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LABORATORY AND THEORETICAL SIMULATION OF 3.4 μm SPECTRA OF HYDROCARBONS IN INTERSTELLAR SOURCES

W. W. Duley,[1] V. I. Grishko,[1,2] J. Kenel,[1] G. Lee-Dadswell,[1,3] and A. Scott[1,4]

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ABSTRACT

The presence of hydrocarbons in interstellar clouds and in some emission objects can be inferred from the appearance of spectral features near 3.4 μm that are characteristic of CH_2 and CH_3 groups. While the 3.4 μm band attributable to these hydrocarbons has been found to be similar in sources such as GC IRS 6E and CRL 618 (Chiar et al. 1998), there are significant variations in the relative amplitude of individual components in other sources such as NGC 7538 IRS9 (Allamandola et al. 1992). This indicates that the composition of these hydrocarbons may depend on ambient conditions in interstellar clouds. To investigate this possibility, we have analyzed observational IR spectra of GC IRS 6E, CRL 618, IRAS 05341+0852, and NGC 7538 IRS9 to extract spectral bands associated with CH_2 and CH_3 groups in each of these sources. These components are compared with the features that appear in laboratory absorption and emission spectra of hydrogenated amorphous carbon. It is found that significant differences exist in the CH_2/CH_3 ratio in individual sources. In particular, we find that CH_3 groups are suppressed in dense cloud dust but that CH_2 groups are still abundant. The properties of individual spectral components within the 3.4 μm interstellar band are discussed and compared to laboratory and theoretical data on IR spectra of certain hydrocarbon molecules, as well as that of hydrogenated amorphous carbon. Simulation of 3.4 μm spectra using a random covalent network model is shown to provide a useful way to extract structural and bonding information for specific chemical groups in interstellar material.

Subject headings: astrochemistry — infrared: ISM — ISM: lines and bands — ISM: molecules — methods: laboratory

1. INTRODUCTION

Infrared (IR) absorption spectroscopy of interstellar clouds and circumstellar sources has revealed the presence of saturated and unsaturated hydrocarbon molecules and dust (Chiar et al. 2000; Pendleton & Allamandola 2002; Pendleton et al. 1994). Similar absorption spectra are also seen in Seyfert and ultraluminous IR galaxies (Mason et al. 2004). The intensity of spectral features produced by these materials indicates that at least 3%–4% of available carbon occurs as CH_2 and CH_3 groups in hydrocarbon compounds (Sandford et al. 1995). In addition, over 5% of carbon is bound in aromatic hydrocarbons (Pendleton et al. 1994). While these limits are generally applicable on average, it is evident that there must be considerable variation in both the composition and distribution of hydrocarbons in specific sources. For example, the aliphatic hydrocarbons that are so ubiquitous in the diffuse interstellar medium (DISM) may not be present in dark clouds associated with protostars (Allamandola et al. 1992), while a further CH component observed in these objects is not apparently abundant in the DISM.

It is also found that the relative intensities of the 3.4 μm bands of CH_2 and CH_3 groups seen in emission spectra of some protoplanetary nebulae can be quite different from those observed in absorption in the DISM (Joblin et al. 1996). Observations also show that the relative strength of these features, as well as that of the 3.28 μm aromatic CH band, can vary dramatically within an emission source (Goto et al. 2003). Other protoplanetary objects show absorption at 3.4 μm that is remarkably similar to that predicted from the absorption spectrum of cold DISM hydrocarbon dust. (Chiar et al.1998). However, the narrow 3.28 μm feature detected in many interstellar emission sources seems to be replaced by a broader weak absorption band in the DISM spectrum (Chiar et al. 2002) and a broad absorption band at 3.25 μm in IR spectra of certain dense clouds (Brooke et al. 1999). The stretching vibration of C=C bonds, evident in emission at 6.2–6.3 μm in interstellar sources (Allamandola et al. 1989; van Diedenhoven et al. 2004) can be seen in absorption near this wavelength in carbon-rich, late-type Wolf-Rayet stars and in the DISM (Schutte et al. 1998; Chiar & Tielens 2001).

These observations indicate that the hydrocarbon component in the interstellar medium could be subject to modification by chemical reactions with hydrogen and other gaseous species and by photochemical processing in response to changes in the ambient radiation field (Duley 2000; Mennella et al. 2001; Munoz Caro et al. 2001). Under these conditions, many reactions lead to the conversion of C–C to C=C bonds, which would diminish the concentration of aliphatic hydrocarbon groups while increasing that of olefinic components and enhancing absorption in the 6.2 μm band (Duley 2000). In other reaction scenarios, the calculated effects of hydrogenation and photodissociation reactions on the composition of polycyclic aromatic hydrocarbons (PAHs) lead to a prediction of increased saturation and to the production of "super-hydrogenated" PAHs (Schutte et al. 1993; Joblin et al. 1996). More generally, theory suggests that small PAHs (containing less than $\approx$25–30 C atoms) will be dehydrogenated in the DISM (Allain et al. 1996a, 1996b; Joblin et al. 1996; LePage et al. 2001, 2003). The relative abundance of side-groups such as CH_2 and CH_3 on PAH is also found to be

[1] Physics Department, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L 3G1, Canada; wwduley@uwaterloo.ca.
[2] Current address: Nanolytics, Inc., 5905 Triangle Drive, Raleigh, NC 27617.
[3] Current address: Physics Department, University of Guelph, 158-50 Stone Road East, Guelph, ON N1G 2W1, Canada.
[4] Current address: EMS Technologies, 1725 Woodward Drive, Ottawa, ON K2C 0P9, Canada.

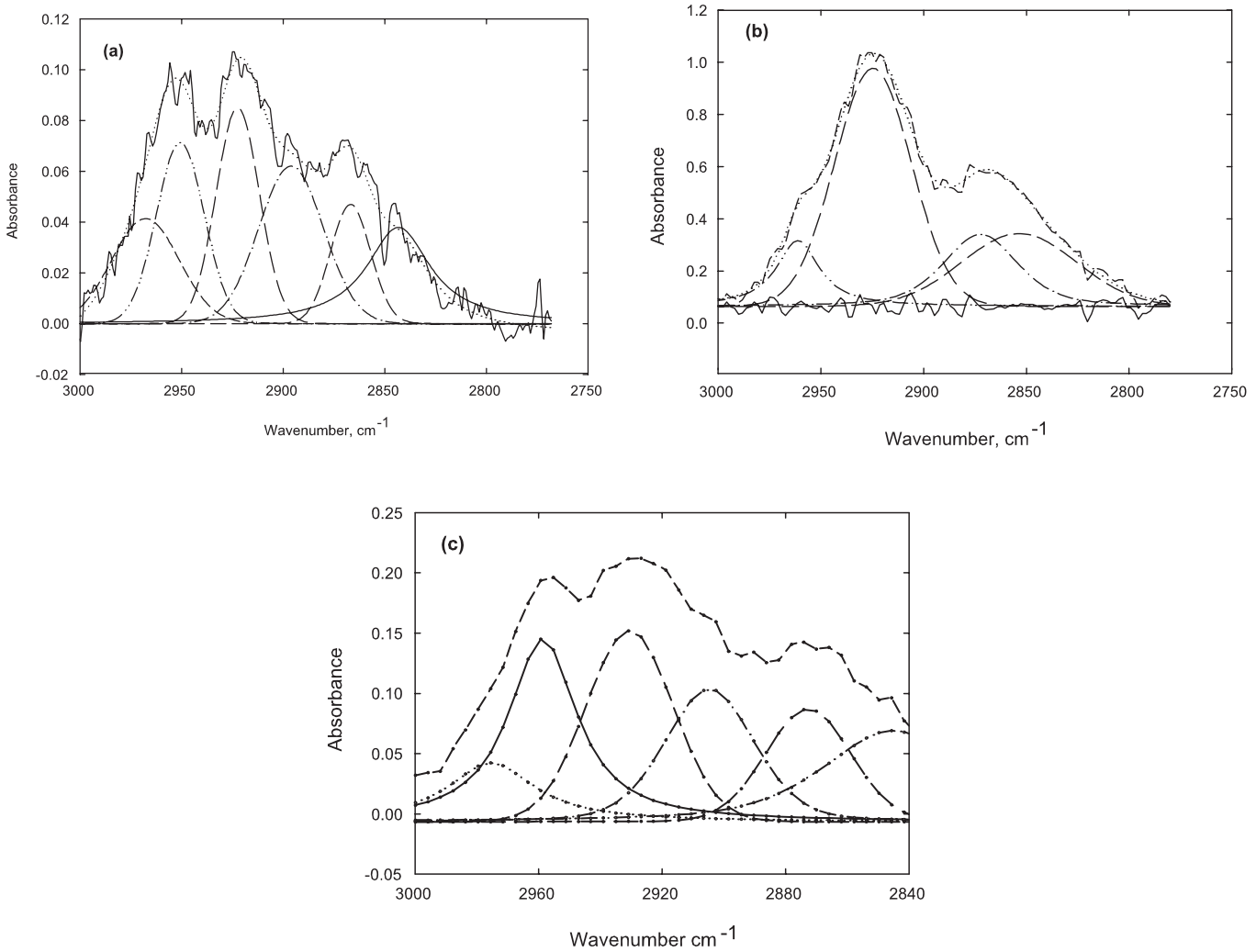


FIG. 1.—(*a*) Components in the 3.4 μm spectrum of CRL 618 (Chiar et al. 1998). (*b*) Components in the 3.4 μm emission spectrum of IRAS 05341+0852 (Geballe & van der Veen 1990). (*c*) Components in the 3.4 μm spectrum of GC IRS 6E (Pendleton & Allamandola 2002).

sensitive to radiative and chemical processing (Joblin et al. 1996; Jochims et al. 1999; Munoz Caro et al. 2001; Mennella et al. 2001; Le Page et al. 2001, 2003).

The primary effect of chemical processing of carbonaceous material in interstellar clouds is then expected to be reflected in infrared absorption and emission spectra, primarily through changes in the relative amplitude and the wavelength of features arising from CH, CH_2, and CH_3 chemical groups. These changes could be subtle, for example, a shift of several cm^{-1} in the energy of a specific feature or a slight variation in profile. In any case, the recognition and analysis of such effects will yield further insight into the composition of interstellar hydrocarbons and their sensitivity to ambient conditions.

Some of these matters have already been discussed in general terms (Duley 2000), but additional laboratory data (Grishko & Duley 2000, 2002; Goto et al. 2003; Duley & Grishko 2001; Grishko et al. 2001; Dartois et al. 2005) are now available. These data allow some questions addressed in earlier studies (Dadswell & Duley 1997; Duley 2000) to be examined in more detail. In particular, the role of CH_3 groups as indicators of the composition and state of carbonaceous material in interstellar sources are investigated. We also find that further understanding of the nature of interstellar hydrocarbon materials can be obtained from ab initio simulations of the 3.4 μm feature.

2. 3.4 μm SPECTRAL COMPONENTS

Representative 3.4 μm spectra for several interstellar sources are shown in Figure 1. To facilitate curve fitting, the observational data have been converted to line form. Deconvolved spectral components are indicated in these figures, and line-fit parameters are summarized in Table 1. All spectra are found to contain at least three individual components, two of which (near 2960 and 2920 cm^{-1}, 3.38 and 3.42 μm) can be clearly identified with the asymmetric stretching modes of CH_3 and CH_2 groups, respectively. The third component, near 2860 cm^{-1} (3.50 μm), can be resolved into components at $\approx$2870 and $\approx$2850 cm^{-1} (3.48 and 3.51 μm) that may correspond to the symmetric stretching modes of CH_3 and CH_2 groups, respectively (see, however, the discussion concerning the 3.50 μm feature in Sandford et al. 1991). A further broad spectral component is present at $\approx$2900 cm^{-1} (3.45 μm) in the spectrum of GC IRS 6E and CRL 618 but does not appear in the spectrum of the protoplanetary nebula IRAS 05341+0852. This feature can be identified as the first overtone of the deformation modes of $CH_{2,3}$ groups at $\approx$1460 cm^{-1} (Szymanski 1964).

Similarities between the 3.4 μm absorption spectrum of the DISM source GC IRS 6E and that of the protoplanetary nebula CRL 618 have been previously noted by Chiar et al. (1998). A

TABLE 1
DECONVOLUTION OF SPECTRA FOR REGION 3000–2800 cm^{-1}

Wavenumber (cm^{-1})	Wavelength (μm)	Peak Height (arbitrary)	Peak Width (cm^{-1})	Peak Area (% of total)
		CRL 618		
2968	3.37	0.413	39	14.6
2951	3.39	0.713	28	17.9
2922	3.42	0.851	25	19.3
2896	3.45	0.620	38	21.1
2867	3.49	0.469	23	9.9
2843	3.52	0.379	38	17.2
		IRAS 05341+0852		
2961	3.38	0.253	25	10.2
2925	3.42	0.913	44	50.1
2872	3.48	0.276	43	16.8
2854	3.50	0.279	65	22.9
		GC IRS 6E		
2975	3.36	0.049	34	8.5
2959	3.38	0.152	27	22.6
2931	3.41	0.159	33	23.0
2905	3.44	0.110	34	17.5
2873	3.48	0.094	32	13.4
2845	3.51	0.076	54	15.0
		HAC (300 K) Absorption		
3035	3.29	0.045	102	8.6
2961	3.38	0.139	34	8.9
2923	3.42	0.287	53	39.1
2886	3.46	0.152	121	34.6
2872	3.48	0.026	38	2.0
2851	3.51	0.082	44	6.8
		HAC (600 K) Emission		
3073	3.25	0.007	139	16.8
3035	3.29	0.008	53	6.9
2959	3.38	0.011	24	5.2
2920	3.42	0.023	30	16.4
2899	3.45	0.016	155	49.2
2850	3.51	0.013	18	5.5

NOTE.—GL618 data from Chiar et al. (1998), IRAS 05341+0852 data from Geballe & van der Veen (1990), and GC IRS 6E data from Pendleton & Allamandola (2002).

spectrum virtually identical to that of GC IRS 6E has also recently been reported for the Seyfert galaxy NGC 1068 (Mason et al. 2004), suggesting that similar types of hydrocarbon material are found in all three sources. Deconvolution of the 3.4 μm spectrum of GC IRS 6E and CRL 618 supports this conclusion, since the major components attributable to CH_2 and CH_3 groups appear with almost the same amplitude in both sources. The only difference is that the amplitude of the CH_3 components may be somewhat ($\approx$25%) weaker in CRL 618 than in the GC IRS 6E source, although this difference may be attributable to the mediocre quality of the DISM spectrum. Small variations in the relative amplitude of 3.4 μm components have also been reported in other objects (Mason et al. 2004).

The 3.4 μm spectrum of IRAS 05341+0852 is, however, quite different from those of the other two sources. This spectrum shows strong emission in the CH_2 components at 2925 and 2854 cm^{-1} (3.42 and 3.51 μm) and little emission from CH_3 groups. In addition, components in IRAS 05341+0852 are $\approx$50% wider than those in the other two objects. This implies that there may be a real difference in the composition of hydrocarbon material in IRAS 05341+0852 compared to that in CRL 618, GC IRS 6E, and NGC 1068.

Absorption and emission spectra of hydrogenated amorphous carbon (HAC) have been reported by several groups (Scott & Duley 1996; Scott & Jahani 1997; Schnaiter et al. 1998; Mennella et al. 1999; Grishko & Duley 2000; Duley & Grishko 2001; Dartois et al. 2005). Absorption and emission components for HAC derived from our laboratory data are given in Table 1. A general correspondence between the central wavelengths of the primary spectral components in HAC and those of the astronomical sources is apparent. In particular, the two major peaks near 2960 and 2920 cm^{-1} (3.38 and 3.42 μm) assigned to the asymmetric stretching modes of $CH_{3,2}$ groups are reproduced in both astronomical and laboratory spectra. A broad component observed at $\approx$2890 cm^{-1} (3.46 μm) in the absorption spectrum and at $\approx$2900 cm^{-1} (3.45 μm) in emission from HAC (Table 1) is not

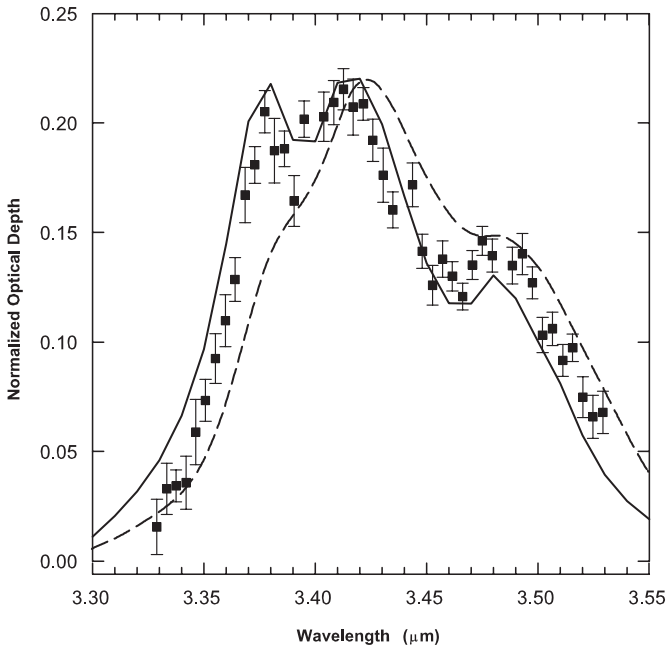


FIG. 2.—The 3.4 μm absorption band in GC IRS 6E (*squares*) compared to that of an HAC sample deposited at 77 K (*solid line*) and one that was deposited at 300 K and heated to 750 K (*dashed line*).

reproduced in the astronomical spectra, although a narrower feature appears at this energy in spectra of IRS 6E and CRL 618. This difference in width may be due, in part, to difficulties in determining background continuum in both laboratory and astronomical spectra in this region.

3. SPECTRAL FITS AND SIMULATION

Fits to the observed spectra of IRS 6E, CRL 618, and IRAS 05341+0852 with laboratory data are given in Figures 2–4. The fits for the sources IRS 6E and CRL 618 were obtained using absorption spectra of HAC, while that for the emission source is from laboratory emission spectra. In general, laboratory spectra provide a satisfactory fit to observational data and reproduce the relative amplitude of individual components. This is especially true for the IRS 6E absorption band, where the observational spectrum is well matched by an absorption spectrum of an HAC

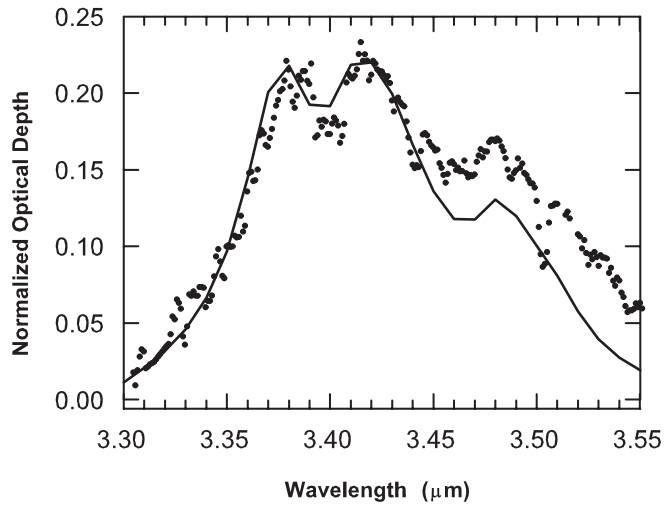


FIG. 3.—The 3.4 μm absorption band in CRL 618 (*lines*; Chiar et al. 1998) compared to that of HAC deposited at 77 K (*filled diamonds*).

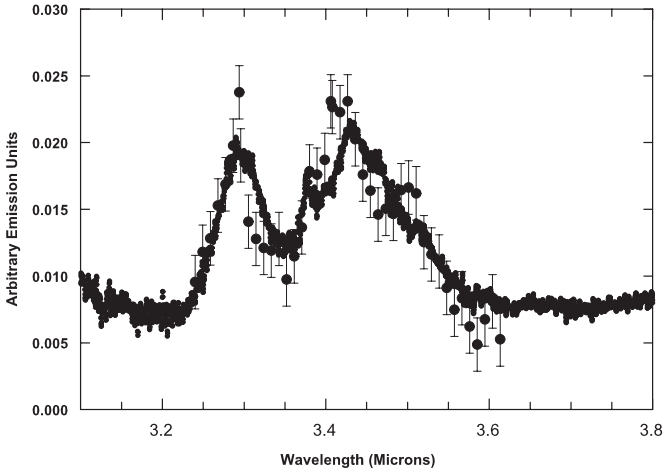


FIG. 4.—Emission spectrum of IRAS 05341+0852 (*circles*; Geballe & van der Veen 1990) compared to emission from HAC. In the HAC spectrum, the 3.4 μm peak arises from dust deposited at 77 K and recorded in emission at 650 K, while the 3.3 μm feature is from dust deposited at 300 K and recorded in emission at 800 K.

sample that was deposited at 77 K. Significantly, the absorption spectrum of an HAC sample previously heated to 750 K but recorded at 300 K does not fit the IRS 6E data. The absorption spectra of IRS 6E and CRL 618, which are nominally the same (Chiar et al. 1998), reveal some small differences when compared to the 77 K HAC spectrum. Specifically, the secondary CH_2 component at 3.48 μm is shifted ≈ -0.1 μm ($+8$ cm^{-1}) from the corresponding peak in the laboratory spectrum. In addition, this CH_2 component appears more intense relative to the other $CH_{2,3}$ features in the spectrum of CRL 618 than in the laboratory spectrum. These differences might, in part, be attributable to the broadness of the individual peaks and the fact that these components are not well resolved in either the laboratory or observational spectra. Alternatively, this shift could arise because of a difference in composition of the hydrocarbons in CRL 618 and in IRS 6E. This difference in amplitude could arise from uncertainties in assigning the background continuum in the CRL 618 spectrum (Chiar et al. 1998).

The spectrum of IRAS 05341+0852 shows an additional emission band attributable to aromatic CH groups at 3.29 μm, and so a fit to the combined 3.3/3.4 μm spectrum is found to require two dust components (Scott et al. 1997). Comparison between the observational spectrum and this fit shows that the primary CH_2 emission band in HAC is shifted by $\approx +0.02$ μm (17 cm^{-1}) to longer wavelengths from the corresponding feature in the observational spectrum. In addition, the amplitude of the secondary CH_2 component at 3.51 μm in IRAS 05341+0852 is greater than that in the laboratory spectrum.

4. DISCUSSION

The comparison between laboratory and observational spectra shown in Figures 2–4 indicates that the 3.4 μm band in these astronomical sources is well represented by that of HAC. This implies that the average composition of interstellar hydrocarbons is similar to that found in these laboratory condensates. With this information, it is possible to infer that the hydrocarbon material observed in absorption in many interstellar and extragalactic sources has a significant concentration of CH_3 groups (relative to CH_2 groups) and may never have been exposed to high temperatures (>300 K) after hydrogenation. This is an important conclusion, since it suggests that the interstellar hydrocarbons

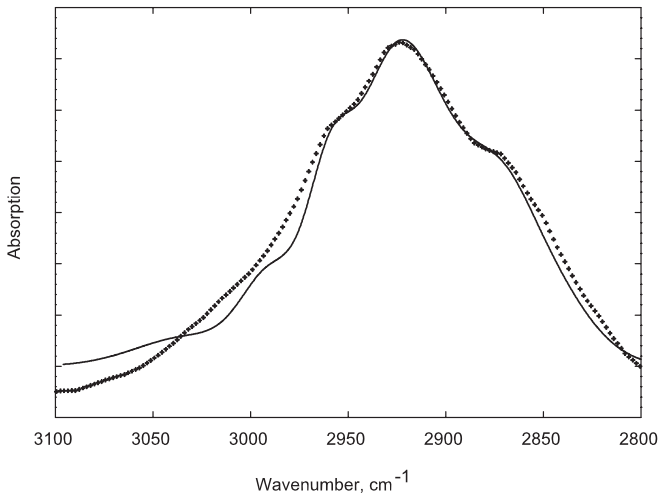


FIG. 5.—Absorption spectrum of a HAC sample deposited at 300 K (*plus signs*). Simulation using the RCN formalism for a material having H/C = 0.33 and 2.5% of carbon contained in sixfold aromatic rings (*solid line*).

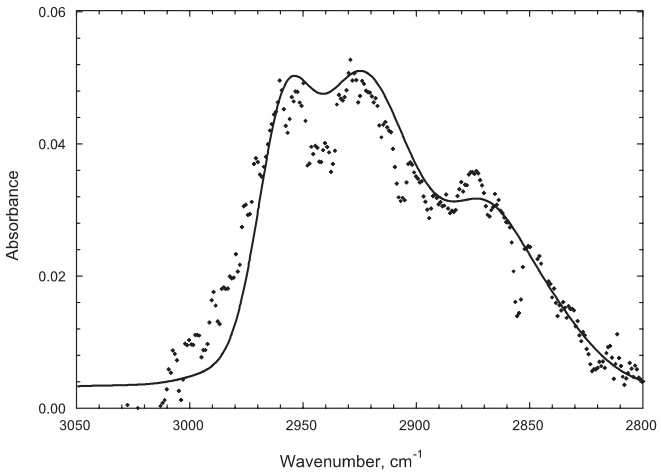


FIG. 6.—RCN simulation of the 3.4 μm band in CRL 618. The simulated material has H/C = 0.42 and 2% of carbon in sixfold aromatic rings.

responsible for the 3.4 μm absorption band could have been formed in situ under relatively low temperature conditions. Alternatively, if formed in a high-temperature environment such as the outflow from an evolved carbon star, they appear to have been modified through further hydrogenation in the interstellar medium (Mennella et al. 2001; Pendleton & Allamandola 2002). The CH_2/CH_3 ratio derived from these observations will, however, depend on the assumed bonding environment for these species (see below).

The effect of hydrogenation on the 3.4 μm band can be investigated theoretically using the random covalent network (RCN) formalism (Duley 1994; Dadswell & Duley 1997). This method essentially creates a network of sp^2 and sp^3-bonded carbon from the properties of individual bonds. The overall RCN network is optimized to increase stability and has been found to yield a good representation of the properties of HAC (Angus & Jansen 1988; Jones 1990). A simulation of the 300 K 3.4 μm absorption band of HAC from the RCN model is shown in Figure 5. This fit assumes that, on average, the sample contains 0.33 H atom/C atom, a value that is consistent with laboratory measurements of the hydrogen concentration in HAC (Angus & Jansen 1988).

The corresponding RCN simulation of the absorption spectrum of CRL 618 is shown in Figure 6 and has 0.42 H atom/C atom, approximately 30% higher than that existing in HAC deposited at 300 K. In addition, the modeled material contains only 2% of sp^2 carbon in the form of sixfold aromatic rings. This confirms that the composition of the dust in CRL 618 as well as that in GC IRS 6E is primarily nonaromatic, with a high concentration of saturated hydrocarbon components. The conversion of this material into a more aromatic composition would require heating or exposure to an enhanced UV flux. Both processes result in a decrease in hydrogenation and the creation of C=C bonds (Duley 2000; Mennella et al. 2001).

It has been reported that CH_2 and CH_3 groups in hydrocarbons appear to be suppressed in dark protostellar clouds, at least as indicated from IR spectra in the 3.4 μm region (Allamandola et al. 1992). This conclusion was reached after an absorption background attributed to methanol (CH_3OH) ice was subtracted from the observed spectra. The absorption spectrum of NGC 7538 IRS9 showing the residual hydrocarbon band (Allamandola et al. 1992) is reproduced in Figure 7 and is compared with an absorption spectrum of HAC deposited at 300 K. This comparison shows that, while CH_3 groups are indeed underabundant in NGC 7538 IRS9, the spectrum still shows clear evidence for the presence of CH_2 groups at 2920 cm^{-1} (3.42 μm). This can be seen by the appearance of shoulders in the observational spectrum corresponding to absorption in the CH_2 bands of HAC at 2920 and 2860 cm^{-1} (3.42 and 3.50 μm). The most intense spectral component in the residual spectrum of NGC 7538 IRS9 is, however, that peaking at 2880 cm^{-1} (3.47 μm). Since the amplitude of this feature has been found to correlate with that of the ice band (Brooke et al. 1999), it seems likely that the carrier of this feature is a component of interstellar ice, rather than a chemical group in HAC. Nevertheless, a broad feature at 2880 cm^{-1} (3.47 μm) does appear in the absorption spectrum of HAC, although this may not be related to the interstellar feature. This feature in HAC can be identified with the overtone vibration of $CH_{2,3}$ groups near 1470 cm^{-1} (6.8 μm).

The enhancement of the concentration of CH_2 groups relative to that of CH_3 in dark cloud material indicates that there is a real difference between the composition of hydrocarbon dust in these objects and that observed in the DISM. The simplest explanation

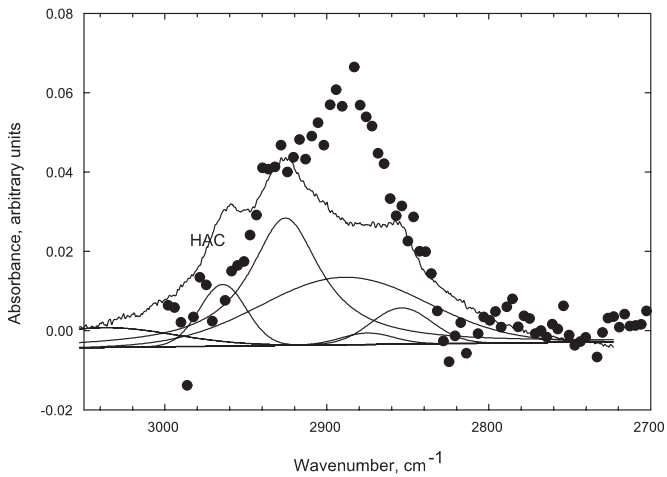


FIG. 7.—Residual absorption spectrum of NGC 7538 IRS9 (*circles*; Allamandola et al. 2002). Absorption spectrum and components of HAC at 300 K (*lines*). Note the appearance of CH_2 components in the observational spectrum at 2920 and 2850 cm^{-1}. The CH_3 band at 2960 cm^{-1} is absent from the observational spectrum.

for this effect is that alkane chains, either in HAC or in some other form, are much longer in dark clouds than in the DISM. Since the structure of these molecules is $CH_3(CH_2)_nCH_3$, an increase in length generally enhances absorption by CH_2 at the expense of CH_3. For example, in octacosane ($C_{28}H_{58}$), where $n = 26$, the CH_3 absorption feature at 2960 cm^{-1} (3.38 μm) has only 20% of the amplitude of the CH_2 feature at 2920 cm^{-1} (3.42 μm). These relative strengths would be consistent with the spectrum of NGC 7528 IRS9 (Fig. 7). While this simple solution is attractive, there are many other ways in which CH_2 can be enhanced relative to CH_3. One possibility is that aromatic rings have been hydrogenated to form cyclohexane-like structures. Vinyl-cyclohexane (C_8H_{14}), for example, has no CH_3 groups, is a simple derivative of cyclohexane (C_6H_{12}), and absorbs at 2930 and 2860 cm^{-1} (3.41 and 3.50 μm).

The four primary components of the 3.4 μm band observed in astronomical sources and in laboratory spectra of HAC are, as noted, readily correlated with the asymmetric and symmetric vibrational modes of CH_3 and CH_2 groups. Unfortunately, it is apparent that it is impossible to assign these features to *specific* hydrocarbon species. For example, one cannot say that the CH_3 groups in HAC or in the material in CRL 618 are in the same chemical environment as those in hexane or decane, two saturated hydrocarbon molecules. Although there are many *individual* hydrocarbon molecules whose spectra would reproduce those of the astronomical sources (Duley & Grishko 2003), any detailed overlap between spectra of specific individual hydrocarbon compounds and that observed in astronomical sources like GC IRS 6E must be considered fortuitous. Such coincidences do, nevertheless, reveal potentially useful information concerning the bonding environment of the groups in interstellar matter, since the integrated strengths of the CH_3 and CH_2 bands in specific molecules can be used to derive the relative concentration of these chemical groups in interstellar hydrocarbons. For example, Pendleton & Allamandola (2002) and Sandford et al. (1991) have compared 3.4 μm absorption spectra of simple alkane hydrocarbons such as hexane, C_6H_{14}, and octane, C_8H_{18}, with those of some galactic center sources and, on the basis of this comparison, suggest that the CH_2/CH_3 ratio in DISM dust is typically 2.5 ± 0.4. This estimate was based primarily on general agreement between laboratory IR data and observed wavelengths for individual CH_2 and CH_3 components in astronomical spectra and would be consistent with that derived from the RCN fit shown in Figure 6. Pendleton & Allamandola (2002) found that a chemical model for dust derived from these data (taking into account additional observational constraints) implies that the CH_2 and CH_3 groups responsible for the 3.4 μm absorption band are present on short chains that act as bridges between aromatic networks. However, as the CH_2/CH_3 ratio is an important parameter in characterizing the composition of interstellar hydrocarbons, and varies considerably with chemical structure, it is useful to ascertain if the observed spectral properties of this material can also be replicated with molecular species *without* alkane chains. The IR database contains many examples of hydrocarbon compounds, other than alkanes, whose spectra reproduce those of the interstellar 3.4 μm bands and for which the CH_2/CH_3 ratio is much less than 2.5. For example, we find that the average CH_2/CH_3 ratio in a number of cyclohexene and cyclohexadiene compounds with spectra that match the 3.4 μm band in CRL 618 is ≈ 1.15. These compounds consist of simple hydrocarbon side-groups attached to nonaromatic hexagonal rings containing one or two double bonds.

Simulation of a "generic" 3.4 μm band based on a mixture of six of these compounds is shown in Figure 8. It is obvious that

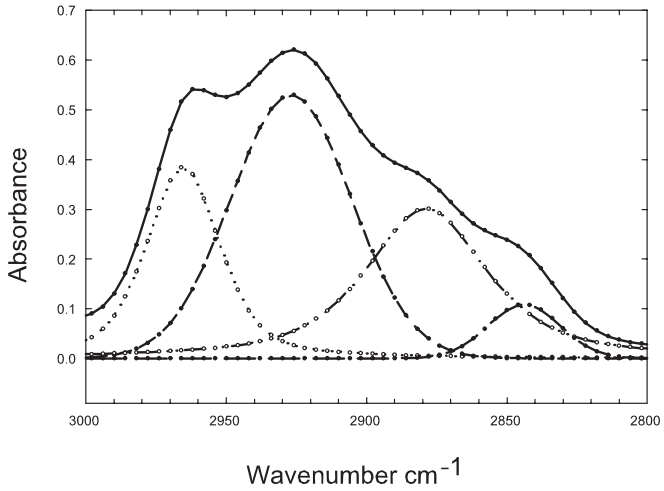


FIG. 8.—Synthetic 3.4 μm band produced by summing bands of individual cyclohexene and cyclohexadiene molecules. The deconvolved components of this spectrum are shown. The synthetic absorption band is similar to observational bands in DISM sources, as well as that of HAC deposited at 300 K.

the relative intensities of the (2960, 2877) and (2929, 2848 cm^{-1}) line pairs could be changed by varying the fractional abundance of one or more compounds in this mixture. In these compounds, some CH_2 groups are present at the periphery of nonaromatic hexagonal rings rather than in side-chains, while CH_3 groups may be attached either as substituents on the ring or in side-chains having mixed sp^2/sp^3 bonding.

The comparison between laboratory and observational spectra shows quite clearly that the relative abundance of hydrocarbon groups in interstellar sources is variable, with enhancement of CH_3 relative to CH_2 in DISM and the depletion of CH_3 groups (relative to CH_2) in dark cloud dust. CH_2 groups seem to be present in all objects. This variability must arise because of differences in the photodissociation rate of $CH_{2,3}$ and the effect of variations in the overall rates of the chemical reactions that influence the concentration of CH_2 and CH_3 groups in different sources (Duley 2000; Mennella et al. 2001; Munoz Caro et al. 2001). In this scenario, the enhanced stability of CH_2 occurs because the carbon atom has two single bonds to other carbons, or a double bond to a single carbon. On the other hand, CH_3 groups can only be attached to the parent hydrocarbon with a single C—C bond, making them especially susceptible to chemical and photochemical erosion

In a simple chemical model for HAC, which includes aromatic PAH groups (Jones et al. 1990; Pendleton & Allamandola 2002; Dartois et al. 2005), the (CH_3/CH_2) ratio inferred from observational spectra will be determined by the relative number of CH_2 and CH_3 attached to ring compounds in the form of bridging groups and side-chains. This assumes that the concentration of "independent" aliphatic molecules is small. In this approximation, the abundance of CH_3 will be strongly influenced by chemical reactions with ambient species, particularly H atoms. An important exoergic channel is the abstraction of CH_3 by H to form CH_4, which can be represented as $R{-}CH_3 + H \rightarrow R{-} + CH_4$, where R is another chemical group. The addition of C, C^+ in reactions such as $R{-}CH_n + (C,\ C^+,\ H) \rightarrow R{-}CH_mCH_3$ would act to reform CH_3. In equilibrium, the (CH_3/CH_2) ratio in a specific location would then depend on the relative rates of these reactions, together with the relative photodissociation rates of CH_2 and CH_3 groups.

Finally, as noted by Chiar et al. (2000) and Pendleton & Allamandola (2002), mid-IR absorption spectra of interstellar

sources provides additional constraints on the composition of interstellar hydrocarbons. Further laboratory experiments are needed to clarify these constraints. The analysis of Pendleton & Allamandola (2002) has demonstrated that the relative strength of CH stretch and deformation modes observed in interstellar spectra is consistent with a hydrocarbon composition similar to that of HAC.

5. CONCLUSIONS

We have compared individual spectral components within the 3.4 μm band observed in the IR sources GC IRS 6E, CRL 618, NGC 7538 IRS9, and IRAS 05341+0852 with laboratory and theoretical spectra. We find that spectra of GC IRS 6E and CRL 618 are well fitted with spectra of HAC that have been deposited at 77 K and less well with spectra of samples deposited at 300 K or higher temperature. This suggests, but does not prove conclusively, that the dust in these objects has never been heated above 300 K. While the relative concentration of CH_2 and CH_3 groups is similar in GC IRS 6E and in CRL 618, we find that there are slight differences in the wavelength and intensity of these components in the two objects. Nevertheless, our results support the suggestion of Chiar et al. (1998) that a similar type of hydrocarbon material is present in both objects. The relative CH_2/CH_3 concentration in IRAS 05341+0852 is much larger than that in IRS 6E and CRL 618, indicating that CH_3 groups are suppressed in this protoplanetary nebula. This would be consistent with higher dust temperatures and/or an increased rate of reaction with H atoms.

Analysis of the 3.4 μm spectrum of dark cloud material as typified by NGC 7538 IRS9 shows that the CH_2 hydrocarbon component seen in the DISM is also present in this object. The corresponding CH_3 component is, however, much less abundant NGC 7538 IRS9 than in the other sources. This results in a notable increase in the CH_2/CH_3 ratio and would be consistent with the presence of long alkane chain molecules, although we show that other types of hydrocarbon could produce a similar effect.

Finally, we note that the relative abundance of CH_2 and CH_3 groups in the ISM inferred from the observational data is highly dependent on the presumed composition of hydrocarbons containing these chemical groups. If the presumed carriers of these groups are alkane chains, then our simulations suggest that the CH_2/CH_3 ratio is $\approx$2.5, in agreement with the results of Pendleton & Allamandola (2002). We find that this ratio can be quite different if the CH_2 and CH_3 groups are contained in other compounds. For example, a simulation of the 3.4 μm band using a mixture of cyclohexene molecules also yields a good fit to observed spectra and predicts a CH_2/CH_3 ratio of $\approx$1.15 in DISM dust.

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