chemical complexes of H_2CO with surrounding molecules in the grain. Furthermore, a discussion is presented of various possible excitation mechanisms for this emission. The conclusion is, that for the features near 3.5 μm in HD 97048, UV pumped IR fluorescence is the most likely mechanism.

Key words: infrared radiation – lines: identification – spectroscopy – stars: circumstellar matter

1. Introduction

A number of stellar objects, planetary and reflection nebulae, H II regions and extragalactic sources show broad emission features in the middle infrared region of the spectrum. The features are associated with high UV flux regions and at present at least 7 are known at wavelengths 3.3, 3.4, 3.5, 6.2, 7.7, 8.6, and 11.3 μm (Aitken, 1981).

The 3.5 μm emission feature was discovered by Blades and Whittet (1980) in HD 97048, a likely pre-main-sequence star of spectral type B9-A0 Ve in the Chamaeleon *T* association, which illuminates a reflection nebulae in the Chamaeleon dark cloud at a distance of 150 pc from the sun. Variable hydrogen line emission (Irvine and Houk, 1977) and an infrared excess (Grasdalen et al., 1975) indicate that this star is losing mass and is surrounded by a circumstellar dust shell.

Compared to the other IR emission features the 3.5 μm emission is quite rare and up to now has only been seen in one other object, Elias I (Allen et al., 1982). In addition to the unusual 3.5 μm feature, HD 97048 shows emission features near 3.3, 3.4, and 11.3 μm (Blades and Whittet, 1980; Aitken and Roche, 1981). While in other objects the 3.4 μm feature is weak relative to that at 3.3 μm , the situation is reversed in HD 97048, suggesting an additional contribution near 3.4 μm , perhaps correlated with the 3.5 μm feature as Baas et al. (1983) have pointed out.

Based on the suggestion of Allamandola and Norman (1978a), Blades and Whittet (1980) proposed the H_2CO molecule (formaldehyde) or its polymeric form, *n*- H_2CO (polyoxymethylene), as the most likely candidate for the 3.5 and 3.4 μm features. Later, Aitken and Roche (1981) rejected polyoxymethylene because 8–13 μm spectrophotometry of HD 97048 did not show the expected strong features of *n*- H_2CO near 9, 10.5, and 12 μm . Baas et al. (1983) presented high resolution spectra of HD 97048 in the 3 μm region (resolving power of 450) and identified the 3.4 and 3.5 μm features as H_2CO . The identification was based on a comparison of the features with previously published laboratory infrared and Raman spectra of H_2CO suspended in low temperature argon and nitrogen matrices. These spectra showed that the vibrational frequencies of H_2CO in these matrices were shifted compared to the gas phase values. Although the shifts were not sufficiently large to match the observed features in HD 97048, Baas et al. argued that interactions of H_2CO with adjacent molecules in the grain could give rise to such shifts.

In this paper we present the results of a laboratory study of H_2CO suspended in low temperature molecular matrices with compositions similar to what may be found in the “dirty ice” mantles of grains. We have found that chemical complexes of H_2CO with surrounding molecules can indeed account for the large frequency shift between laboratory and observed spectra. In addition we present further evidence that the 3.4 and 3.5 μm emission in HD 97048 is caused by ultraviolet pumped infrared fluorescence rather than by thermal emission.

2. Experimental

Since the experimental details have been described elsewhere (Hagen et al., 1979), only the relevant aspects will be summarized here.

In a vacuum chamber, gas mixtures were deposited onto the surface of an aluminium block, cooled to 10 K by a closed cycle helium refrigeration system (Air Products CSW-202A dispex). Infrared absorption spectra between 4000 and 500 cm^{-1} (2.5 and 20 μm), with a resolution of 2 cm^{-1} , were obtained with a Fourier transform spectrometer (Digilab FTS-15 BD).

Formaldehyde was prepared by thermal cracking of polyoxymethylene at 390 K, using a simplified version of the method of Spence and Wild (1935), and stored at 77 K. It was then deposited simultaneously with the other gases, via a separate deposition line. The vapor pressure of H_2CO was fixed by means of slush baths at 131 K or 143 K surrounding the H_2CO container.

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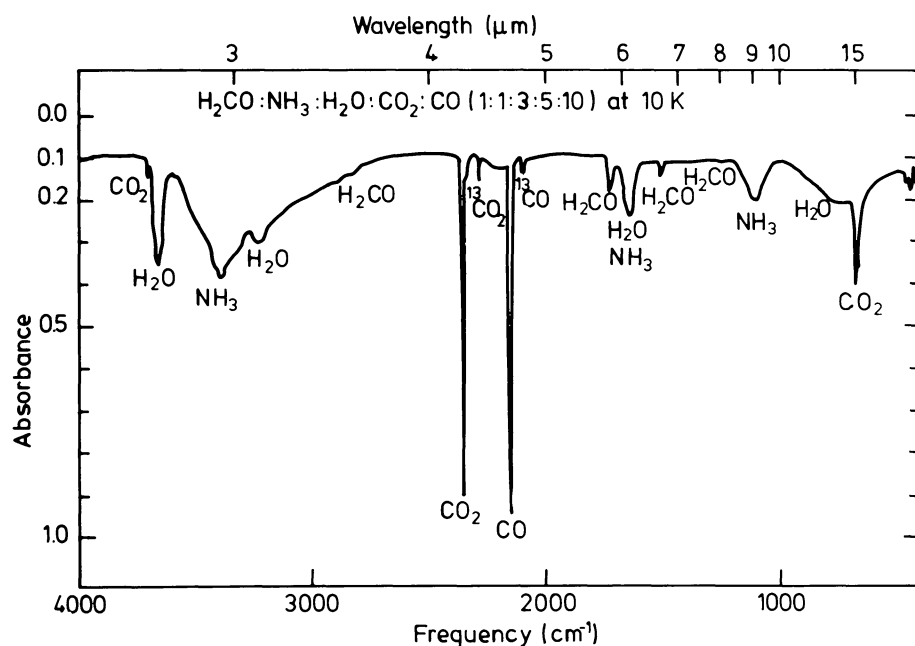


Fig. 1. Infrared absorption spectrum from 4000 to 500 cm^{-1} of an H_2CO containing solid molecular mixture at 10 K

3. Laboratory spectra

3.1. Results

Figure 1 shows the absorption spectrum from 4000 to 500 cm^{-1} (2.5 to 20 μm) of an $\text{H}_2\text{CO}:\text{NH}_3:\text{H}_2\text{O}:\text{CO}_2:\text{CO}$ (1:1:3:5:10) mixture at 10 K. The fundamental vibrational frequencies of formaldehyde in this mixture are listed in Table 1. Carbon dioxide (CO_2) and formaldehyde were deposited separately via non-calibrated deposition lines and the amounts condensed, relative to the other species, estimated from the absorption depths in the spectrum. The region from 2970 to 2745 cm^{-1} (3.4–3.6 μm), containing the symmetric and antisymmetric C–H stretching vibration (ν_1 and ν_5 , respectively) of formaldehyde, is shown in Fig. 2a, while the spectrum of HD 97048 is shown in the same wavelength region in Fig. 2b. The position of the absorption feature at 2835 cm^{-1} (3.527 μm) in the laboratory spectrum, which is assigned to the ν_1 vibrational mode of formaldehyde, closely matches that of the main emission band at 3.53 μm in HD 97048.

In order to understand the nature of the unusually large blue-shift of the ν_1 and ν_5 bands of formaldehyde from the gas phase values which are 2766 and 2843 cm^{-1} , respectively (Blau and Nielson, 1957), the individual effects of the different components of the mixture on this band have been studied. The 2960–2760 cm^{-1} regions of these spectra are shown in Fig. 3a–f, with the position of

Table 1. The fundamental vibrational frequencies of H_2CO in an $\text{H}_2\text{CO}:\text{NH}_3:\text{H}_2\text{O}:\text{CO}_2:\text{CO}$ (1:1:3:5:10) mixture

| Fundamental mode | Frequency (cm^{-1}) |
|------------------|--------------------------------|
| ν_1 | 2835 |
| ν_2 | 1719 |
| ν_3 | 1500 |
| ν_4 | 1183 |
| ν_5 | 2896 |
| ν_6 | 1249 |

the emission features of HD 97048 indicated by arrows on the abscissa scale. In all cases the ν_1 and ν_5 bands are blue-shifted with respect to the gas phase values. The positions of these bands are summarized in Table 2.

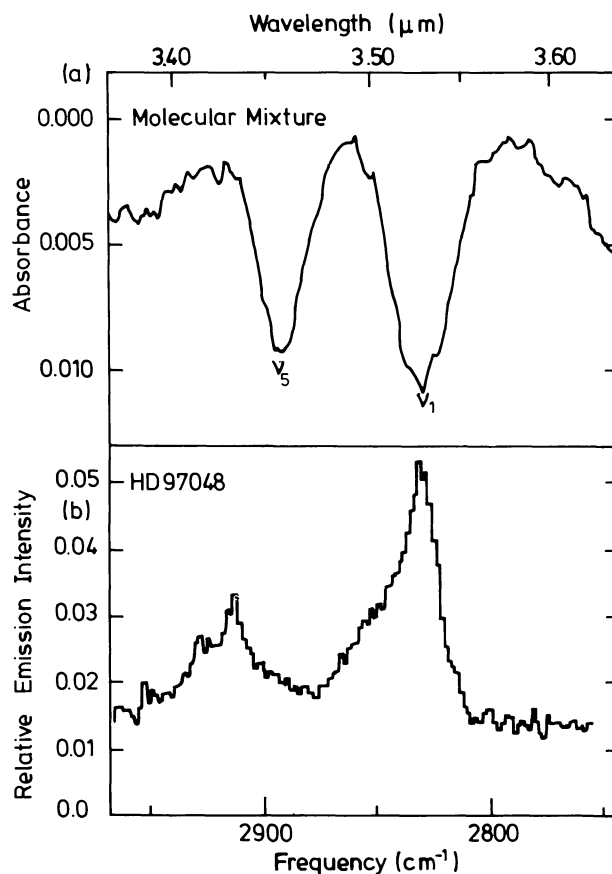


Fig. 2. **a** The 2960–2760 cm^{-1} region of the spectrum of Fig. 1, showing the symmetric and antisymmetric C–H stretching vibration (ν_1 and ν_5 , respectively) of formaldehyde. **b** The spectrum of HD 97048 in the same wavelength region

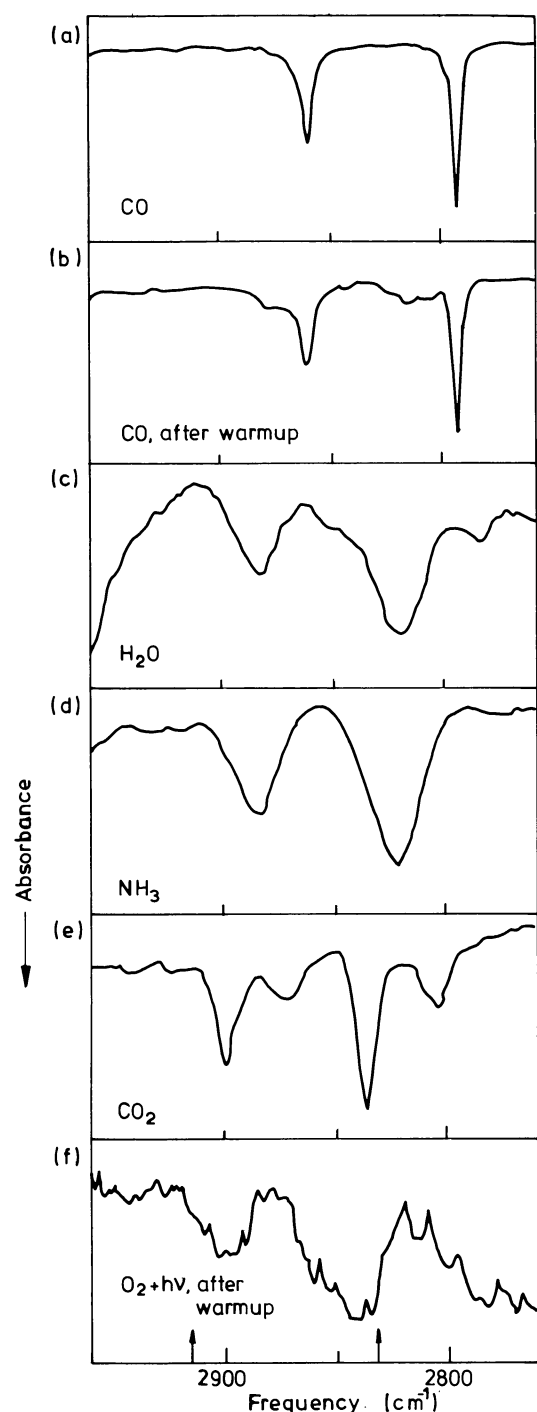


Fig. 3a-f. The 2960–2760 cm^{-1} region of the spectra of formaldehyde suspended in various molecular ices: **a** $\text{H}_2\text{CO}:\text{CO}$ (1:250), 10 K; **b** $\text{H}_2\text{CO}:\text{CO}$, 10 K, after warmup to 32 K; **c** $\text{H}_2\text{CO}:\text{H}_2\text{O}$ (1:20); **d** $\text{H}_2\text{CO}:\text{NH}_3$ (1:20); **e** $\text{H}_2\text{CO}:\text{CO}_2$ (1:600); **f** $\text{H}_2\text{CO}:\text{O}_2$, ratio of the spectrum taken at 40 K to that at 30 K of a photolyzed sample. The positions of the emission features of HD 97048 are indicated by arrows on the abscissa scale

In carbon monoxide ($\text{H}_2\text{CO}:\text{CO}=1:250$) at 10 K (Fig. 3a) two bands appear at 2795 and 2862 cm^{-1} . The shifts of ν_1 and ν_5 , relative to the gas phase values, are caused by weak interactions of monomeric formaldehyde with surrounding CO molecules. After warmup of the sample to 32 K (Fig. 3b), CO is partly evaporated and dimeric and higher associated complexes of formaldehyde

Table 2. The ν_1 and ν_5 fundamental vibrational frequencies of H_2CO in various solids

| Solid | ν_1 | ν_5 |
|---------------------------------------|---------------|---------|
| | (cm $^{-1}$) | |
| CO | 2795 | 2862 |
| H_2O | 2785 | 2853 |
| NH_3 | 2775 | – |
| CO_2 | 2837 | 2900 |
| | 2806 | 2874 |
| O_2^a | 2845 | 2901 |
| Associated H_2CO | 2823 | 2886 |
| Polycrystalline H_2CO | 2832 | 2887 |
| HD 97048 | 2833 | 2915 |
| Gas phase H_2CO | 2766 | 2843 |
| Polyoxymethylene | 2919 | 2980 |

^a Photolyzed and warmed up sample

have formed, giving rise to additional, further blue-shifted features at 2808, 2817, 2871, and 2880 cm^{-1} .

Frozen in water ($\text{H}_2\text{CO}:\text{H}_2\text{O}=1:20$, Fig. 3c) formaldehyde shows two weak bands at 2785 and 2853 cm^{-1} . The formaldehyde concentration in this mixture, as well as in the mixtures with ammonia and oxygen, is much higher than in the other matrices. Therefore, most of the formaldehyde occupies sites adjacent to other formaldehyde molecules forming associated complexes which produce the two broad bands at 2823 and 2886 cm^{-1} (Harvey and Ogilvie, 1961). This assignment has been tested and confirmed by experiments with different concentrations of H_2CO in H_2O . The intensity of the bands assigned to associated formaldehyde relative to the intensity of the bands assigned to matrix isolated formaldehyde decreases as one goes to lower concentrations.

Suspending a high concentration of H_2CO in ammonia ($\text{H}_2\text{CO}:\text{NH}_3=1:20$, Fig. 3d), again gives rise to the two strong, broad, associated formaldehyde bands at 2823 and 2886 cm^{-1} . Figure 3d also shows that formaldehyde isolated in NH_3 absorbs very weakly at 2775 cm^{-1} , with the ν_5 feature presumably obscured by the 2823 cm^{-1} associated H_2CO band.

In the case of carbon dioxide ($\text{H}_2\text{CO}:\text{CO}_2=1:600$, Fig. 3e), the isolated formaldehyde undergoes a somewhat stronger shift than in the other matrices, with ν_1 and ν_5 absorbing at 2806 and 2874 cm^{-1} . A much stronger interaction is clearly also possible in solid CO_2 , as shown by the two strong absorption features at 2837 and 2900 cm^{-1} . These two lines cannot be due to associated formaldehyde because the concentration of formaldehyde is thirty times less than in the H_2O and NH_3 matrices. In the H_2O matrix at this low concentration of formaldehyde, the associated H_2CO bands were not present.

Figure 3f shows the result of an experiment in which a molecular ice consisting of formaldehyde and oxygen (O_2) was photolyzed for two hours with a hydrogen discharge lamp and subsequently warmed up. The ratio of the spectrum taken at 40 K to that at 30 K is shown in this figure. Two broad bands centered roughly at 2845 and 2901 cm^{-1} appear upon warmup from 30 to 40 K, due to one or more different formaldehyde complexes. The complexing species is (are) produced by photolysis, because nonphotolyzed mixtures failed to show these bands. The most

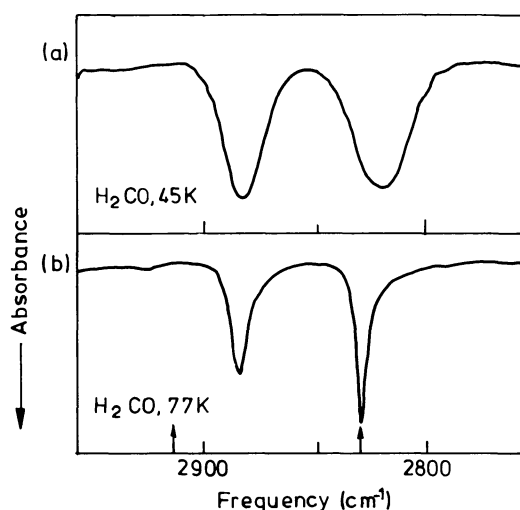


Fig. 4a and b. The 2960–2760 cm^{-1} region of the spectrum of pure associated H_2CO at 45 K (a), and polycrystalline H_2CO at 77 K (b). The positions of the emission features of HD 97048 are indicated by arrows on the abscissa scale

likely candidate is ozone (O_3), which is readily formed upon photolysis.

Figure 4 shows the 2960–2760 cm^{-1} region of the spectrum of pure associated H_2CO at 45 K (4a), and polycrystalline H_2CO at 77 K (4b) which appears upon warmup of the associated formaldehyde (Harvey and Ogilvie, 1961). This is a crystalline phase of formaldehyde showing sharp bands at 2832 and 2887 cm^{-1} .

3.2. Discussion

The shift to higher frequencies of the ν_1 and ν_5 vibrational modes of H_2CO in different matrices with respect to the gas phase values can be qualitatively explained in simplified terms as follows: the characteristic symmetric and antisymmetric C–H stretching frequencies of simple saturated or unsaturated hydrocarbons (C_xH_y) lie between 2900 and 3300 cm^{-1} (Bellamy, 1958). The C–H bond in formaldehyde is adjacent to a double bonded oxygen atom. The oxygen atom, possessing free electrons, has the ability to donate part of these electrons into the antibonding orbital of the C–H bond, thereby weakening it and shifting the symmetric and antisymmetric C–H stretching frequency to a lower value (Bellamy and Mayo, 1976). For gas phase formaldehyde these values are 2766 and 2843 cm^{-1} , respectively (Blau and Nielson, 1957).

It is the behavior of the carbonyl (C=O) group of the formaldehyde which plays a key role in determining the shifts of ν_1 and ν_5 : in noble gas and CO matrices, weak dispersive interactions attract the electrons from the C=O group towards the surrounding molecules, thus lowering the electron density in the carbonyl group and hence also in the antibonding C–H orbital. The result is a shift of the C–H stretching vibrations to higher frequencies.

The ability of H_2CO to interact more strongly with other molecules, forming chemical complexes, is illustrated by considering the interaction with an acidic molecule, for example H_2O : Nelander (1980) has shown that 1:1 complexes of H_2O and H_2CO are formed in argon and nitrogen matrices, via hydrogen bonding between a hydrogen atom of the water and the oxygen atom of formaldehyde. Part of the free electrons of the formaldehyde oxygen are involved in this hydrogen bond, again lowering the electron density in the antibonding C–H orbital and blue-shifting the symmetric and antisymmetric C–H stretching frequency. In

argon for example, these values are 2817 and 2882 cm^{-1} , respectively. For H_2CO in an H_2O matrix, the situation is much more complicated, because different kinds of interactions may be involved.

Formaldehyde is also known to form 1:1 complexes with bases, such as NH_3 (Nelander, 1982), also producing blue-shifts of the C–H stretching frequencies. Again, because of the possibility of many types of interactions, it is difficult to predict the way in which ν_1 and ν_5 of H_2CO isolated in a NH_3 matrix would be affected.

For associated formaldehyde, intimate contact between the carbonyl groups of neighbouring molecules promotes concerted effects, which perturb the C=O group to a much larger extent (Schneider and Bernstein, 1956). The coincidence in frequency of this kind of complex with the bands in solid CO_2 and possibly O_3 (which has an electronic structure almost equal to that of CO_2), suggests that a similar mechanism occurs in these solids.

The bands at 2806 and 2874 cm^{-1} in the CO_2 matrix are probably due to formaldehyde complexed to a much lesser extent than the higher frequency bands. In fact, the positions of these bands are about the same as in the 1:1 complex of H_2CO and CO_2 in argon and nitrogen matrices (van der Zwet et al., 1985).

The above experiments show that suspending H_2CO in molecular matrices which are comprised of molecules likely to be constituents of grain mantles will, in general, result in chemical complexes of formaldehyde with surrounding matrix molecules, with corresponding blue-shifts of the ν_1 and ν_5 vibrational modes of H_2CO compared to the gas phase values. Comparing Figs. 3a–f with 2a indicates that the features in the spectrum of Fig. 2a are mainly due to a blend of absorption bands of associated H_2CO complexes and complexes of H_2CO with CO_2 .

4. Identification

The identification of an infrared band is seldom possible on the basis of one band alone. However, in the case of the 3.5 μm emission feature additional evidence exists which justifies the assignment to H_2CO .

The position of this band (2835 cm^{-1}) points to a C–H stretching vibration, N–H and O–H stretching vibrations generally having values higher than 3000 cm^{-1} . However, C–H stretching vibrations of simple hydrocarbons can be excluded because these occur at frequencies between 2900 and 3300 cm^{-1} (Bellamy, 1958). The stretching frequency of a C–H group which is adjacent to a nitrogen or oxygen atom shifts to lower frequencies as explained in the previous section, and thus molecules containing such combinations are likely. Simple molecules which satisfy this criterion and which absorb in this region are formaldehyde, methanol (CH_3OH) and, although less abundant in the interstellar medium than the first two (Mann and Williams, 1980), methylamine (CH_3NH_2).

Laboratory experiments in which frozen gas mixtures containing methanol were photolyzed by vacuum ultraviolet light show that methanol is readily photodissociated at 10 K. The regions of space where the 3.5 μm emission feature originates are exposed to a substantial UV flux, so that survival of methanol in grain mantles is quite unlikely. In addition, Baas et al. (1983) calculated that the minimum temperature of core-mantle grains in the circumstellar dust shell of HD 97048 is 70 K. Our experiments show that CH_3OH has largely evaporated at this temperature.

Formaldehyde, on the other hand, is a molecule likely to be present in interstellar matrices, as it is readily formed upon photolysis of interstellar ice analogs at 10 K. In the solid phase

photolysis experiments a few percent of the ice is quickly converted into formaldehyde which then appears to follow steady state behavior, presumably due to the availability of CO and photolytic hydrogen atom sources (molecules such as H₂O and NH₃). These latter two conditions are likely to prevail in grain mantles. Moreover, at 70 K H₂CO remains in the ices, presumably due to its ability to form strong complexes.

Methylamine has never been detected in our photolysis experiments and we conclude that the build-up of a substantial concentration of this molecule in grain mantles is far less favorable than for formaldehyde.

Model calculations on the composition of grain mantles by Tielens and Hagen (1982) and d'Hendecourt et al. (1984) indicate that both H₂CO and CO₂ are constituents of the mantles under a variety of conditions, providing theoretical support for the identification of the 3.5 μm feature with formaldehyde.

Thus, in view of the shifts of the symmetric and antisymmetric C–H stretching frequencies of formaldehyde frozen in the molecular ices described in the previous section, and the additional evidence presented above, we agree with the conclusion of Baas et al. (1983), that the 3.53 μm emission band arises from H₂CO frozen on the grains surrounding HD 97048. The asymmetric lineshape of the 3.53 μm emission feature in HD 97048 may be the result of a blend of lines arising from several different complexes of formaldehyde with surrounding molecules in grain mantles, each emitting with a different efficiency (see the next section for a discussion of the mechanism evolved).

It is unlikely that the 3.5 μm feature is due to associated and/or polycrystalline H₂CO because these complexes would polymerize to polyoxymethylene upon exposure to UV radiation (Goldanskii, 1976). Polyoxymethylene is the polymerized form of H₂CO (Baas et al., 1983) and has its symmetric and antisymmetric C–H stretching frequencies at 2919 (3.43 μm), and 2980 cm⁻¹ (3.36 μm) (Piseri and Zerbi, 1968).

In the laboratory spectrum shown in Fig. 2a, the ν₅ component of H₂CO occurs at 3.45 μm (2896 cm⁻¹). While there seems to be a weak feature at this wavelength in HD 97048, the strongest emission is observed at 3.43 μm. There is no counterpart of the 3.43 μm feature in the laboratory spectra, although Fig. 3f indicates that very strong interactions between H₂CO and other species in the molecular mantle may produce the required shift. Another possible candidate for the 3.43 μm feature is the symmetric C–H stretching mode of polyoxymethylene. This would mean that the asymmetric C–H stretching mode of polyoxymethylene emits only weakly or not at all, because no emission is observed at 3.36 μm in HD 97048.

It should be emphasized at this point that one cannot compare the relative intensities of the 3.5 and 3.4 μm interstellar features with those of the corresponding absorption bands measured in the laboratory, because different vibrations are involved and these may have very different emission efficiencies in the solid (again, see the next section for a discussion about this point).

5. Excitation mechanisms

The evidence presented above points to H₂CO frozen in dirty ice mantles of core-mantle grains as the carrier of the emission features near 3.5 μm in HD 97048. This constrains the excitation mechanisms possible by putting an upper limit on the temperature of such grains, as formaldehyde evaporates from these mantles above 100–120 K. Baas et al. (1983) calculated that the minimum temperature for 0.1 μm radius core-mantle grains, in the region

where the emission originates, would be 70 K. Given this we now consider the possible excitation mechanisms.

Several models have been proposed to account for the infrared emission bands originating in the dust: first, Allamandola and Norman (1978a, b) ascribed these bands to infrared fluorescence from vibrationally excited simple molecules frozen in grain mantles. The most likely excitation mechanism was considered to be absorption of UV photons (UV pumped IR fluorescence). Later, Dwek et al. (1980) pointed out that the required UV→IR photon conversion efficiency (α_{ph}) for all the bands taken together, pumped by 10 eV photons (λ ≈ 120 nm), is slightly greater than unity, a value they felt unacceptably high. While most of the energy is emitted in the 7.7 μm band, they argued that, since these features generally occur together, they should all be excited in the same way. It was suggested that two grain populations exist: large (a = 0.1 μm), cool grains which are responsible for infrared absorptions, and small (a = 0.01 μm), hot grains (T = 200–300 K) which produce the emission features by thermal excitation. It was further postulated that the small grains, heated by absorption of UV radiation, should emit very inefficiently in the infrared except at resonant frequencies of the emitting species. Recently, Sellgren (1984) has suggested that even smaller, 10 Å radius grains, momentarily excited to very high temperatures (1000 K) by UV photon absorption, might be responsible for the continuum emission in visual reflection nebulae. Each mechanism will now be considered in turn.

5.1. UV pumped thermal emission

There are several difficulties in accounting for the 3.5 and 3.4 μm bands in HD 97048 with a thermal mechanism. First, emission from the 100 K grains required to retain the H₂CO, is not sufficient to produce the intensity observed. An additional difficulty arises from the band to continuum ratio: Olofsson (1983) has shown that the ratio of the intensity of the well known 3.28 μm band to the continuum at 3 μm, in two nebulae (the Orion bar and S235A), is impossible to reconcile with a thermal excitation mechanism. Olofsson considered hydrogen-atom covered 0.01 μm carbon grains and calculated that the band to continuum ratio would be less than 0.1 if both the 3.3 μm band and the continuum were thermally excited, whereas the ratios observed are 3 and 7. While the physical situation considered by Olofsson does not strictly apply to the 3.5 and 3.4 μm emission bands, the general argument is valid and the observed band to continuum ratio of 10 for these features in HD 97048 (as deduced from the spectra of Aitken and Roche, 1981), makes a thermal emission model highly unlikely.

The large discrepancy between the calculated and observed band to continuum ratios may be reconciled if, as implicitly assumed by Dwek et al. (1980), emission in the band is 1000 times more efficient than in the continuum. In order to obtain the observed intensity in the band, they derived a value of $\tilde{f}/A \geq 1.7 \cdot 10^{-3}$, in which \tilde{f} is the product of the oscillator strength and the number density of oscillators in the grain relative to the density of graphite, and A the oscillator mass in atomic mass units. This implies an oscillator strength f of the order of 1 (Sellgren, 1981). The well known relation between the oscillator strength and the cross-section is:

$$f = \frac{mc^2}{\pi e^2} \int \sigma dv. \quad (1)$$

Taking a width of 30 cm⁻¹ and an oscillator mass of 1 a.m.u. for the 3.3 μm emission feature, an f -value of 1 implies a σ of 3 · 10⁻¹⁷ cm². This value is much too high, since C–H stretching

vibrations generally have cross-sections which are orders of magnitude lower: for example, the cross-section of the C–H stretching mode of CH_4 is $4 \cdot 10^{-21} \text{ cm}^2$ (Pugh and Rao, 1976), and for the ν_1 of H_2CO a value of $6 \cdot 10^{-21} \text{ cm}^2$ has been calculated from our experiments. Thus, in the thermal equilibrium model the abundance of the emitting species has to be increased by at least a factor of one thousand in order to account for the observed flux in the 3.3 μm band.

Another way to account for the observed band to continuum ratio with a thermal emission model, is to assume that the emission features near 3.5 μm in HD 97048 are caused by a population of grains different from those responsible for the continuum emission. However, this is very unlikely because the infrared excess of HD 97048 is dominated by 800 to 1200 K grains (Grasdalen et al., 1975; Glass, 1979), and the assumption of a stable molecular species at the even higher grain temperature required to boost the line to continuum ratio at 3.5 μm seems unlikely. The recent suggestion that thermal fluctuations up to about 1000 K in very small grains might account for the 1–5 μm continuum observed in reflection nebulae (Sellgren, 1984), cannot explain the 3.5 and 3.4 μm bands since H_2CO containing ices, even in the unlikely event that they could condense on such small particles, would not survive on these hot grains.

5.2. UV pumped fluorescence

Baas et al. (1983) estimated the UV \rightarrow IR energy conversion efficiency α_{en} to be as low as $3 \cdot 10^{-3}$ for the 3.5 and 3.4 μm features. They argued that, since the black-body radiation of HD 97048 peaks at 300 nm and H_2CO has a broad absorption centered near that wavelength, the pumping UV flux should be integrated up to 360 nm. The UV spectrum of HD 97048 has recently been measured with the IUE satellite and does not show significant absorption at 300 nm (IUE data bank). It should be noted, however, that the oscillator strength of the ${}^1A_2 \leftarrow {}^1A_1$ transition at 300 nm of (gas phase) H_2CO is only $2.4 \cdot 10^{-4}$ (Sidman, 1958), corresponding to a forbidden electronic transition, whereas much stronger electronic transitions, with f -values of $> 10^{-2}$ (Mentall et al., 1971) are present in the far-ultraviolet region (120–180 nm). Since the extinction for classical-sized grains with $a=0.15 \mu\text{m}$ would be completely saturated at far-ultraviolet wavelengths (Greenberg, 1978), the strongest electronic absorptions would not show up in the IUE spectra at all, while the expected absorption feature at 300 nm would partly affect the stellar spectrum. In view of this, a better way to estimate α_{en} is to ignore the absorption at 300 nm completely and integrate the UV flux (which is absorbed by the much stronger bands) up to 180 nm. In this case a value of $\alpha_{en} = 3 \cdot 10^{-2}$ is obtained.

The UV pumped fluorescence model depends critically on the lifetimes of the vibrationally excited molecules. It is known that different fundamental modes in solids can have very different lifetimes, depending on the size of the molecule, the energy, the symmetry of the vibration involved, and the strength of the coupling with lattice vibrations (Legay, 1977; Bondybey, 1977). If the energy gap between the excited vibrational mode and other energy levels in the solid (at lower energy) is small, the coupling may become very efficient and nonradiative decay fast. If, on the other hand, the energy gap is larger, the coupling will probably be less efficient and the lifetime of that particular state of the molecule may be increased to the point where it is comparable to the radiative lifetime, providing the opportunity for radiative decay. Experimental evidence for long lived vibrational excitations in solids does exist, but to date the systems in which it has been

studied and for which it has been observed are so limited, that at the moment one can only speculate about similar effects in dirty ice mixtures. The C–H stretching mode is a good candidate for IR fluorescence because, in the molecular ice mixtures studied here (Fig. 1) as well as likely in the interstellar medium, a rather large energy gap exists between this band and the next one at lower energy (the ν_3 band of CO_2 at 2350 cm^{-1}).

The absorption bands of other molecules which are present in grain mantles can also contribute to the pumping process, by transferring their energy to formaldehyde via nonradiative processes. This will reduce α_{en} , since the integration of the UV flux can then be partially extended into the visible region and even into the near IR. After nonradiative relaxation from one of these acceptors to formaldehyde, it is left vibrationally excited in the ground state. If the $\nu = 1$ level of the C–H stretching fundamental vibration of H_2CO has a long enough lifetime, energy can pool at this point.

Taken together, the arguments suggest that for the 3.5 and 3.4 μm emission features in HD 97048, UV pumped IR fluorescence from formaldehyde on grains is a more likely mechanism than thermal emission. Moreover, it is worth mentioning that we have recently detected UV pumped IR fluorescence between 2 and 5 μm in H_2CO containing low temperature matrices. The results of these experiments will be reported in a future publication.

From the above discussion it follows that the pumping mechanism of a particular mode and its associated lifetime are sensitive functions of the solid state environment and the symmetry of the vibration involved, resulting in strong selection effects. Consequently, the appearance of other H_2CO fundamental vibrational modes in emission are not necessarily required. In this sense, while 5–8 μm observations of the objects which show the 3.5 μm emission, searching for the 5.8 μm band (the strongest formaldehyde absorption), is important, the absence of this band would not necessarily contradict the identification of the features near 3.5 μm with H_2CO .

6. Recent developments

During the final stage of preparation of this manuscript, it became evident that polycyclic aromatic hydrocarbons may account for the 3.3, 6.2, 7.7, 8.6, and 11.3 μm emission bands (Leger and Puget, 1984; Allamandola et al., 1985). One may speculate about a possible interpretation of the 3.5 and 3.4 μm emission of HD 97048 using this model. In this case, the emission would probably arise from aldehydic groups $\left(-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \right)$ attached to the side of aromatic ring systems. However, the survival of functional groups other than –H in these molecules in the harsh UV radiation field is questionable. Moreover, an aldehydic group attached to an aromatic molecule would also emit at 3.65 μm (Duley and Williams, 1981; Aldrich Library of Infrared Spectra, 1981), although the specific state of the molecule (i.e. being in a neutral, ionic or radical form) may effect these vibrational frequencies. These problems have to be solved before this hypothesis can be accepted as a possible explanation for the 3.5 and 3.4 μm emission features in HD 97048.

7. Conclusion

Spectroscopic evidence supporting the assignments of the emission features near 3.5 μm in HD 97048 to H_2CO , initially made by

Blades and Whittet (1980), and later supported by Baas et al. (1983), has been presented. Implications concerning dust composition and temperature can be derived from this assignment. The positions and line profiles of the emission features near 3.5 μm can be explained in terms of formaldehyde complexes in dirty ice mantles of grains present in a circumstellar shell surrounding the star. UV pumped IR fluorescence is the most likely mechanism for these features.

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