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APPROACHING THE INTERSTELLAR GRAIN ORGANIC REFRACTORY COMPONENT

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ABSTRACT

Infrared spectra have been obtained for laboratory residues of photoprocessed low-temperature ices which have been exposed to long-term solar ultraviolet radiation on the *EURECA* satellite. This is an analog to the ultraviolet processing of interstellar dust mantles in diffuse clouds after leaving molecular clouds. The 3.4 μm absorption features of these organic materials match those of the diffuse cloud interstellar dust better than any other previously suggested analog to the interstellar organics.

Subject headings: dust, extinction — infrared: ISM: lines and bands — ISM: individual (GC IRS 6E)

1. INTRODUCTION

The presence of a carbonaceous component in interstellar dust that exhibits the 3.4 μm features characteristic of CH stretches in CH_2 and CH_3 groups is now well established (Butchart et al. 1986; Sandford et al. 1991). Although many carbon compounds exhibit features similar to the interstellar one, a recent survey (Pendleton et al. 1994) shows that no previously produced laboratory analog candidate absorbs exactly like the interstellar dust. We report here on a simulation of cyclic interstellar dust evolution which provides a remarkably close match to the observed 3.4 μm absorption. The cyclic ultraviolet processing of interstellar dust which occurs sequentially in molecular and diffuse clouds is accomplished in two stages. In the first stage we produce laboratory residues, which result from ultraviolet photoprocessing of analog grain mantles that start out as simple ices (H_2O, CO, CH_4, NH_3, etc.) at 10 K (Greenberg 1978). These “first generation” organics are then exposed to long-term ultraviolet radiation. The reason for this is that in the lifetime of an interstellar grain the organic grain mantles are further subjected to very substantial ultraviolet irradiation, which inevitably leads to chemical and physical modifications of these first generation organics as simulated in the laboratory (Jenniskens et al. 1993). The ERA (Exobiology Radiation Assembly) platform on the *EURECA* satellite (Innocenti & Mesland 1995) offered the opportunity to expose our laboratory samples to very long-term irradiation by the Sun. The Sun may not be an ideal representation of the interstellar radiation field, but it provided a significant advantage over any laboratory experiments not only in the long-term irradiation but also in that it permitted simultaneous irradiation of many different samples.

2. BACKGROUND TO THE EXPERIMENTS: INTERSTELLAR GRAIN MANTLE EVOLUTION

Laboratory ultraviolet processing experiments already under way in 1970 (Greenberg et al. 1972) led to the prediction by Greenberg (1973) that the absence of an H_2O ice band in the line of sight to VI Cygni 12 was a clue to the presence of organic material in the diffuse cloud medium. The expected 3.4 μm feature was first observed in the Galactic center toward Sgr A W (Willner et al. 1979) and in GC IRS 7 by Wickramasinghe & Allen (1980), but it took 15 years before it was seen toward the former object (Adamson, Whittet, & Duley 1990), where it was originally predicted. The cyclic evolutionary model (Greenberg 1982, 1986) for interstellar dust starts with small silicate particles emitted by cool evolved stars which serve as nuclei for accretion of volatile ices which are partially converted to complex organic refractories by ultraviolet photoprocessing during the time spent in molecular clouds. The second part of the cycle occurs when the grains are ejected (following star formation) into the low-density diffuse clouds, where the volatiles are evaporated or eroded away by various destruction processes (supernova shocks, etc.) but where only partial erosion of the organic refractory mantle occurs (Draine & Salpeter 1979; Greenberg 1982). The cycle is repeated when the grains reenter a molecular cloud; i.e., an outer mantle of ices is accreted on the remaining organic refractory mantle and photoprocessing replenishes the organic refractory lost in the diffuse cloud phase, etc. The critical point to note here is that while in the diffuse cloud the organic mantle is subjected to a relatively intense bombardment of ultraviolet photons that should partially remove H, O, and N from the organic molecules (Jenniskens et al. 1993), thus changing their chemical composition and associated infrared absorption features relative to those created in the first molecular cloud phase. For an average grain the cycle is repeated many times because while each complete cycle takes about 10^8 yr, the mean lifetime for an interstellar grain is about 5×10^9 yr before it is consumed by star formation (Greenberg 1984).

3. LABORATORY ANALOG PRODUCTION OF ORGANIC RESIDUES AND SPACE ULTRAVIOLET PROCESSING

A number of samples of “first generation” organics which have been called “yellow stuff” were produced by ultraviolet irradiation and subsequent warm-up of a variety of ice mixtures consisting of H_2O, CO, NH_3, CH_4, CH_3OH, and C_2H_2 deposited on small blocks of aluminum at 10 K. The gas deposition rate was $\sim 10^{16}$ molecules s^{-1} with simultaneous irradiaton of 10^{15} photons s^{-1} from a vacuum ultraviolet lamp for times of 22–68 hr. See Mendoza-Gómez (1992) for details of the procedure. The blocks containing the yellow residues were mounted in the ERA sample carrier in a glove box with a slight overpressure N_2 atmosphere. The sealed sample carrier was carried into space on the ERA platform of the *EURECA* satellite, which remained at an altitude of 500 km for about 11 months during which all the samples were subjected to irradiation by the full solar spectrum for a total of 4 months (Innocenti & Mesland 1995). Before returning to the

TABLE 1

GAS MIXTURES

	INITIAL MIXTURE[a]				
SAMPLE	H_2O	CO	NH_3	CH	LIT[b]
A...........	5	2	2	2(CH_4)	68
B...........	5	2	2	1(C_2H_2)	22
C...........	5	5	1	1(CH_3OH)	46

NOTES.—Gas mixtures deposited at 10 K, photoprocessed, and brought to room temperature in the laboratory to create residues which were irradiated by the Sun on the ERA platform of the *EURECA* satellite.

[a] The numbers are ratios of ice mixtures.

[b] Laboratory irradiation time (hr).

Earth, the sample carrier was sealed in an argon atmosphere and returned to Leiden. In Table 1 are shown three of the 16 interstellar analog residue samples which span the full variety of mixtures taken into space. Although molecular abundances in grain mantles served as a guide, the initial abundances were actually selected to represent the depleted elemental ratios characteristic of diffuse clouds.

The ultraviolet flux at 1 AU from the Sun at energies $h\nu \geq 4.5$ eV ($\lambda \leq 3000$ Å) on the samples was $\sim 3 \times 10^{15}\ h\nu\ s^{-1}\ cm^{-2}$. The total fluence was $3.1 \times 10^{22}\ h\nu\ cm^{-2}$, which is equivalent to the photon dose received in about 10^7 yr in the diffuse cloud medium in interstellar space. The mean penetration depth of the ultraviolet in the organic residue is about 0.1 μm, which is comparable with the mean sample thickness (Mendoza-Gómez 1992; Jenniskens et al. 1993). Because of the unevenness of the residue thickness some but not all of the material is fully irradiated. However, a comparison of the infrared spectra obtained at different positions does not indicate any gross dissimilarities. Except for the somewhat lower energy range of the ultraviolet photons (for $E \geq 5$ eV the effective interstellar time is about 10^6 yr) this should produce effects which approach those on an average interstellar grain after leaving the shelter of a molecular cloud and before reentering another molecular cloud; i.e., the solar ultraviolet irradiated samples are expected to resemble the interstellar organic mantles which have undergone at least one complete evolutionary cycle.

4. GROSS CHANGES IN THE ORGANIC REFRACTORIES

The immediately obvious effect of the solar irradiation of the organic refractories was the change in color from yellow to brown. Other than that, the samples appeared as before launch; i.e., they showed the same morphological structure. The color change indicates an increase in the carbonization and associated greater visual absorptivity, which results from photodissociation and depletion of the oxygen, nitrogen, and hydrogen from the samples. A coronene sample which was sent up as a control retained its original yellow color and its infrared spectrum (see next section) was unchanged. Coronene is an example of polycyclic aromatic hydrocarbons which are notoriously resistant to ultraviolet irradiation (Mendoza-Gómez, de Groot, & Greenberg 1995).

5. INFRARED SPECTRA OF ERA SAMPLE RETURN

Infrared spectra of the residue samples were obtained by a Bio-Rad FTS-40A spectrometer equipped with a diffuse reflection accessory while maintaining the entire system in a nitrogen atmosphere. The diffuse reflection technique was necessary because of the highly inhomogeneous nature of the samples, which consist of patches of material ranging in size from less than 1 μm up to almost 1 mm (Jenniskens et al. 1993; Mendoza-Gómez 1992). The penetration depth of the infrared radiation into the samples is of the order of a few microns, which is fully adequate. The position and width of the features produced by the diffuse reflection technique coincide with those obtained by measuring in transmittance, which was checked with a first generation residue. The position and width of the features were identical within ≤0.1% and ≤5%, respectively, for the two techniques. In all cases the ERA spectra were taken at a number of different areas of the sample including "blank" spots for control of a possible contamination. The amount of material on these blank spots as indicated by the very low strength of their spectra in comparison with the spectra in the rest of the samples proved that contamination was less than 1%. This was also confirmed by the lack of organic refractory features in the coronene sample.

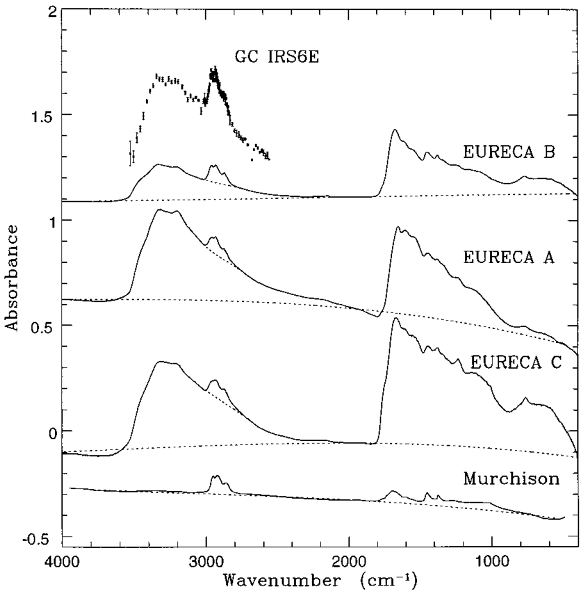

FIG. 1.—Comparison of the absorbance of the Galactic center GC IRS 6E (Pendleton et al. 1994) with three solar irradiated residues on the *EURECA* satellite ERA platform. *EURECA* A, B, and C are as in Table 1. The Murchison acid residue is from Cronin & Pizzarello (1990). All spectra except the Galactic center are normalized to equal 3.4 μm strengths.

The spectra of samples A, B, and C in Table 1 are shown in Figure 1 for comparison with the near-infrared spectrum of the Galactic center (IRS 6E) and the acid dissolved residue of the Murchison meteorite (Cronin & Pizzarello 1990). The two regions of interest in addition to that at 3.4 μm (3200 cm^{-1}) are at around 3 μm and longward of $\lambda \sim 5\ \mu m$ ($\lambda^{-1} \sim 1900\ cm^{-1}$). The first corresponds to the OH stretch as in alcohols and carboxylic acid groups (Briggs et al. 1992), the last to various C=C, C=O, C—OH, C≡N, C—NH_2, etc., stretches, to CH, OH, and NH_2 deformations, and, at the longest wavelengths, and to H wagging in the organic molecules. We note that all samples reproduce the general features of IRS 6E quite well. It is clear that the Murchison spectrum is relatively deficient in the absorptions at 3 μm as well as those beyond 1900 cm^{-1}. The 3 μm feature in the interstellar dust is not always observed and at least part of what is observed has been attributed to ice mantles in molecular cloud dust along the line of sight (Schutte & Greenberg 1988). When it is fully absent

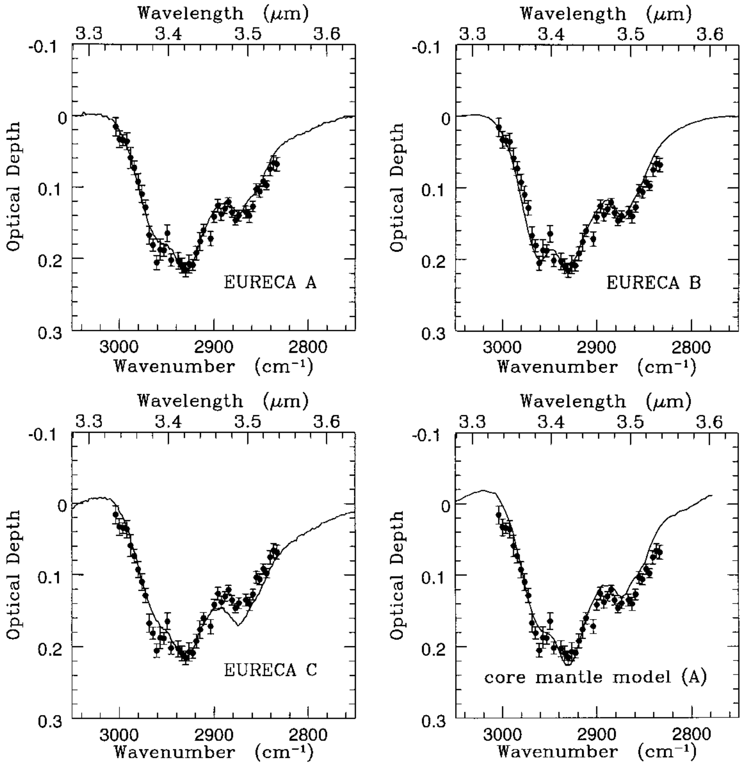

FIG. 2.—Comparison of the 3.4 μm spectra of *EURECA* A, B, and C with the Galactic center spectrum of IRS 6E (*dots*). The lower right is a calculated absorption by a prolate (3:1) spheroidal silicate core–organic refractory mantle particle, where the optical constants at 3.4 μm are derived from the *EURECA* data (Greenberg & Li 1995).

this indicates reduction in the oxygen and probably nitrogen and hydrogen content, which would result from greater photoprocessing. One should then observe, as well, a reduction in the features beyond 6 μm.

6. THE 3.4 MICRON FEATURE

Following Pendleton et al. (1994) we have selected the IRS 6E source as the best observed interstellar example of the 3.4 μm feature with the highest resolution. In Figure 2 we present comparisons with the three individual samples. The correspondence between the peak frequencies of the three subfeatures of the ERA analog samples at 2960, 2925, and 2870 cm^{-1} corresponding to the symmetric C—H stretches in CH_3 and CH_2 and the asymmetric C—H stretch in aliphatics with those of the interstellar organics is remarkable in all cases when compared with all the previous interstellar analogs: e.g., hydrogenated amorphous carbon (HAC), quenched carbonaceous condensate (QCC), and photolyzed ice residues shown in Figure 3. Relative to the latter (Fig. 3*a*) we see how the ultraviolet (*EURECA*) irradiation of the residues in Table 1 provides a significant improvement over the unirradiated one. We note that with the exception of ion irradiated CH_4 (which is not a realistic analog to interstellar chemistry) the closest correspondence to the IRS 6E spectrum is given by the Murchison meteorite and that, even for this, the peak absorptions are shifted to longer wavelengths (see Fig. 3*f*). No matter what, the CH stretch positions in the *EURECA* sample are in all cases the best to date of the interstellar analogs. The fact that irradiated methane has the same features implies that it may be a good structural analog to the *EURECA* (and interstellar) molecules even though it may not be a good chemical analog. Figure 2 shows that using the derived optical constants for the 3.4 μm ERA organics (Greenberg & Li 1995) as mantles on elongated silicate cores to obtain particle cross sections does not distort the position and strength of the features with respect to the material absorption.

7. CONCLUDING REMARKS

The evolution of interstellar dust organics resulting from extensive exposure in diffuse clouds to ultraviolet irradiation of organic mantles produced in interstellar clouds is well simulated by the long-term ultraviolet irradiation of laboratory organic residues in the solar environment. The 3.4 μm infrared feature of the solar irradiated laboratory organic residues is much closer to that of diffuse cloud interstellar dust than that of a wide variety of other suggested sources of organics. The precise match in position to the CH_2 and CH_3 absorptions in the interstellar 3.4 μm feature suggests that the interstellar processes of formation and irradiation of organic refractories that we have postulated are the most likely way to achieve an understanding of the origins of the organic grain mantles on interstellar grains. The fact that the final 3.4 μm spectra are quite uniform for the three representative samples suggests that the structural characteristic of highly processed organics are only weakly dependent on the initial composition. Future experiments should explore further the effects of initial composition, the ultraviolet spectral distribution, and the irradiation dose. The success of these *EURECA* experimental results confirms the importance of chemical analysis of laboratory produced organics (Briggs et al. 1992) to obtain a better understanding of the material composition of comets. This is additionally important if comets are, indeed, primordial ag-

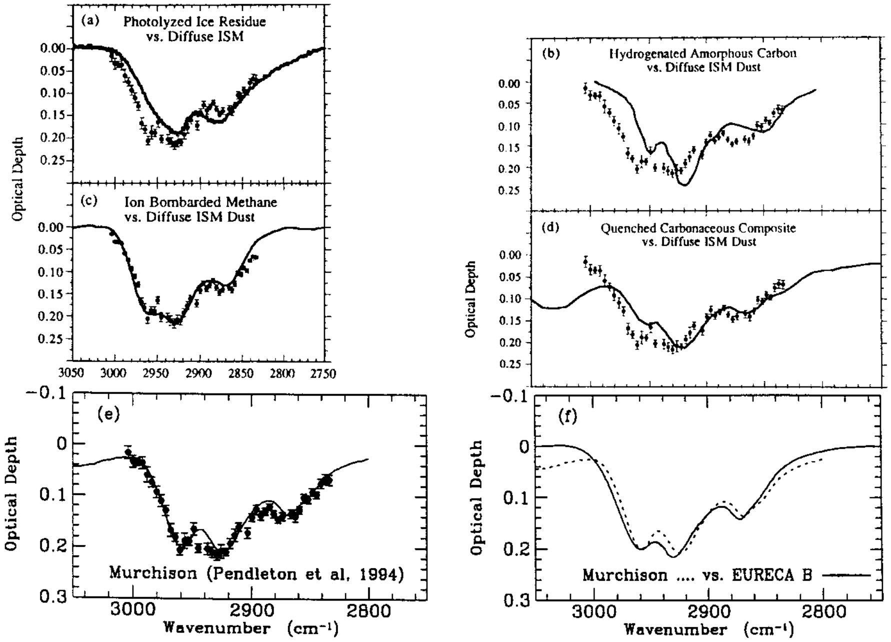

FIG. 3.—Comparison of the Galactic center spectrum IRS 6E (*points*) with: (*a*) the spectrum of a photolyzed ice residue of a 10 K H_2O:CH_3OH : NH_3 :CO = 10 : 5 : 1 : 1 interstellar ice analog followed by warm-up to 200 K (Allamandola et al. 1988); (*b*) the spectrum of hydrogenated amorphous carbon (Borghesi et al. 1987); (*c*) ion bombarded methane (from Pendleton et al. 1994, as provided by Strazzulla); (*d*) the spectrum of quenched carbonaceous condensate (Sakata & Wada 1989); (*e*) the spectrum of organic Murchison meteorite acid residue (Cronin & Pizzarello 1990); (*f*) Comparison of *EURECA* B with the Murchison organic.

gregates of interstellar dust and comets were the bearers of the prebiotic molecules on the earth (Greenberg et al. 1994).

Based on the ERA sample spectra there is incentive to more thoroughly investigate with future satellites (*ISO*) the $\lambda \geq 5$ μm spectral region as related to the 3 μm spectra of diffuse cloud dust because it gives information on the oxygen and nitrogen containing groups in the organics and provides an additional test of the interstellar origins of complex organics.

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