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DIAMOND, AROMATIC, AND ALIPHATIC COMPONENTS OF INTERSTELLAR DUST GRAINS: RANDOM COVALENT NETWORKS IN CARBONACEOUS GRAINS

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ABSTRACT

A formalism based on the theory of random covalent networks (RCNs) in amorphous solids is developed for carbonaceous dust grains. RCN solutions provide optimized structures and relative compositions for amorphous materials. By inclusion of aliphatic, aromatic, and diamond clusters, solutions specific to interstellar materials can be obtained and compared with infrared spectral data. It is found that distinct RCN solutions corresponding to diffuse cloud and molecular cloud materials are possible. Specific solutions are derived for three representative objects: VI Cyg No. 12, NGC 7538 (IRS 9), and GC IRS 7. While diffuse cloud conditions with a preponderance of sp^2 and sp^3 bonded aliphatic CH species can be reproduced under a variety of RCN conditions, the presence of an abundant tertiary CH or diamond component is highly constrained. These solutions are related quantitatively to carbon depletions and can be used to provide a quantitative estimate of carbon in these various dust components. Despite the abundance of C_6 aromatic rings in many RCN solutions, the infrared absorption due to the aromatic stretch at ~3.3 μm is weak under all conditions. The RCN formalism is shown to provide a useful method for tracing the evolutionary properties of interstellar carbonaceous grains.

Subject headings: dust, extinction — infrared: ISM: lines and bands — ISM: clouds

1. INTRODUCTION

The presence of carbonaceous compounds in interstellar materials was first detected in the absorption spectrum of the galactic center source GC & IRS 7 (Soifer, Russell, & Merrill 1976; Willner et al. 1979; Wickramasinghe & Allen 1980). Subsequent observations (Butchart et al. 1986; Adamson, Whittet, & Duley 1990; Sandford et al. 1991) have demonstrated that condensed carbonaceous material containing CH_2 and CH_3 functional groups is a common and abundant constituent of dust in the diffuse interstellar medium. This material may contain as much as 35% of the available carbon in the interstellar medium (ISM). The spectrum is compatible with that of hydrogenated amorphous carbon (HAC) (Duley & Williams 1983; Duley 1994) which can be created by direct deposition on dust in interstellar clouds (Duley 1993) or as the photolysis product of irradiated ices (Sandford et al. 1991).

Observations of spectra of some protostars in the CH stretching region (3.2–3.9 μm) has recently revealed the presence of a spectral feature attributed to tertiary carbon near 2880 cm^{-1} (3.47 μm) (Allamandola et al. 1992). This tertiary carbon can be associated with sp^3-bonded diamond clusters. When the 2880 cm^{-1} absorption feature is observed in these spectra, features attributable to aliphatic CH_2 and CH_3 groups are weak or absent, suggesting that diamond clusters are the predominant carbonaceous dust component in dense molecular clouds (Allamandola et al. 1993). The tertiary CH absorption feature may also have been detected in the 3.2–3.6 μm spectrum of the protostar Mon R2/IRS 3, where it is paired with an additional absorption feature at 3076 cm^{-1} (3.251 μm) (Sellgren, Smith, & Brooke 1994). Neither absorption feature is detectable in Elias 16, which shines through the Taurus molecular cloud (Sellgren et al. 1994).

Aliphatic compounds have also been detected in cometary spectra (Knacke, Brooke, & Joyce 1986; Encrenaz, d'Hendecourt, & Puget 1988) as well as in meteoritic organic material (Ehrenfreund et al. 1991). The 3.4 μm spectrum observed in cometary emission is similar in many respects to the absorption spectrum of diffuse cloud material, although a recent observation of the comet P/Swift-Tuttle (Davies et al. 1993) reveals a single emission peak at ~2915 cm^{-1} (3.43 μm) rather than the full range of diffuse cloud spectral features.

These data suggest that the composition and structure of carbonaceous dust vary within the ISM and that these variations involve changes in the relative abundance of sp^2 and sp^3 hybridized bonded components. Similar variations are observed in laboratory samples of hydrogenated amorphous carbons (Smith 1984; Robertson 1986; Angus & Hayman 1988; Ogmen & Duley 1988) and can be attributed to changes in structure and composition driven by such factors as hydrogen content, temperature, and radiative exposure (Duley 1993). Modeling of these amorphous carbons as a random covalent network (RCN) has been shown to provide a useful insight into these changes (Angus & Jansen 1988; Jones 1990). The RCN provides constraints on both composition and structure of an amorphous solid and, in the case of HAC, yields a prediction of the relative proportion of sp^2 and sp^3 components when the hydrogen content is specified.

The RCN formalism is used here to quantitatively estimate the relative proportion of aromatic, aliphatic, and diamond components in carbonaceous dust. The range of possible compositions permitted under RCN conditions has been determined and specific solutions consistent with observed astronomical IR spectra are obtained. Solutions compatible with diamond-rich materials are shown to exist formally and to be distinct from solutions which yield a "diffuse cloud"

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spectrum. The relative intensities of individual IR components in the 3.2–3.7 μm spectral region are predicted from this model.

2. THE RANDOM COVALENT NETWORK FOR INTERSTELLAR CARBON

The theory of RCNs has been developed by Phillips (1979), Döhler, Dandaloff, & Bilz (1980), and Thorpe (1983). Application of this theory to describe the bonding in hydrocarbons has been discussed by Angus & Jansen (1988) and Jones (1990). Constraints on composition and structure are provided by the requirement that the atom fractions, x_i, of all components of the amorphous solid sum to unity:

$$\sum_{i=1}^{n} x_i = 1 \ . \tag{1}$$

A further constraint is provided by bonding (Döhler et al. 1980), which in turn depends on the coordination number, m, at each site. Then

$$\begin{aligned} N_{\mathrm{con},i} &= (m^2/2) \qquad m \le 2 \ , \\ &= (2.5m - 3) \quad m > 2 \end{aligned} \tag{2}$$

is the number of constraints at site i. Since there are 3 degrees of freedom per site,

$$\sum x_i N_{\mathrm{con},i} = 3 \ . \tag{3}$$

For a simple network consisting of sp^1, sp^2, and sp^3 carbon atoms (m = 2, 3, and 4, respectively) together with hydrogen atoms (m = 1), equations (1)–(3) yield

$$x_1 + x_2 + x_3 + x_4 = 1 \ , \tag{4}$$

$$0.5x_1 + 2x_2 + 4.5x_3 + 7x_4 = 3 \ . \tag{5}$$

In the following analysis it will be assumed that $x_2 = 0$ since spectral features due to sp^1 bonded carbon are not evident in astronomical spectra (Whittet 1992). At low hydrogen concentrations sp^2 clusters are anticipated (Angus & Jansen 1988; Jones 1990). For an RCN with ethylene-type C_2 and benzene-like C_6 units, equations (4)–(5) can be rewritten as (Jones 1990)

$$x_1 + x_3 + x_4 = 1 \ , \tag{6}$$

$$0.5x_1 + 3.5(1 - f)x_3 + 2fx_3 + 7x_4 = 3 \ , \tag{7}$$

where f is the fraction of sp^2 bonded carbon atoms in C_6 rings. The ratio x_4/x_3 and the average coordination number $\bar{m}$ can be obtained by combining equations (6) and (7). This solution can be used to estimate the relative proportion of aromatic and aliphatic species, but it does not explicitly include diamond-like clusters. The structure of the smallest sp^3 bonded carbon cluster that explicitly contains tertiary carbon-hydrogen bonds is the C_6 cluster shown schematically in Figure 1. This cluster has m = 10 and N_{con} = 22. If d is the fraction of sp^3 bonded carbon in such clusters, equations (1) and (3) become

$$x_1 + x_3 + x_4 = 1 \ , \tag{8}$$

$$0.5x_1 + 3.5(1 - f)x_3 + 6(1 - d)x_4 + 2fx_3 + \frac{22}{6}\,dx_4 = 3 \ . \tag{9}$$

Then

$$\frac{x_4}{x_3} = \frac{(0.5 - 3x_1 - 1.5f + 1.5fx_1)}{(5.5x_1 - 3 + 2.33d - 2.333dx_1)} \ , \tag{10}$$

where $x_1 \equiv x_{\mathrm{H}}$, the fraction of H atoms in the solid. This ratio can be used to predict the relative intensity of IR absorption features arising from primary, secondary, and tertiary CH dust components.

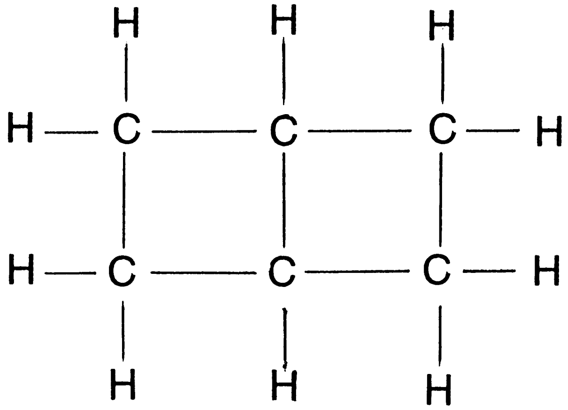

FIG. 1.—C_6 cluster exhibiting tertiary CH bonding as used in RCN calculation.

3. INFRARED SPECTRAL FEATURES

The relationship between IR optical depth $\tau(\nu)$ at frequency ν, spectral width, integrated absorbance A (cm molecule^{-1}) and column density N (cm^{-2}) is given by

$$\int \tau(\nu) d\nu = NA \ . \tag{11}$$

This can be approximated as

$$\tau_{\max} \Delta\nu_{1/2} = NA \ , \tag{12}$$

where $\tau_{\max}$ is the optical depth at the center of a line with a full spectral width at half-maximum of $\Delta\nu_{1/2}$ (cm^{-1}). The column density N_i for component i in carbonaceous dust is

$$N_i = 3.7 \times 10^{-4} n_{\mathrm{H}} L p_i x_i \delta \ , \tag{13}$$

where $n_{\mathrm{H}} L$ is the column density of hydrogen, $3.7 \times 10^{-4}\ \delta$ is the abundance of available carbon in dust, δ is the fraction of carbon in dust, which can be treated as an empirical parameter to be derived from a fit to IR spectra, and p_i is the fraction of sites i containing H atoms. Then, for tertiary CH in diamond clusters, one has

$$(\tau_{\max} \Delta\nu_{1/2})_{\mathrm{diamond}} = 3.7 \times 10^{-4} n_{\mathrm{H}} L p_4^d \frac{d}{3} x_4 \delta A_{\mathrm{CH}} \ . \tag{14}$$

It will be assumed that $p_4^d = p_4$ in the analysis that follows.

The extra factor of 3 in the denominator arises since only $\frac{1}{3}$ of C atoms in the C_6 diamond cluster (Fig. 1) can participate in tertiary bonds to H atoms. Similar expressions for other species are as follows:

$$(\tau_{\max} \Delta\nu_{1/2})_{\mathrm{aromatic}} = 3.7 \times 10^{-4} n_{\mathrm{H}} L p_3 f x_3 \delta A_{\mathrm{CH}}^{\mathrm{arom}} \ , \tag{15}$$

$$(\tau_{\max} \Delta\nu_{1/2})_{\mathrm{CH_3}} = 3.7 \times 10^{-4} n_{\mathrm{H}} L p_4 (1 - d) x_4 \delta A_{\mathrm{CH_3}} \ , \tag{16}$$

$$\begin{aligned} (\tau_{\max} \Delta\nu_{1/2})_{\mathrm{CH_2}} = {} & 3.7 \times 10^{-4} n_{\mathrm{H}} L[(1 - f)p_3 x_3 \\ & + 0.667 p_4 x_4 d] \delta A_{\mathrm{CH_2}} \ . \end{aligned} \tag{17}$$

Table 1 summarizes values of A that are used in the present calculations. With these values of A, ratios of the various spectral components are as follows (abbreviating $\tau_{\max} \Delta\nu_{1/2}$ to

TABLE 1

INTEGRATED ABSORBANCE A FOR AROMATIC, ALIPHATIC, AND DIAMOND BONDED H

Group	ν (cm^{-1})	A (cm per group)	Reference
Diamond—CH	2880	4×10^{-18}	1
—CH$_2$	2925	7.4×10^{-18}	2
—CH$_3$	2955	1.2×10^{-17}	2
Aromatic—CH	3030	2×10^{-19}	3

REFERENCES.—(1) Allamandola et al. 1992; (2) Sandford et al. 1991; (3) Dyuley 1993.

$\tau \Delta\nu$):

$$\frac{(\tau \Delta\nu)_{\rm diamond}}{(\tau \Delta\nu)_{\rm CH_3}} = \frac{0.1111 d}{(1-d)} \frac{p_4^d}{p_4} , \tag{18}$$

$$\frac{(\tau \Delta\nu)_{\rm diamond}}{(\tau \Delta\nu)_{\rm CH_2}} = \frac{0.18 p_4 x_4 d}{[(1-f) p_3 x_3 + 0.667 p_4 x_4 d]} , \tag{19}$$

$$\frac{(\tau \Delta\nu)_{\rm diamond}}{(\tau \Delta\nu)_{\rm aromatic}} = \frac{6.66 p_4^d x_4 d}{f p_3 x_3} . \tag{20}$$

4. RESULTS AND DISCUSSIONS

Equations (8)–(9) can be used to define a range of solutions for $x_1 \rightarrow x_4$ compatible with the requirements of an RCN amorphous structure. These results can be conveniently expressed in terms of the ratio $x_3/(x_3 + x_4)$ which measures the relative fraction of sp^2 hybridized bonded carbon in the material. Figure 2 shows the allowed range of solutions to equations (8)–(9) plotted as $x_3/(x_3 + x_4) \equiv sp^2/(sp^2 + sp^3) = \beta$ versus $x_1 \equiv x_{\rm H}$, the atom fraction of hydrogen. The region of permitted solutions extends from a limit where $f = 0$, $d = 0$ (*right-hand curve*) to $f = 1$, $d = 1$ (*left-hand curve*). Between these limits, solutions are possible for combinations with $0 < f < 1$, $0 < d < 1$. The solution for $f = 1$, $d = 0.5$ is shown as the intermediate curve in Figure 2. Some features of the solution are the following:

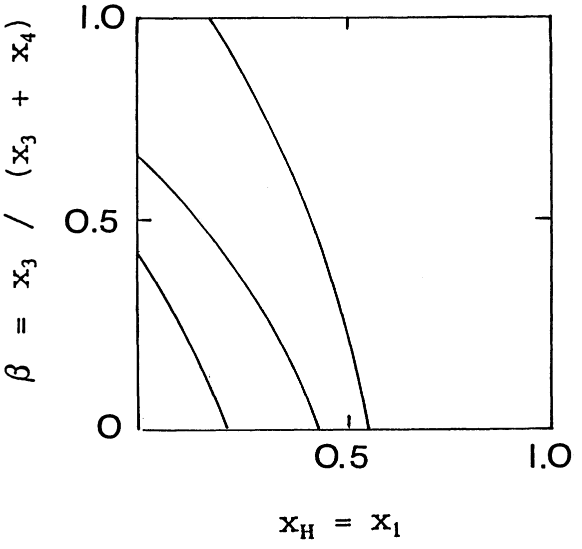

FIG. 2.—Permitted RCN solutions for carbon solids (eqs. [8]–[9]). $\beta = x_3/(x_3 + x_4)$ is the ratio of sp^2 bonded to ($sp^2 + sp^3$) bonding carbon, $x_{\rm H} = x_1$ is the atom fraction of hydrogen. *Right curve*: ($f = 0$, $d = 0$); *middle curve*: ($f = 1$, $d = 0.5$); *lower curve*: ($f = 1$, $d = 1$).

1. The point for crystalline diamond ($\beta = 0$, $x_{\rm H} = 0$) is not included as a solution, while that for graphite ($\beta = 1$, $x_{\rm H} = 0$) is within the permitted range.
2. Solutions with $\beta = 0$, $0.21 < x_{\rm H} < 0.545$ consist of pure sp^3 bonded material with the ratio (diamond/CH$_3$) increasing as $x_{\rm H}$ decreases.
3. Solutions with $x_{\rm H} = 0$ exist over the range $0.4 \leq \beta \leq 1$ and correspond to mized aromatic-diamond composition.
4. The region $x_{\rm H} \leq 0.166$, $\beta = 1$ is the solution for pure sp^2 bonded material with the ratio (aromatic/CH$_2$) increasing as $x_{\rm H}$ decreases.
5. The region from the middle to upper right of the diagram yields solutions with comparable fractions of CH$_2$ and CH$_3$ components, but with little aromatic or diamond material.
6. Solutions for materials with $x_{\rm H} < 0.1$ can also be described using a "defected graphite" model (Tamor & Wu 1990), which may be a more appropriate description when large atom clusters dominate. However, only materials with appreciable hydrogen content ($x_{\rm H} > 0.1$) will be detectable by absorption in the CH stretching region under astrophysical conditions; therefore, the RCN model is expected to represent the appropriate composition for these materials.

Specific RCN solutions for astrophysical solids can be obtained (if they exist) from equations (8)–(10) and (14)–(17). An additional requirement is provided by the constraint that x_1 must include all hydrogen atoms in the solid. Formally, this requirement can be expressed as

$$x_1 = p_3 f x_3 + 2 p_3 (1-f) x_3 + \frac{4 p_4}{3} x_4 d + 3 p_4 (1-d) x_4 + p_4^d \frac{x_4}{3} d . \tag{21}$$

Solutions for diffuse cloud material are characterized by the requirement that $(\tau \Delta\nu)_{\rm CH_3} \simeq (\tau \Delta\nu)_{\rm CH_2}$ (Sandford et al. 1991). This condition is a valid RCN solution for the region near ($\beta = 0.6$, $x_{\rm H} = 0.3$) in Figure 2 and permits small amounts of both aromatic and diamond material in addition to aliphatics. The simplest solution is obtained, however, with $f = 0$ and $d = 0$. Under these conditions,

$$p_3 x_3 = 2.7 \times 10^3 \frac{N_{\rm CH_2}}{\delta N_{\rm H}} , \tag{22}$$

$$p_4 x_4 = 2.7 \times 10^3 \frac{N_{\rm CH_3}}{\delta N_{\rm H}} . \tag{23}$$

A summary of parameters obtained for fits with ($f = 0$, $d = 0$) to the CH$_n$ absorption features in VI Cyg No. 12 and GC IRS 9 using the data of Sandford et al. (1991) is given in Table 2. Solutions can be obtained only over the limited range $0.117 < \delta < 0.375$ and $0.128 < \delta < 0.42$ for VI Cyg No. 12 and GC IRS 9, respectively. Those solutions in which the level of hydrogenation of sp^2 and sp^3 sites are comparable ($p_3 \sim p_4$) would seem to be most plausible, although at low H concentrations one might expect that hydrogenation might be enhanced at sp^2 sites. Table 3 compares RCN fitting parameters for the VI Cyg No. 12 data using other (f, d) combinations. It is apparent that a wider range of possible solutions extending to high values of δ can be obtained when f is permitted to increase. Solutions are also possible for materials in which the diamond cluster component is nonzero and for mixed diamond-

TABLE 2

RCN PARAMETERS

δ	x_1	x_3	x_4	p_3	p_4
			VI Cyg 12		
0.117......			No solution		
0.20.......	0.325	0.5	0.175	0.20	0.24
0.30.......	0.216	0.73	0.05	0.09	0.56
0.375......			No solution		
			GC IRS 7		
0.128......			No solution		
0.20.......	0.35	0.43	0.22	0.23	0.23
0.30.......	0.23	0.69	0.08	0.097	0.42
0.42.......			No solution		

NOTES.—RCN parameters derived from IR absorption in VI Cyg No. 12 and GC IRS 7 using $f = 0$, $d = 0$. Values for x_1, etc., are exact to the significant figures quoted for particular δ. However, all allowed RCN solutions are equivalent in the absence of additional information that would favor one solution over another.

aromatic components (e.g., $f = 0.3$, $d = 0.3$). Under the conditions of these solutions, the column density of the aromatic dust component can be comparable to or can exceed those of CH_2 and CH_3 (Table 4). However, the low absorption strength of aromatic CH bonds (Table 1) results in $(\tau\,\Delta\nu)_{\rm aromatic} \leq 0.04$ for the VI Cyg No. 12 sight line in which $(\tau\,\Delta\nu)_{CH_3} = 0.71$ and $(\tau\,\Delta\nu)_{CH_2} = 1.11$. For tertiary hydrogen (i.e., the diamond component) $(\tau\,\Delta\nu)_{\rm diamond} = 0.034$ for $d = 0.3$ in VI Cyg No. 12. Thus, neither aromatic nor diamond components are likely to be detectable in absorption under the conditions that yield a fit to the diffuse ISM aliphatic components. On the other hand, the RCN fit to the diffuse ISM observations is not unique and is given by a range of possible carbon compositions.

TABLE 3

RCN FIT TO VI CYG NO. 12 IR ABSORPTION DATA FOR SEVERAL (f, d) COMBINATIONS

f	d	δ	x_1	x_3	x_4	p_3	p_4	β
0........	0	0.117			No solution			
		0.20	0.325	0.5	0.175	0.20	0.24	0.74
		0.30	0.216	0.73	0.05	0.09	0.56	0.93
		0.375			No solution			
0.3......	0	0.135			No solution			
		0.20	0.37	0.33	0.30	0.43	0.14	0.52
		0.30	0.25	0.56	0.19	0.17	0.15	0.75
		0.40	0.185	0.68	0.135	0.10	0.16	0.83
		0.50	0.15	0.74	0.11	0.07	0.15	0.87
0.6......	0	0.17			No solution			
		0.30	0.32	0.38	0.30	0.44	0.09	0.56
		0.40	0.24	0.51	0.25	0.25	0.08	0.67
		0.50	0.19	0.58	0.23	0.17	0.07	0.72
		0.60	0.16	0.63	0.21	0.13	0.07	0.75
		0.70	0.135	0.67	0.195	0.11	0.06	0.77
0.0......	0.3	0.148			No solution			
		0.20	0.36	0.33	0.31	0.30	0.19	0.52
		0.30	0.24	0.65	0.11	0.10	0.36	0.86
		0.42			No solution			
0.3......	0.3	0.135			No solution			
		0.2	0.37	0.2	0.43	0.63	0.14	0.32
		0.3	0.25	0.49	0.26	0.17	0.15	0.65
		0.4	0.185	0.62	0.195	0.10	0.15	0.76
		0.5	0.15	0.70	0.15	0.07	0.16	0.82
		0.6	0.12	0.75	0.13	0.06	0.16	0.85
0.6......	0.3	0.196			No solution			
		0.30	0.31	0.29	0.40	0.51	0.10	0.42
		0.40	0.23	0.43	0.34	0.25	0.09	0.56
		0.50	0.19	0.52	0.29	0.17	0.08	0.64
		0.60	0.155	0.57	0.27	0.13	0.07	0.67
0.0......	1.0				No solution			

TABLE 4

REPRESENTATIVE COLUMN DENSITIES

f	d	$N(CH_3)$	$N(CH_2)$	N(Aromatic)	N(Diamond)
		VI Cyg No. 12 $N_H = 1.9 \times 10^{22}$ cm^{-2}			
0........	0	5.9×10^{16}	1.5×10^{17}	0	0
0.3......	0	5.9×10^{16}	1.5×10^{17}	6.0×10^{16}	0
0.6......	0	5.9×10^{16}	1.5×10^{17}	2.1×10^{17}	0
0........	0.3	5.9×10^{16}	1.5×10^{17}	0	8.4×10^{15}
0.3......	0.3	5.9×10^{16}	1.5×10^{17}	6.0×10^{16}	8.4×10^{15}
0.6......	0.3	5.9×10^{16}	1.5×10^{17}	2.1×10^{17}	8.4×10^{15}
		GC IRS 7 $N_H = 6.5 \times 10^{22}$ cm^{-2}			
0........	0	2.4×10^{17}	5.0×10^{17}	0	0
0.3......	0	2.4×10^{17}	5.0×10^{17}	$2.1 \times 10^{17}0$	0
0.6......	0	2.4×10^{17}	5.0×10^{17}	7.5×10^{17}	0
0........	0.3	2.4×10^{17}	5.0×10^{17}	0	3.4×10^{16}
0.3......	0.3	2.4×10^{17}	5.0×10^{17}	1.9×10^{17}	3.4×10^{16}
0.6......	0.3	2.4×10^{17}	5.0×10^{17}	6.7×10^{17}	3.4×10^{16}

NOTES.—Representative column densities (cm^{-2}) for aromatic and diamond carbon components in VI Cyg No. 12 and GC IRS 7 predicted from the RCN model.

For the tertiary H component associated with sp^3 diamond (Allamandola et al. 1992), the observational requirement is that $CH : CH_2 : CH_3 \simeq 10:3:1$. This requirement cannot be met by the RCN model unless it is assumed that the last term in the bracket in equation (17) is essentially zero, since otherwise the diamond clusters themselves would contribute CH_2 in the ratio (see Fig. 1) $CH_2 : CH = 2:1$. If this assumption is made, namely, that the secondary hydrogen sites in the diamond cluster shown in Figure 1 are nonbonding for hydrogen, then a solution can be found. Parameters describing this solution are given in Table 5. The solution is quite specific and requires $d \sim 1$ and a relatively high level of hydrogenation for the sp^3 diamond. They also imply a higher carbon depletion ($\delta = 0.6$–0.65 when $f = 0$ and $\delta = 0.8$–0.9 when $f = 0.6$). Solutions where diamond and aromatic clusters are present in the same RCN mixture exist and are enhanced at high overall carbon depletion.

The narrow range over which the diamond component dominates is in sharp contrast to the wide range that pertains to the diffuse ISM solution as typified by VI Cyg No. 12. RCN solutions for diamond- and aliphatic-dominated materials are shown on a β versus x_H plot in Figure 3. The diamond-dominated mixtures require $x_H \sim 0.2$ and show no overlap with the diffuse ISM solutions, although this and other conclusions concerning the diamond rely heavily on the spectrum of NGC 7538 (IRS 9), in particular, the requirement that $CH{:}CH_3 = 10:1$ yields $d = 0.968$.

Distinct RCN solutions for diffuse ISM and dense cloud dust supports the conclusion of Allamandola et al. (1992, 1993) that different carbonaceous dust components exist in these two environments. It suggests, in addition, that other carbonaceous dust components characterized by different RCN solutions may exist in different interstellar environments. Figure 4 traces the evolution of an RCN solution ($f = 0.3$, $d = 0$), initially fitting the VI Cyg No. 12 data as the level of hydrogenation is allowed to change while maintaining $\delta = 0.2$. As x_H decreases, as would occur, for example, when dust is exposed to UV

TABLE 5

RCN SOLUTIONS

d	f	δ	x_1	x_3	x_4	p_3	p_4	β
0.968……	0	0.53			No solution			
		0.60	0.20	0.34	0.46	0.056	0.42	0.43
		0.65	0.185	0.55	0.265	0.034	0.73	0.67
		0.70	0.174	0.73	0.097	No solution		
		0.73			No solution			
0.968……	0.6	0.655			No solution			
		0.70	0.21		No solution			
		0.80	0.19	0.12	0.69	0.49	0.36	0.15
		0.90	0.165	0.125	0.66	0.30	0.34	0.21

NOTES.—RCN solution for diamond using data measured from the spectrum of NGC 7538 (IRS 9) (Allamandola et al. 1992) and assuming $CH:CH_2:CH_3 = 10:3:1$.

radiation or heat (Duley 1993; Smith 1984), β increases, and the proportion of sp^2 bonded carbon increases at the expense of sp^3 bonded carbon. If x_H is permitted to increase, for example, in response to exposure to H atoms (Furton & Witt 1993), sp^3 bonding is enhanced relative to sp^2 bonding, i.e., β decreases. The effect of these compositional changes on IR spectra in the 3.2–3.7 μm region cannot be predicted quantitatively since p_3 and p_4 are not known. However, as $x_4 \rightarrow 0$ $(\tau\,\Delta\nu)_{CH_3}/(\tau\,\Delta\nu)_{CH_2} \rightarrow 0$ while as $x_4 \rightarrow 0.5$, this ratio is enhanced above its diffuse ISM solution. For $x_H \sim 0.5$, absorption due to CH_3 species will dominate the 3.2–3.7 μm spectrum.

The effect of decreasing x_H while maintaining f, δ, and d constant for the NGC 7538 (IRS 9) solution is also shown in Figure 4. Once again a decrease in x_H forces an increase in the sp^2 bonded component. The effect on the spectrum is to decrease $(\tau\,\Delta\nu)$ for all components. Aliphatic CH_2 absorption dominates over tertiary CH in the IR spectrum when $x_H = 0.1$.

Somewhat surprisingly, under no RCN conditions for $x_H \gtrsim 0.1$ does the absorption due to the aromatic component become comparable to that due to the other nonaromatic components. This occurs even though the fraction of sp^2 C_6 ring material can become large, particularly when $f \rightarrow 1$ and $x_H \rightarrow 0$. In most cases $(\tau\,\Delta\nu)_{\mathrm{aromatic}} \leq 0.1\ (\tau\,\Delta\nu)_{CH_2,CH_3}$. This situation could be improved somewhat if A (aromatic CH) (Table 1) were to increase substantially. However, the large increase in A that would be required is incompatible with the known low strength of the aromatic CH stretching band (Wexler 1967). The weakness of the aromatic CH stretch in astronomical spectra has been recognized for some time (Duley & Williams 1979; Léger & Puget 1984).

Recently Sellgren et al. (1994) have reported a 3 μm spectrum of the protostar Mon R2/IRS 3 which shows absorption features at 2871 ± 6 cm^{-1} (3.483 ± 0.007 μm) and 3076 ± 2 cm^{-1} (3.251 ± 0.002 μm). The former is close to that of absorption by tertiary CH in diamond, while the latter feature lies in the aromatic CH stretching region. If the absorption feature at 3076 cm^{-1} in this source is indeed due to aromatic CH, then the present analysis suggests that the carriers of this feature are not incorporated with other sp^2 and sp^3 bonded carbons in an RCN network such as that of HAC since the relative strengths of the 2871 and 3076 cm^{-1} absorptions ($\tau\,\Delta\nu = 2.87$ and 2.96 cm^{-1}, respectively) are not consistent with RCN solutions. This implies that the 3076 cm^{-1} absorption in Mon R2/IRS 3, if attributable to aromatic CH, must be due to either gas-phase polycyclic aromatic hydrocarbons (PAHs) or to PAH molecules that have accreted on carbonaceous dust grains. Absorption due to accreted PAHs would seem to be more plausible since the energy of the absorption feature (3076

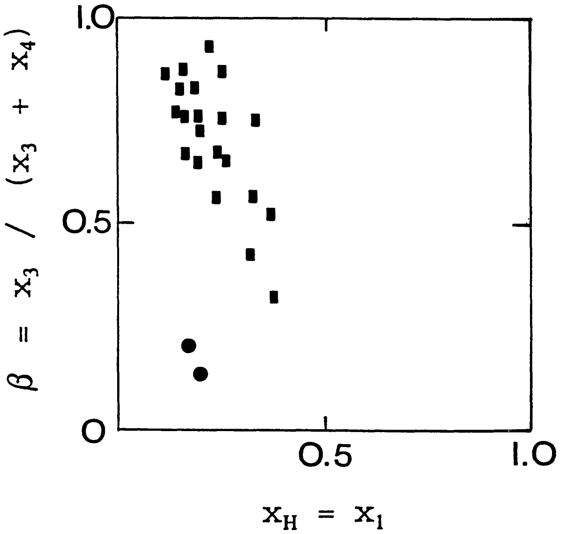

FIG. 3.—RCN solutions for diamond-rich (*circles*) and aliphatic-rich (*squares*) solids. These are derived for NGC 7538 IRS 9 and VI Cyg No. 12 conditions, respectively.

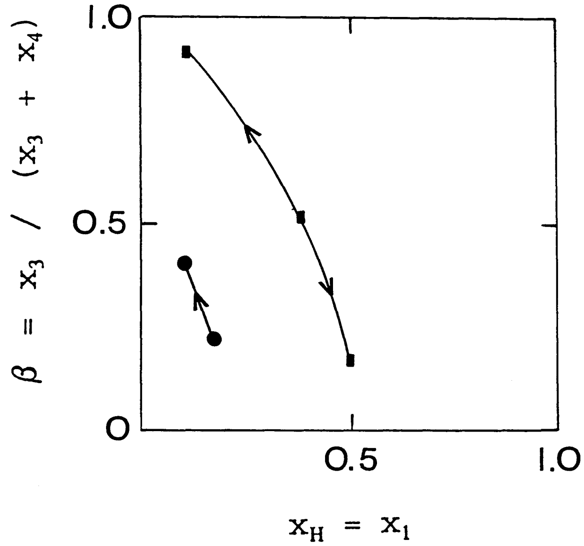

FIG. 4.—Evolution of VI Cyg No. 12 solution with $f = 0.3$, $d = 0$, and $\delta = 0.2$ with changes in x_H (*upper curve*). Evolution of NGC 7538 IRS 9 for "diamond" dust with changing x_H (*lower curve*).

cm^{-1}) is shifted from that of the emission feature normally associated with PAHs (3030 cm^{-1}). The accretion of unreactive molecules such as PAHs would yield a solid that was underconstrained and would provide a wider range of possible solutions than permitted by the RCN formalism. On this basis the RCN formalism may provide a means to distinguish regions where grains have grown by accretion of gaseous PAH molecules from those formed by accretion of C, C^+, and simple molecular species.

Additional solutions including those for polymeric and crystalline materials can exist outside the RCN range (Angus & Hayman 1988). For example, polyethylene $(CH_2)_n$ with no sp^2 component lies at $\beta = 0$, $x_H = 0.67$ in Figure 2 and is an example of an underconstrained material. Crystalline diamond and graphite occur at $\beta = 0$, $x_H = 0$ and $\beta = 1$, $x_H = 0$, respectively.

5. CONCLUSIONS

RCN theory which is applicable to the description of the relative composition and structure of amorphous carbons and hydrogenated amorphous carbons (Angus & Jansen 1988) has been used to estimate these parameters for interstellar carbons. Consistent RCN solutions compatible with IR absorption data have been obtained for representative diffuse cloud and dense cloud conditions, although the parameters describing dust in these two environments form distinct subsets within the RCN formalism. The association of diffuse cloud material with aliphatic carbons and dense cloud material with diamond clusters has been confirmed by this analysis. Diamond clusters may also be present in diffuse cloud material, but at a much lower concentration than in the dust in dense clouds. When diamond is present at a high concentration, 60%–90% of available interstellar carbon is contained in dust. This dust can also contain an appreciable concentration of C_6 aromatic rings, but absorption due to the CH strengthening vibration of this material is always weak compared to CH_2, CH_3, and tertiary CH features. Observation of what could be an aromatic CH absorption band at 3.25 μm in the spectrum of Mon R2/IRS 3 (Sellgren et al. 1994) is inconsistent with aromatic rings within the RCN solution that describes other carbonaceous dust components and may signal either absorption by gas-phase PAH molecules or, more likely, absorption by PAH molecules accreted onto dust grains.

RCN solutions can also be used to generate synthetic IR spectra for carbonaceous dust in specific interstellar environments. When some information on carbon dust composition is available, for example, through detection of CH_2 or CH_3 absorption bands at 3.4–3.5 μm, the RCN formalism can be used to constrain the abundance of other grain components such as aromatic and diamond-like carbon species. In addition, a self-consistent estimate of carbon depletion can be obtained using this technique, as RCN solutions are often compatible with only a limited range of carbon depletions.

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