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POSSIBLE IDENTIFICATIONS OF THE $3.4\mu\text{m}$ FEATURE

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INTRODUCTION

A feature at $3.4\mu\text{m}$ was first detected in Comet P/Halley by the IKS spectrometer on board the Vega 1 probe, Combes *et al.* (1986a,b); and subsequently from the ground by Danks *et al.*, Knacke *et al.* (1986), Wickramasinghe and Allen (1986) and Baas *et al.* (1986). The feature has since been reported in Comet Wilson (1986l), Tokunaga *et al.* (1987). The presence of the feature is of considerable interest for a number of reasons. First, it may represent the detection of a new parent molecule, and when combined with data from Giotto and Vega yield new information on cometary chemistry and the early solar system composition. Secondly, it may represent a link to the interstellar medium, the feature corresponds in wavelength and shape with an interstellar feature seen in absorption in a luminous star, towards the Galactic center known as GC-IRS7, Allen and Wickramasinghe (1981). The feature in turn is thought to be related with a growing family of unidentified infrared emission features seen in stellar objects, planetary nebulae, reflection nebulae, HII regions and extra galactic sources, Aitken (1981). These features occur at wavelengths 3.3, 3.4, 3.5, 6.2, 7.7, 8.6, and $11.25\mu\text{m}$.

IDENTIFICATION

Consider first the highest spectral resolution observation of the 3.4μ feature in Halley taken by Baas *et al.* (1986) shown in Figure 1. The spectrum has a resolution of $0.008\mu\text{m}$ and some structure can be seen in the profile. At first sight the structure corresponds remarkably well with the wavelengths of the rotation lines of the CH(1-0) ground electronic state. The R branch extends blueward from the band origin at $3.6\mu\text{m}$ to peak at approximately R12 at $3.4\mu\text{m}$, the short wavelength limit corresponding to the R-branch band head. The larger portion of the spectrum is shown in Figure 2 from Danks *et al.* and many P-branch lines can be seen to correspond with structure seen in the observed profile. However, peaking at R12 would imply a thermal-rotational temperature of approximately 300 K. At this temperature, the individual rotation line widths would be narrow and should be resolved by Baas *et al.* Although the temperature of the molecule could perhaps be explained by excitation processes during release of dust from the nucleus, how would the temperature be maintained? The molecule CH is seen in the visible and known to be excited by resonance-fluorescence; however, the dipole moment of CH is sufficiently large that it would be difficult to maintain a high J population. It is difficult to argue, then, that the feature arises from CH directly, although there is likely to be a small contribution.

The feature occurs at $3.4\mu\text{m}$ as a natural consequence of the vibrational energy or bond strength of the CH molecule. However, the bond strength can be modified by the near presence of other atoms, for instance when CH bonds occur naturally within larger molecular structures, i.e., polymers or cyclic molecules. These aspects are demonstrated

in Allamandola (1984). The region between 2-15 μm corresponds with energies typical of bond strengths which dictate the molecular vibrational frequencies, and this spectral region is known by chemists as the "fingerprint" region where particular groups of atoms give rise to "characteristic" absorption bands, e.g., C-H stretch olefinic 3.3 μm , C-H aromatic 3.4 μm , C-H-saturated 3.5 μm , C-C stretch 6.1 and 7.2 μm , C-C stretch 6.2 and 6.7 μm , =C-H out of plane bend 10 and 10.4 μm , etc. The width, shape and central wavelength of the C-H signature can be modified in a specific molecule depending on the structure and how many C-H bonds it has, but it essentially retains its personality. There are also abundance constraints which limit the choice of molecule; some favorite candidates based on models are CH₄, NH₃, CHN, H₂O, CO, CO₂, etc. (Crovisier and Encrenaz 1983). The 3.4 μm emission is characteristic of the CH-stretching frequency (CH₃, CH₂) of saturated hydrocarbons, while the 3.3 μm emission is characteristic of the CH stretching of unsaturated hydrocarbons - in particular alkenes (-CH=CH-, CH=CH₂) and aromatic compounds (Bellamy, 1975). But it is probably not possible to discriminate if the IR emission originates from a gaseous or solid phase, or uniquely identify the saturated H-C from the 3.4 μm feature.

An analogous situation exists for the UIBs which have been suggested to originate from polycyclic aromatic hydrocarbons (PAHs). As the name suggests these are cyclic molecules which can probably only form through condensation of grains. The argument is that once formed they are hard to destroy. Extinction in the interstellar medium tells us small grains exist, and depletion of C in the gas phase suggest the grains are made of graphite. Graphite, in turn, can give rise to the 2200A feature. The graphite planes are held together by weak Van der Waals forces which are easily broken, providing PAHs in the gaseous- or single-molecule form. But many details are left unexplained. Donn *et al.* (1987) have addressed some objections, i.e., significant differences in wavelengths and intensities of the features, neglecting to take into account intramolecular vibrational relaxation in large molecules which can significantly change population distributions. Donn *et al.* agree, however, that hydrogen-rich carbonaceous material is probably responsible for the features based on laboratory data. The chemist would follow the same approach and would not make an identification of a sample based on an IR spectrum from the "fingerprint" region alone, but would also make a NMR measurement.

The 3.4 μm feature in Halley must be approached in the same way; identification will probably come only through a combination of spectroscopy with spacecraft data. For instance, data from PICCA (Positive Ion Cluster Composition Analyzer) on board Giotto has recently been analyzed by Huebner *et al.* (1987) who report mass peaks at 105, 91, 75, 61, and 45 at a regular spacing of approximately 15 amu. These data are consistent with decay products of a polymer, and by making up polymers from the most abundant elements H, O, C, and N, only a few possibilities exist - (NH)_n and (H₂CO)_n. (H₂CO)_n is known as paraformaldehyde or as polyoxymethylene (POM), which was first predicted by Wickramasinghe (1974). It has an affinity for graphite and silicon and grows in whiskers on dust particles. It is stable to heating by solar radiation. In fact, in the spectrum of Danks *et al.* features are also seen at 3.3, 3.37, 3.51 and weakly at 3.58 μm . Features beyond 3.5 μm are easier to interpret in terms of gaseous emissions, as the number of candidates increases rapidly. Possible identifications of the 3.51 and 3.58 μm features are the fundamentals of H₂CO, ν_5 , and ν_1 , centered at 2843 cm⁻¹ and 2783 cm⁻¹ respectively. Gas phase chemistry of the interstellar medium predicts the abundances of diatomic molecules well, and also the formation of some linear molecules; certainly the molecules observed in the dark clouds at radio wavelengths are linear. In addition, Giotto and Vega both found large numbers of small grains rich in C, H, O, and N. All this re-enforces the hydrogenated carbonaceous ideas, and we should probably concentrate on linear molecules in the gas phase. Some of this data lead Chyba and Sagan to propose small organic grains or grains with mantles of organic material formed from a methane clathrate bombarded by p⁺ and γ rays to process the methane ice into an organic residue. The model fits the observations globally and could serve as a good basis for specifying what future space missions should look for.

CONCLUSION

In order to advance further, the identification of the $3.4\mu\text{m}$ feature and detection and identification of other parent molecules in general requires complementary probe data.

From the ground the $3.4\mu\text{m}$ feature should be re-observed in as many comets as possible. It has now been seen in Halley (old) and Wilson (new), but has not been detected in Enke (old), West (new), or IRAS (new). Technology is advancing fast, and it should be possible to obtain higher resolution observations and eventually mapping.

Observations from the KAO should be carried out in the $5\text{-}12\mu\text{m}$ region to search for the complementary bands of C-H, C=C, etc. The absence of features in this region to date is disquietening.

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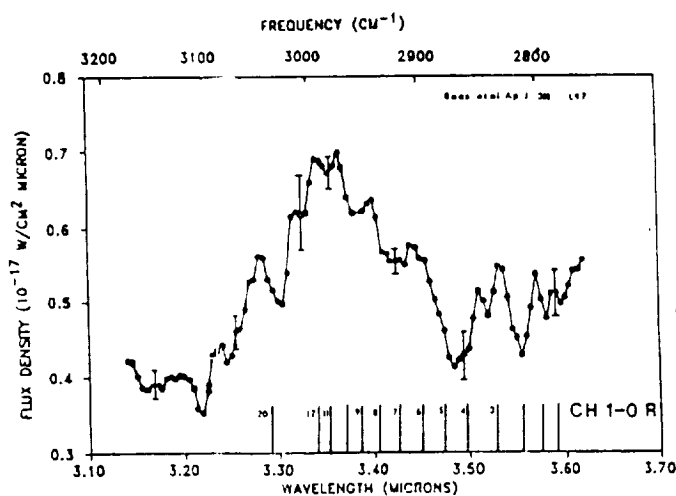


Fig (1) The $3.4\mu\text{m}$ feature in P/Halley taken from Baas *et al.* (1986).

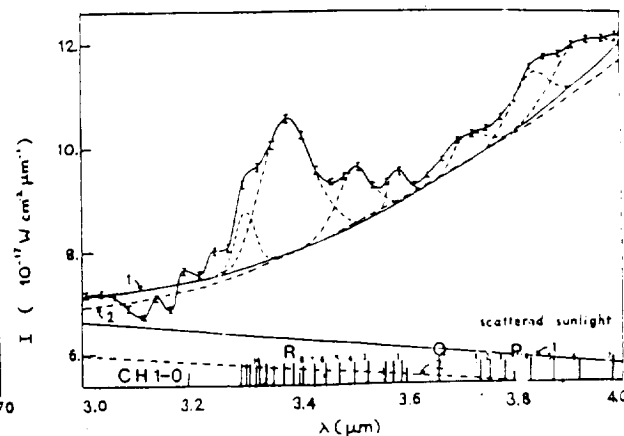


Fig (2) The spectrum of P/Halley from 3.0 to $4.0\mu\text{m}$ taken from Danks *et al.*

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DISCUSSION AND RECOMMENDATIONS

Ground-based and space-probe measurements of P/Halley yielded a wealth of information about the chemical composition and size distribution of cometary grains.

The most important result to come from the PIA/PUMA data is the ground-truth demonstration that grains with chemical compositions similar to those seen in terrestrial, interplanetary interstellar grains exist in the nuclei of comets. It is evident, however, that many questions remain unanswered and new questions have been raised. We summarize the conclusions reached by the participants in this session, and outline their recommendations for future cometary investigations.

Spectroscopic Studies

The data returned during the Halley apparition provided a wealth of information about cometary dust grains. Realization of the potential of the data requires supplementary laboratory studies of grain materials. These should include experimental investigations of grain-processing mechanisms as well as laboratory spectroscopy of prospective grain constituents.

Spectroscopic studies of the emission features that appear in comets are extremely important to elucidate the origin of these features. Further observations of both new and evolved comets over a wide range in heliocentric distance are required. These should be supplemented by laboratory studies of materials thought to be similar to cometary constituents.

The detailed spectral shape of the $3.4\mu\text{m}$ feature in comets has yet to be well determined by observations at high-spectral resolution. Such observations, as well as comparative spectra of laboratory samples, will be necessary to distinguish between such mechanisms as emission by solid organic grains and resonance fluorescence by organic gases. Some of these models can be discriminated by documentation of temporal variations in the $3.4\mu\text{m}$ feature and by the presence or absence of features at other wavelengths as a function of heliocentric distance.

There are several broader questions that such observations of these emission features in a large sample of comets and stars can address. How do the comet features compare with those observed in circumstellar and interstellar dust? What are the connections between the hydrocarbon functional groups which produce the $3.36\mu\text{m}$ emission and those that produce the 3.29 and longer wavelength features in interstellar sources? Are the organic residues in comets formed after capture in the inner solar system, in the Oort cloud, or in the interstellar grains which were accreted into the comet nucleus?

Interplanetary Dust Particles

The interplanetary dust particles (IDPs) seem to be the closest analogue of comet dust accessible to laboratory study. At least one subset of IDPs, the anhydrous chondritic aggregates, are very likely to be comet dust, albeit "weathered" in the solar system for up to 10^4 years. It is important to study their physical structure, chemical and mineralogical make-up and to relate to these to physical and chemical processes in the comet. These data will form the basis for comparison with future *in situ* measurements of comet grains. An understanding of their alteration in the interplanetary medium and in the earth's atmosphere is also necessary.

It is also important to measure the optical properties of these IDPs, including their infrared emission features (if possible, as a function of temperature), for analogy with the

comet dust observed remotely. An attempt should then be made to model the optical properties, to test the adequacy of theoretical predictions for non-spherical particles.

Direct Sampling from Space Missions

It is apparent that the proposed space missions, such as the Comet Rendezvous Asteroid Flyby (CRAF), Comet Sample Return, and the Orbit Determination and Capture Experiment (ODACE) are of the highest priority for increasing our understanding of the composition and mineralogy of cometary grains and their relationship to interplanetary and interstellar grains. The results from PUMA/PIA and from analyzing IDPs show that much can be learned from the dust composition at the submicron level. From CRAF, dust samples can be analyzed by a variety of techniques including x-ray fluorescence, gas chromatography, secondary ion mass spectroscopy, and electron microscopy (see Chapter 5). These measurements can address the questions: Under what conditions did the mineral dust grains form? Have they been subjected to thermal and aqueous alteration? How do isotope ratios such as D/H and C_{12}/C_{13} compare with terrestrial vs. the ISM? What is the composition of the organic material in grains? By sampling the dust coma at different times, the heterogeneity of the nucleus can be investigated.

Earth-based remote sensing, however, will remain the bridge between the target comet, other new and evolved comets and the interstellar medium.