Table III. Equilibrium Constants for Extraction of Picrate with Dicyclohexyl-18-crown-6

Isomer	Cation	Solvent	K_e, M^{-2}	K_s,[a] M^{-1}	P_e	P_c, M^{-1}	P_cK_d
A	K^+	CH_2Cl_2	4.0×10^6	1.5×10^2	2.5×10^{-4}	1.1×10^8	3×10^3
B	K^+	CH_2Cl_2	1.1×10^6	6.0×10^1	2.7×10^{-4}	7×10^7	2×10^3
Mixture	K^+	$CFCl_2CF_2Cl$	1.9×10^4	1×10^2 [b]	7×10^{-2}	2.7×10^3	
Mixture	K^+	$n\text{-}C_6H_{14}$	3.8×10^3	1×10^2 [b]	1.5×10^{-1}	2.5×10^2	
Mixture	Na^+	CH_2Cl_2	1.5×10^4	4×10^1 [b]	2.6×10^{-4}	1.5×10^6	1.5×10^2

[a] From ref 4. [b] Average values.

to the reaction

$$MCr^+_{aq} + A^-_{aq} \rightleftharpoons MCr^+_{org} + A^-_{org} \qquad (17)$$

and is relevant when the complex ion pairs are largely dissociated in the organic phase.

The equilibrium constants in Table III give some insight into the effect of the solvent on extraction. While the overall equilibrium constant K_e decreases in the solvent sequence $CH_2Cl_2 \rightarrow CFCl_2CF_2Cl \rightarrow C_6H_{14}$, the partition coefficients of the complex, P_c or P_cK_d, decrease even more dramatically through more than six decades, and thus appear to be the dominating influence. The partition coefficient of the polyether, P_e, works in the opposite direction, since the lower polyether solubility in the less polar solvents actually furthers complexing in the aqueous phase. The difference in K_e of the two isomers is only partly due to strength of complexing, as measured by K_s, for the partition coefficients of their complexes also vary measurably. Similarly, the less efficient extraction of sodium compared to potassium is in large part caused by the partition coefficient, which is almost two decades lower, and only in small part by weaker complexing, which accounts for less than a factor of three.

The above considerations demonstrate how very important the solubility relations are in determining extraction properties and that strength of complex formation, while no doubt important, is not necessarily the governing factor. All the measurements reported here concern one anion, picrate, but it is evident that the very strong anion effect (*e.g.*, no measurable extraction of hydroxide or fluoride[2a]) comes from its effect on the complex partition coefficient.

The absolute magnitude of the partition coefficients leads to some interesting conclusions. The picrate complexes in the form of ion pairs are far more soluble in methylene chloride and moderately more soluble in the two less polar solvents than they are in water. Indeed this is the principal reason why extraction occurs. What is more noteworthy, however, is that even the dissociated ions of the picrate complex are considerably more soluble in methylene chloride than in water (*cf.* P_cK_d in Table III).

Acknowledgments. A considerable debt is owed to Charles J. Pedersen, who laid the foundations for this work and assisted it with much sage counsel. The author also wishes to acknowledge the assistance of the following colleagues: Paul J. Bente, III, who obtained much of the extraction data; D. J. Sam, who helped with the isomer separation; E. G. Brame, who provided the nmr information; and B. F. Winkel, who undertook the nonlinear regression analysis. Professor G. Eisenman, University of California, Los Angeles, contributed unpublished data and informative discussions.

Spectroscopy of Carbon Molecules. IV. C_4, C_5, C_6 (and C_9)[1]

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Abstract: The carbon molecules C_4, C_5, C_6, and perhaps C_9, have been formed in argon matrices by the reaction of C, C_2, and C_3. Highly enriched ^{13}C graphite was vaporized to form the isotopically substituted molecules. Analysis of the ir spectra of "pure" and mixed-isotope molecules made possible definite vibrational assignments for the Σ_u^+ frequencies. For $^{12}C_4$, $^{12}C_5$, and $^{12}C_6$ these are 2164; 1952, 1544; and 1997, 1197 cm^{-1}, respectively. The data on each molecule, including mixed-isotope species, were used to calculate stretching force constants. C_4 was found to have a strong C≡C outer bond with $f = 16.5$ mdyn/Å, in general agreement with theory. The force constants for the two outer bonds of C_6 were reliably determined to be 11.9 and 8.1 mdyn/Å. Larger carbon molecules were formed but not identified.

It has been established that the vapor over graphite at 2500°K contains C, C_2, and C_3 molecules[2-4] which have now been rather thoroughly studied.[5,6] Mass spectrometry[7] has also detected very small quantities

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[1] This research was supported by the Air Force Office of Scientific Research (SRC)-OAR, USAF, Grant No. 68-1588.

[2] W. A. Chupka and M. G. Inghram, *J. Chem. Phys.*, **21**, 371 (1953); *J. Phys. Chem.*, **59**, 100 (1955).

[3] R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).

[4] An excellent review of all aspects of the vaporization of carbon has been given by H. B. Palmer and M. Shelef, *Chem. Phys. Carbon*, 4, 85 (1968).

[5] C_2, E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 84 (1963); C_3, L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *ibid.*, **142**, 45 (1965).

($<0.1\%$) of C_4 and C_5 in the vapor, and it is likely that the saturated vapor at higher temperatures contains even larger carbon molecules. The rapid heating of sparks, arcs, and lasers[8] does vaporize graphite to yield these larger species and reveals an interesting variation in the concentration of C_n with n, the size of the molecule. Although generally decreasing as n becomes larger, the concentration of the nth molecule is an oscillating function of n (for $n < 10$) and is larger for n odd. This has been explained very clearly by Clementi, Pitzer, and Strickler[9] as being a direct consequence of simple MO theory applied to linear carbon chains, and these and other authors[10] have calculated the relative stabilities and approximate electronic properties of the series. Accordingly, C_n molecules are expected to be linear, at least up to about $n = 10$, with strong electronic delocalization occurring along the chain. Odd molecules would probably have a singlet and even ones a triplet ground state.

These interesting molecules are difficult to study in the gas phase since their concentrations are small and they are very reactive. Their reactivity has been demonstrated in earlier work in this series[6] (hereafter referred to as III) when the large molecules were formed by controlled diffusion of carbon vapor, *i.e.*, C, C_2, and C_3, trapped in solid neon at temperatures near 4°K. Evidence for their formation was provided by infrared spectroscopy, where it was observed that many new bands appeared when the temperature was raised to about 12°K. The implications were that rapid reactions continue to occur as C_n molecules are formed during solid-state diffusion. The observed ir bands were assigned to various C_n molecules after consideration of their diffusion behavior, and their bonding, as derived from these vibrational frequencies, was briefly discussed.

In the preparation of such matrices from the vaporization of graphite at ~2800°K it is difficult to eliminate CO as a trapped impurity. It is well known[11] that carbon atoms react readily with CO to form the radical CCO, and it is possible that this and other species can be formed in the matrix during the quenching process or when the matrix is warmed.

The experiments described here were carried out to identify those spectral bands belonging to "pure" carbon molecules by the vaporization of highly enriched ^{13}C-substituted graphite. Having identified the C_n bands, one can then use calculated and observed isotope shifts for bands in mixed-isotope molecules, *e.g.*, $^{13}C-^{12}C-^{13}C-^{13}C$, to establish which bands arise from C_4, C_5, etc. In this way the allowed ir (Σ_u^+) stretching frequencies of molecules $C_3, \ldots, C_6$ have been assigned,[12] and those for the larger chains observed but not definitely assigned. Utilizing these assignments and those for mixed-isotope molecules, force constants for each molecule have been calculated.

We assume that all of the carbon molecules C_n reacting in the matrix are in their ground states which, in accord with theory, are $^3\Sigma_g^-$ when n is even and $^1\Sigma_g^+$ when n is odd (for $n > 2$). Then reactions which can occur in the matrix at 4°K to yield products in their ground states are

$$\begin{aligned}
2C(^3P_g) &= C_2(^1\Sigma_g^+)\\
C_2(^1\Sigma_g^+) + C_3(^1\Sigma_g^+) &= C_5(^1\Sigma_g^+)\\
C(^3P_g) + C_3(^1\Sigma_g^+) &= C_4(^3\Sigma_g^-)\\
C_2(^1\Sigma_g^+) + C_4(^3\Sigma_g^-) &= C_6(^3\Sigma_g^-)\\
C(^3P_g) + C_4(^3\Sigma_g^-) &= C_5(^1\Sigma_g^+)\\
C_2(^1\Sigma_g^+) + C_5(^1\Sigma_g^+) &= C_7(^1\Sigma_g^+)\\
3C_3(^1\Sigma_g^+) &= C_9(^1\Sigma_g^+)
\end{aligned}$$

Using $\Delta H_f°$ at 0°K for C and C_2 as 170 and 200 kcal/mol, respectively, and the heat of formation values in Table II of Strickler and Pitzer,[9] one finds that the $\Delta H_0°$ of each of these reactions is negative and greater than 120 kcal/mol. Spin-conservation rules require that the following reactions lead to molecules in excited electronic states which would then presumably be quenched to their ground states.

$$\begin{aligned}
C(^3P_g) + C_2(^1\Sigma_g^+) &= C_3(^3\Sigma_g^-)\\
2C_2(^1\Sigma_g^+) &= C_4(^1\Sigma_g^+)\\
2C_3(^1\Sigma_g^+) &= C_6(^1\Sigma_g^+)\\
C_3(^1\Sigma_g^+) + C_4(^3\Sigma_g^-) &= C_7(^3\Sigma_g^-)
\end{aligned}$$

Again, however, even if one assumes the excited states of the products to lie at 3 eV, the thermodynamics are favorable for their formation.

Carbon has also been vaporized in the form of atoms, but CO is always a major impurity in such experiments. Under such conditions an entirely different set of bands is observed due to CCO, C_3O_2, and possibly other C_nO molecules. This is discussed only briefly and will be the subject of a future publication.

Experimental Section

The variable temperature optical dewar used in this research is similar to that described earlier.[6] The rate of flow of liquid helium through the copper block containing the CsI (or CaF_2) window was controlled by a needle valve and the temperature of the window monitored by a Chromel *vs.* Au–0.02 atom % Fe thermocouple. The pressure of the inert gas in the dewar, as measured by an ion gauge, was also found to be a sensitive indication of the window temperature. Upon reaching the desired temperature to allow annealing or diffusion to occur in the matrix, the needle valve was opened and the matrix rapidly quenched.

Since pure isotopes of carbon were to be vaporized, the heating of graphite rods could not be used. A tantalum tube, 0.25 in. in diameter, 0.50 in. long, with about 0.008 in. wall thickness, and with a 0.0625-in. orifice drilled in the side, was packed with a powdered carbon sample. Tantalum plugs filled the ends and the tube was heated by passing a few hundred amperes at about 6 V through it. After heating at about 2400°K for 1 hr, the tantalum cylinder was converted to carbide. The cell could then be raised to 2900–3300°K for vaporization of carbon. The cell would fail structurally at the deposition temperature if it were not carbided thoroughly

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(6) W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.*, **45**, 3096 (1966) (referred to as III in the text). Note that in the caption to Figure 8 in this paper, the words "heavy" and "light" should be interchanged.

(7) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *ibid.*, 31, 1131 (1959).

(8) H. Hinterberger, J. Franzen, and K. D. Schuy, *Z. Naturforsch. A*, **18**, 1236 (1963); J. Berkowitz and W. A. Chupka, *J. Chem. Phys.*, 40, 2735 (1964); P. D. Zavitsanos, *Carbon (Oxford)*, **6**, 731 (1968).

(9) K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.*, **81**, 4477 (1959); E. Clementi, *ibid.*, **83**, 4501 (1961); S. J. Strickler and K. S. Pitzer, "Molecular Orbitals in Chemistry, Physics, and Biology," B. Pullman and P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1964, p 281; E. Clementi and H. Clementi, *J. Chem. Phys.*, **36**, 2824 (1962).

(10) H. Muller, *Z. Chem.*, 10, 369 (1963); R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

(11) M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, *J. Chem. Phys.*, **43**, 3734 (1965).

(12) A calculation of the vibrational frequencies in C_4, C_5, and C_6 has been attempted by R. H. Sanborn, *ibid.*, **49**, 4219 (1968). Recently, the force constants of C_2, C_3, and C_5 have been calculated by M. J. S. Dewar, E. Haselbach, and M. Shanshal, *Angew. Chem., Int. Ed. Engl.*, **9**, 738 (1970).

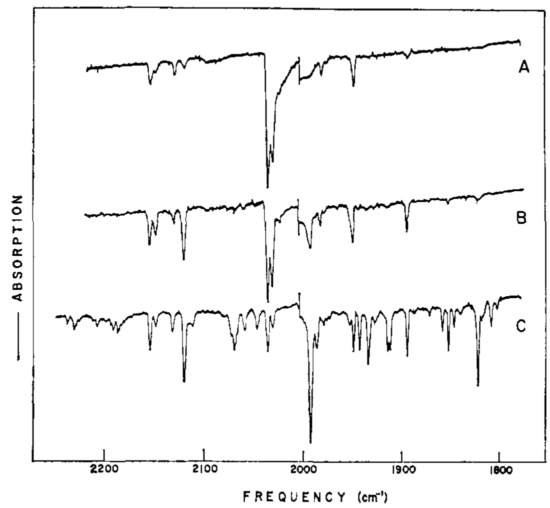

Figure 1. Infrared spectra of carbon-12 vapor trapped in solid argon at 4°K: (A) original matrix, (B) after "weak" diffusion, (C) after "strong" diffusion.

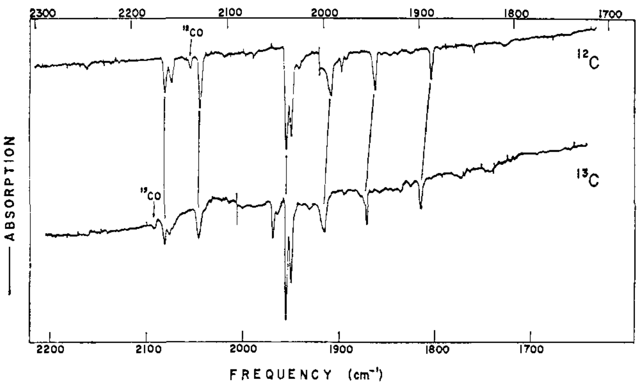

Figure 2. Infrared spectra of carbon vapor trapped in solid argon at 4°K: top, carbon-12 vapor; bottom, 95% isotopically enriched carbon-13 vapor.

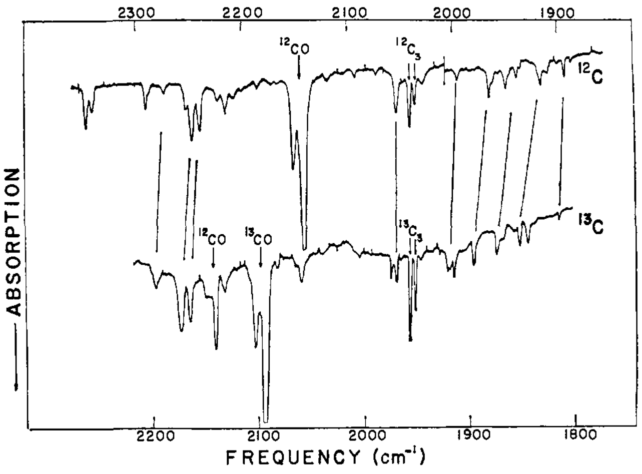

Figure 3. Infrared spectra of trapped carbon vapor, containing CO species, after weak diffusion: top, vaporization of carbon-12; bottom, vaporization of carbon-13.

and maintained as a carbide by a sufficiently large carbon sample. Rapid pumping was necessary to thoroughly outgas the sample of CO_2 and H_2O. CO could never be completely removed but was always observed at least as a weak band in the ir.

If these experiments are carried out with a tantalum cell containing no hole in the cylindrical 0.008-in. thick wall, vaporization of carbon takes place only from the tantalum carbide surface (see II). The vapor then consists of only carbon atoms and tantalum atoms, plus CO, which is especially difficult to pump out with this cell design. Attempts to improve the outgassing of the graphite by putting holes in the tantalum end plugs did not seem to help very much. In order to obtain a sufficient vapor pressure of carbon during these runs, the surface temperatures ranged from about 2900 to about 3300°K, *i.e.*, considerably higher than in those runs where the cells approximated Knudsen cell behavior.

Carbon-13 graphite, 96% enriched, was obtained from the Monsanto Co. (Mound Laboratory, Miamisburg, Ohio). Natural carbon (99% carbon-12) was ground from spectroscopic grade graphite rods (Carbon Division, Union Carbide Corp.). Research grade argon was used in all matrix experiments reported here. It was precooled to 77°K just prior to entering the dewar at a flow rate of about 0.5 l. (STP)/hr. The matrix to trapped molecule ratio (M/A) was estimated to vary from about 1000 to 10,000 during these runs.

The infrared spectra reported here were measured with a Perkin-Elmer 621. The instrument was calibrated using standard gases, and the absolute accuracy of the reported bands is considered to be ± 0.5 cm^{-1}. Ultraviolet and visible spectra were recorded using a Jarrell-Ash 0.5-m Ebert spectrograph with appropriate sources and photomultipliers.

Results

Ir Spectra. The infrared spectra observed were dependent upon the amount of CO trapped in the matrix, and it became apparent that thorough outgassing was needed to obtain good spectra of "pure" carbon molecules. When this was done the spectra shown in Figure 1 were obtained, where only a small CO band occurs at 2138 cm^{-1}. The spectrum of the originally prepared matrix is shown in A; two bands not shown in that figure occur at 1544 and 1197 cm^{-1}. The C_3 doublet at 2038–2034 cm^{-1} is very strong. A "weak" diffusion, brought about by raising the temperature to about 15°K, causes the changes seen in spectrum B. A "strong" diffusion to about 30°K, as shown in C, leads to a drastic weakening of the C_3 bands and, most notably, a large increase in a band at 1997 cm^{-1}. The bands not shown at 1544 and 1197 cm^{-1} continue to grow during the strong diffusion.

Figure 2 compares the spectra of ^{12}C and ^{13}C molecules after weak diffusions; the scales have been shifted to make the similarity evident. (The doublet at 1972 cm^{-1} in the ^{13}C spectrum is due to the ^{13}C–^{13}C–^{12}C species arising from the presence of ^{12}C isotope in the ~95% ^{13}C-enriched graphite.[13] Correspondingly, a small band in the ^{12}C spectrum at 1985 cm^{-1} is due to the ^{12}C–^{13}C–^{12}C molecule from the 1% of ^{13}C in natural carbon. Contributions from ^{13}C–^{12}C–^{12}C are hidden in the large shoulder on the low-frequency side of the $^{12}C_3$ band.)

Figure 3 shows the same region of the infrared spectrum of a ^{12}C matrix containing a large amount of ^{12}CO resulting from insufficient outgassing of the graphite. A CO_2 band also appears at about 2350 cm^{-1} in the original matrix. One can see that the bands dominating the "pure" carbon spectrum after diffusion, *e.g.*, those at 2128 and 1997 cm^{-1}, are much less intense in the spectrum of the CO-containing matrix. Also compared are the ^{12}C and ^{13}C spectra of two matrices containing a large amount of CO; each matrix has been diffused to some extent. The ^{13}C spectrum contains some ^{12}CO arising from the small percentage in the graphite and probably also from $^{12}CO_2$ from the walls of

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(13) W. Weltner, Jr., and D. McLeod, Jr., *J. Chem. Phys.*, **40**, 1305 (1964).

the furnace. Some prominent bands produced by the presence of CO are (for ^{12}C) at 2243, 2052, 1969 (CCO), and 1831 cm^{-1}.

Matrices were also prepared by vaporization of carbon from a thin-walled tantalum cell packed with graphite powder but with no orifice. As in III, the object of such experiments was to vaporize the carbon "through" the tantalum, forming a vapor consisting entirely of carbon atoms (plus perhaps some tantalum atoms). The matrix containing carbon atoms was then warmed to allow the C_n species to form. The difficulty is that here, even more so than in the other vaporizations, any CO impurity is very detrimental to the formation of larger carbon molecules. This is aggravated by the fact that the complete enclosure of the carbon by tantalum makes the outgassing more difficult (see Experimental Section).

It is known that C atoms react readily with CO to form the CCO radical,[11] which is easily identified by a band at 1969 cm^{-1}. This reaction competes with those leading to the formation of C_2, C_3, etc., and if the CO is present in large quantity, continued diffusion leads to the formation of C_3O_2 (indicated by bands at 2289, 2272, and 1595 cm^{-1} in argon)[11,14] and perhaps other C_nO species.[11] This, of course, depletes the C atoms in the matrix and leads to new bands of molecules containing oxygen. Even in the original matrix, because of the rapid diffusion of C atoms, C_3 (2038 cm^{-1}) and CCO (1969 cm^{-1}) are present. Upon diffusion, the most prominent band to grow in is at 2243 cm^{-1}; it is believed to be C_3O, but this remains to be proven.

Isotopic Molecules. The use of highly enriched ^{13}C graphite to investigate the ir spectra of carbon polymers is necessary because of the large number of mixed-isotope species that could result if a nearly equal mixture of ^{12}C and ^{13}C isotopes were vaporized. The six C_3 molecules possible if ^{12}C and ^{13}C atoms can take all positions in the molecule have been observed previously.[13] This number rises rapidly for the larger carbon species; for example, it is ten for C_4, and the allowed ir bands for each of these ten molecules would be spread over about 85 cm^{-1}. With many carbon molecules present, the analysis would become very difficult. Nevertheless, the observation of some mixed-isotope species would be valuable since the spectra of pure ^{12}C and pure ^{13}C molecules can give no information other than to identify the bands as belonging to a "pure" carbon molecule, that is to one containing no oxygen. Thus, assuming linear molecules, the Teller–Redlich product rule for two completely isotopically substituted carbon species reduces to simply[15] (primed are ^{13}C)

$$\frac{\nu_1'\nu_2'\ldots\nu_j'}{\nu_1\nu_2\ldots\nu_j} = \left(\frac{m}{m'}\right)^{j/2} = (0.9606)^j$$

The right-hand side is 0.9606 for the one Σ_u^+ vibration in C_3 or C_4; it is $(0.9606)^2$ for the two allowed stretching frequencies of C_5 and C_6, etc. Furthermore, for these linear symmetric C_n molecules, it can be shown that for *each* individual frequency

$$^{13}\nu_i/^{12}\nu_i = 0.9606$$

(This number will be raised slightly in the observed frequencies because of anharmonicity.) Hence it is a necessary condition that each vibrational frequency $^{12}\nu_i$ in the $^{12}C_n$ molecules be lowered to about $0.961 \cdot (^{12}\nu_i)$ in the corresponding $^{13}C_n$ molecule, so that all frequencies corresponding to "pure" carbon molecules can be identified in this way. Table I lists all of the observed bands which can be attributed to "pure" carbon molecules.

Table I. Vibrational Frequencies of Carbon Molecules in an Argon Matrix at 4°K

$^{12}C_n$, cm^{-1}	$^{13}C_n$, cm^{-1}	$^{13}C/^{12}C$[a]	Molecule
2164	2081	0.9616	C_4
2128	2046	0.9615	C_9
2039	1959	0.9608	C_3
1997	1920	0.9614	C_6
1952	1877	0.9616	C_5
1893	1821	0.9620	C_9
1844	1774	0.9620	
1818	1748	0.9615	
1804	1737	0.9629	
1715	1649	0.9615	
1696	1631	0.9617	
1601	1540	0.9619	
1589	1531	0.9635	
1544	1484	0.9611	C_5
1447	1391	0.9613	C_9
1284	1236	0.9626	
1197	1151	0.9616	C_6

[a] Theoretical ratio, for pure C_n species, is 0.9606. Anharmonicity causes the observed values to be slightly higher.

As indicated above, the complete substitution of ^{13}C for ^{12}C in the carbon polymers serves to identify the bands arising from "pure" carbon molecules, but such isotopic substitution does not give any clues as to the assignment of these bands to the individual polymers. However, molecules containing both ^{12}C and ^{13}C can yield this information if the bands arising from the many possible species can be detected or if the number of isotopic species formed is limited.

If one has present only a relatively small amount of ^{12}C in the ^{13}C graphite, as occurs in the 95% isotopically pure solid, then only molecules containing one, or possible two, ^{12}C-substituted atoms will be produced during vaporization. For example, as pointed out in connection with Figure 2, when 95% ^{13}C graphite is vaporized, an intense doublet band occurs at 1959–1954 cm^{-1} due to $^{13}C_3$, but another weaker doublet appears at 1973–1969 cm^{-1} due to ^{12}C–^{13}C–^{13}C and a still weaker doublet at 2014–2010 cm^{-1} due to ^{13}C–^{12}C–^{13}C. These bands arising from substitution of one ^{12}C in the $^{13}C_n$ molecules should then appear in all of the ir spectra produced by vaporization of 95% ^{13}C graphite on the high-frequency side of the identified "pure" carbon bands. Figure 4 indicates these satellites more clearly. Some are quite definite, as for example a band at 1934 cm^{-1} appearing with that of 1920 cm^{-1}, while others are in more crowded regions and harder to identify. The observed bands designated in Figure 4 are listed in Table II; 5% ^{12}C in the ^{13}C appears to be about optimum, since a run made by mixing 15% ^{13}C with ^{12}C yielded too many isotopically substituted C_3 molecules and diffusion led to a corresponding plethora of larger molecules.

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(14) W. H. Smith and G. E. Leroi, *J. Chem. Phys.*, 45, 1767 (1966). We have prepared C_3O_2 and trapped it in an argon matrix at 4°K. These two bands are from our observations.

(15) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945.

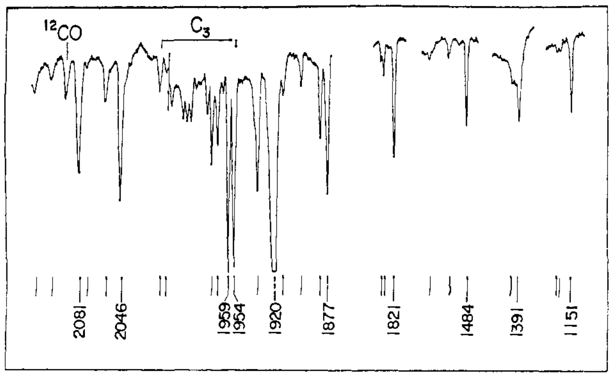

Figure 4. Infrared spectrum of 95% enriched ^{13}C vapor trapped in argon at 4°K showing bands due to mixed ^{12}C–^{13}C molecules.

Identification and Vibrational Assignments.[16] One now has two sets of experimental information plus some theoretical expectations to aid in the assignment of Σ_u^+ stretching frequencies. The experimental data comprise (1) the sequence of appearance of the bands as diffusion is allowed to occur and (2) the observed mixed-isotope frequencies. The crude calculated frequencies given in Figure 8 of III can still serve as a guide in making initial assignments; however, the asymptotic frequency given there is clearly too high, since bands do not appear in the spectra above 2250 cm^{-1} (for ^{12}C) even after strong diffusion.

Table II. Observed and Calculated Shifts (Δ) of Mixed-Isotope Molecules Formed from 95% ^{13}C-Enriched Graphite (see Figure 4)

"Pure" $^{13}C_n$ bands, cm^{-1}	Mixed-isotope $^{12}C_m{}^{13}C_{n-m}$ bands,[a] cm^{-1}	Δ(obsd),[b] cm^{-1}	Assigned C_n molecule	Δ(calcd),[c] cm^{-1}
1151			C_6	0
	1161	10		11*
	1163	12		12*
1391	1395	4		
	1397	6		
1484			C_5	2*
	1499	15		13*
	1514	30		22
1821			C_9	4*, 4*,
	1830	9		4, 15,
	1832	11		15
1877	1883	6	C_5	4*
	1899	22		22*
	1915	38		32
1920			C_6	2*
	1934	14		15*
				27
1954	1968	14	C_3	14*
1959	1972			
2046	2059	13	C_9	1*, 7,
	(2075)	(29)		15*,
				19, 20
2081	2105	24	C_4	19*
	(2118)	(37)		21*

[a] Observed bands appearing as satellites to the $^{13}C_n$ bands in column 1. These bands are expected to be those for $m = 1$ molecules, since there is only a small amount of ^{12}C present. [b] Difference between band positions in column 2 and the $^{13}C_n$ band in column 1. [c] Calculated shifts of satellite bands produced by all possible mixed-isotope molecules containing one ^{12}C atom. For example, for C_6, these are ^{12}C–$^{13}C_5$, ^{13}C–^{12}C–$^{13}C_4$, and $^{13}C_2$–^{12}C–$^{13}C_3$. The bands corresponding to Δ's marked with an asterisk are expected to be more intense; those unmarked belong to mixed-isotope molecules which will be present in low concentration.

The assignments to specific molecules rely partially upon the behavior of the observed bands upon diffusion and this depends upon the initial concentrations, mobilities, and kinetics of reaction of these species. As before, we assume that all carbon molecules can react with one another with essentially zero energy of activation so that the formation of C_n is determined purely by the mobilities and concentrations of its precursors. In general this approach is supported by the observed spectra if the vibrational frequencies approximately conform to the pattern in III.

When graphite is being vaporized, mass spectrometric measurements[7] indicate that the vapor is about 60 mol % C_3, 25% C, and 15% C_2. Since other bands than the $^{12}C_3$ band at 2039–2035 cm^{-1} are observed in the original matrix in Figure 1A, these must be due to C_4, C_5, and C_6. Three-body collisions are required to make C_7, C_8, C_9, . . . so that they can be expected to be absent or very weak initially. Since C_3 is present in such large concentration, one expects it to be depleted last and C_6 to continue to grow as long as C_3 is present. From such reasoning one can make the following assignments, beginning with the originally observed spectrum of identified carbon-12 molecules given in column 1 of Table I.

C_4. Among the initially observed bands there are three choices for the one allowed Σ_u^+ stretching frequency of $^{12}C_4$, these being the bands at 2164, 1952, or 1893 cm^{-1}. The bands at 2128 and 1997 cm^{-1} continue to grow on diffusion and eventually are very strong, so that they must be due to larger species. (The band at 1893 cm^{-1} could probably also be placed in this latter category, but it can easily be eliminated by the mixed-isotope evidence discussed here.)

To choose from among these three, one must now refer to the bands observed when mixed-isotope molecules are formed (see Table II) and compare them with calculated band positions for C_4 species. Let us suppose that we select 2164 cm^{-1} as the Σ_u^+ frequency for $^{12}C_4$. Then for a general force field,[15] one can immediately calculate $f_R - f_{RR} = 16.55$, where R refers to the two outer bonds. This force constant along with assumed values for f_r, f_{Rr}, and f_{RR} may then be used to calculate the frequencies for all of the ten mixed-isotope molecules between $^{12}C_4$ (2164 cm^{-1}) and $^{13}C_4$ (2081 cm^{-1}). (Subscript r here refers to the one inner C–C bond.) However, the only molecules which will appear with any intensity other than $^{13}C_4$ when 95% enriched ^{13}C is vaporized will be those containing one ^{12}C atom, ^{12}C–^{13}C–^{13}C–^{13}C and ^{13}C–^{12}C–^{13}C–^{13}C. So, for example, if one chooses $f_R = 16.55$, $f_{RR} = 0.0$, etc., as in Table III, the frequencies given there are calculated for these two mixed molecules. f_R–f_{RR} is always chosen equal to 16.55 so as to give $^{12}C_4$ and $^{13}C_4$ correctly. Relative to $^{13}C_4$, the mixed molecules should then, according to this force field, produce two satellite lines at higher frequency by about 21 and 19 cm^{-1}. Now this force field can be varied greatly, but these two lines are always calculated to lie about 2 cm^{-1} apart and to vary from about 18 to 22 cm^{-1} in the average value of the shift Δ. Note also that the intensity of the

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(16) In the discussion of vibrational force constants, they will always be given in millidynes per ångström.

Table III. Calculated Mixed-Isotope and Σ_g^+ Frequencies for C_4[a]

	Σ_u^+ frequency, cm^{-1}	Δ,[b] cm^{-1}	Σ_g^+ frequencies, cm^{-1}	
$^{12}C_4$	2164.3		2568.0	1096.9
$^{12}C{-}^{13}C_3$	2100.3	21.2		
$^{13}C{-}^{12}C{-}^{13}C_2$	2098.5	19.4		
$^{13}C_4$	2079.1		2466.9	1053.8

[a] Taking f_R = 16.55 mdyn/Å, f_r = 12.0, f_{rR} = 0.5, f_{RR} = 0.0. [b] Frequency for mixed-isotope molecule minus that for $^{13}C_4$.

$^{12}C{-}^{13}C_3$ band should be at least twice that of the $^{13}C{-}^{12}C{-}^{13}C_2$ molecule, since its formation is favored by the $^{13}C_3$ + ^{12}C reaction. Then, independent of the force field, one should observe a doublet, or more exactly, one band with a shoulder, about 20 cm^{-1} toward higher frequency from the $^{13}C_4$ band. This should serve as identification.

These calculated properties of the C_4 spectrum are now compared with the satellite bands observed near the $^{13}C_n$ band at 2081 cm^{-1}. Table II and Figure 4 show that there is one satellite observed at 2105 cm^{-1}, Δ = 24 cm^{-1} higher in frequency. (Also indicated is a weak band shifted by 37 cm^{-1} which is actually a shoulder on a group of overlapping bands in that region. This shift is only shown to indicate the frequency gap to the next nearest band.) This is then in satisfactory agreement with expectations and the choice of 2164 cm^{-1} for the $^{12}C_4$ stretching frequency is a reasonable one.

If this same procedure is applied to the choice of 1952 or 1893 cm^{-1}, for $^{12}C_4$ one finds that the calculated shifts for the two mixed molecules are about 19 and 17 cm^{-1}, not very different from those for the 2164-cm^{-1} choice. However, the observed satellite bands for their ^{13}C counterparts, 1877 and 1821 cm^{-1}, given in Table III, are not in agreement with calculations. There are three satellite bands next to the 1877 cm^{-1} band which are particularly distinct, while the two next to the 1821 cm^{-1} band are only shifted by Δ = 9 and 11 cm^{-1} (see Figure 4). Force-field changes cannot account for these discrepancies. Hence it appears that the most likely choice for the ir-allowed stretching frequency of $^{12}C_4$ is at 2164 cm^{-1}, yielding $f_R - f_{RR}$ = 16.55.

C_5. Its two ir-allowed stretching frequencies are expected to lie near 2100 cm^{-1} and 1400 cm^{-1} (see Figure 8 of III). Having eliminated 2164 cm^{-1} as $^{12}C_4$, the most logical choice is then the initially observed bands at 1952 and 1544 cm^{-1}. As will be seen, the mixed-isotope shifts corroborate this choice; however, first consider the vibrational analysis based upon these frequencies.

The analysis here (and for C_6) is interesting in indicating the critical nature of the interaction force constants. If one uses the general expression for Σ_u^+ vibrations as given by Smith and Leroi for C_3O_2,[14] along with the observed ν = 1952 and 1544 cm^{-1}, but neglects interaction force constants, no real solutions are obtained for the stretching force constants $f_1 = f_R - f_{RR}$ (R = outer bond) and $f_2 = f_r - f_{rr}$ (r = inner bond). It is found that $f_{12} = f_{Rr_1} - f_{Rr_2}$ must be at least +1.909 in order to obtain real values for f_1 and f_2 and, in that case, one obtains f_1 = 11.90 and f_2 = 7.93. f_{Rr_1} is between adjacent and f_{Rr_2} between nonadjacent bonds. For the extreme case where all bonds are considered equal and only adjacent-bond interaction constants are nonzero, one finds $f_R = f_r$ = 10.88 and $f_{Rr} = f_{rr}$ = 2.12.

Either of these force fields will give frequencies for the mixed-isotope molecules which approximately fit the observed satellites for the corresponding two $^{13}C_5$ bands at 1877 and 1484 cm^{-1}. The most intense bands will be produced by the three molecules $^{12}C{-}^{13}C_4$, $^{13}C{-}^{12}C{-}^{13}C_3$, and $^{13}C{-}^{13}C{-}^{12}C{-}^{13}C{-}^{13}C$, and if one considers all possible routes for their formation, the first two should be more concentrated by a factor of about 5 than the symmetrically substituted molecule.

If the observed shifts in Table II are used, one can specify eight independent frequencies (Δ = 1 cm^{-1} is assumed for the $^{13}C{-}^{12}C{-}^{13}C_3$ molecule relative to the 1484 cm^{-1} band) and the force constants calculated which provide the best fit. Only the f_{RR} force constant was neglected. The results are given in Table IV.

Table IV. Calculated and Observed Σ_u^+ Frequencies and Calculated Σ_g^+ Frequencies for C_5[a]

Molecule	Σ_u^+ frequencies Obsd ν, cm^{-1}	Calcd ν, cm^{-1}	Diff, cm^{-1} [b]
12–12–12–12–12	1952	1953.7	−1.67
	1544	1545.5	−1.48
12–13–13–13–13	1881	1880.3	0.69
	1498	1497.6	0.44
13–12–13–13–13	1897	1898.5	−1.45
	1484	1486.5	−2.45
13–13–12–13–13	1913	1908.8	4.25
	1513	1507.8	5.18
13–13–13–13–13	1875	1876.8	−1.66
	1483	1484.7	−1.78

[a] Using the force constants, mdyn/Å (calculated dispersion): f_R = 10.95 (0.169), f_r = 5.66 (2.80), f_{Rr} = 2.10 (0.08), f_{rr} = −3.06 (2.80). [b] Obsd ν − calcd ν. Calculated Σ_g^+ frequencies for $^{12}C_5$, cm^{-1} (calculated dispersion): 1641.3 (111.5), 422.4 (511.6).

Agreement is satisfactory except for the symmetrical 13–13–12–13–13 molecule. The large dispersion for f_r and f_{rr} indicates the relative insensitivity of the calculations to variations in these two parameters, so that they must be considered as only very roughly determined.

C_6. The band at 1997 cm^{-1} continues to grow and becomes the strongest band in the spectrum as the $^{12}C_3$ band decreases. It and the original weak band at 1197 cm^{-1} are assigned to $^{12}C_6$.

The general force analysis is analogous to that for diacetylene.[17] As in C_5, the neglect of interaction force constants again yields imaginary stretching force constants for the assignment of 1197 and 1997 as Σ_u^+ vibrations. The force constant (f_m) for the central bond does not enter into the calculation so that we will again designate $f_1 = f_R - f_{RR}$ (R = outer bond) and $f_2 = f_r - f_{rr}$ (r = adjacent bond). Real values of f_1 and f_2 are only obtained for $f_{12} \geqslant 0.354$, where f_{rm} is assumed equal to f_{Rr}. When the equality holds $f_1 = f_2 = 9.758$.

There is one strong mixed-isotope band at 1934 cm^{-1} very distinctly associated with the 1920-cm^{-1} band here assigned to $^{13}C_6$. (It resembles in intensity the $^{12}C{-}^{13}C{-}^{13}C$ band relative to that of $^{13}C_3$.) Both the 1934- and the 1920-cm^{-1} bands are not of gaussian shape but

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(17) A. G. Meister and F. F. Cleveland, *J. Chem. Phys.*, **15**, 349 (1947).

have a shoulder on the high-frequency side. The most intense mixed-isotope molecules derived from the 95% ^{13}C-enriched graphite would be expected to be ^{12}C–^{13}C$_5$ (A) and ^{13}C–^{13}C–^{12}C–^{13}C$_3$ (B). The molecule 13–12–13–13–13–13 would be present at much lower concentration, since 13–12–13 is present in the matrix in much smaller amount than 13–13–12, as can be seen by the relative strength of their two bands at 2014 and 1972 cm^{-1}, respectively.

Using almost any force field with the 1197 and 1997 frequencies for ^{12}C$_6$, one calculates that the larger stretching frequency for B above lies within a few reciprocal centimeters of that for ^{13}C$_6$, so that it probably contributes to the shoulder on the high-frequency side of the 1920-cm^{-1} band, let us say with $\Delta = 2$ cm^{-1}. From such calculations one can then also assign the two satellite bands of 1151 cm^{-1} to A or B. The final assigned bands are listed in Table V, column 2.

Table V. Calculated and Observed Σ_u^+ Frequencies and Calculated Σ_g^+ Frequencies of C$_6$[a]

Molecule	Σ_u^+ frequencies Obsd ν, cm^{-1}	Calcd ν, cm^{-1}	Diff, cm^{-1}
12–12–12–12–12–12	1997	1997.9	−0.89
	1197	1197.4	−0.36
12–13–13–13–13–13	1932	1931.3	0.71
	1160	1159.1	0.94
13–13–12–13–13–13	1922	1921.8	0.16
	1163	1163.5	−0.52

[a] Using the force constants, mdyn/Å (calculated dispersion): $f_R = f_m = 11.887$ (0.29), $f_r = 8.064$ (0.19), $f_{Rr} = f_{rm} = 0.783$ (0.11). [b] Obsd ν − calcd ν. Calculated Σ_g^+ frequencies for ^{12}C$_6$, cm^{-1} (calculated dispersion): 2137.7 (15.8), 1834.3 (22.7), 641.9 (3.6).

Finally, the force field can be varied to fit the observed frequencies. A very successful fit could be made by letting $f_R = f_m = 11.89$ and $f_r = 8.064$, with all adjacent interaction constants equal to 0.783. These parameters fit all six frequencies to better than 1 cm^{-1}, as shown in Table V.

C$_7$, C$_8$, and C$_9$. The ^{12}C spectra exhibit three bands at 2128, 1893, and 1447 cm^{-1} which appear relatively early and grow in at the same rate. These would then be assigned to one of the molecules C$_7$, C$_8$, or C$_9$. Crude vibrational calculations indicate that reasonable force constants can be found for each of these molecules to yield frequencies approximately matching the three above, so that a choice cannot be made on that basis. Also, although isotope shifts are observed for the ^{13}C counterparts of the bands (at 2046, 1821, and 1391 cm^{-1}; see Table II), the calculations cannot be made accurately enough to utilize those data.

On the basis of concentration alone, C$_3$ being such a dominant species originally, it seems likely that C$_9$ would be the most likely candidate. For the very simple force field where all bond force constants f_i are equal, all adjacent-bond interaction constants f_{ij} are equal, and all others are zero, $f_i \cong 8.6$ and $f_{ij} \cong 0.5$ will fit the observed frequencies to about 50 cm^{-1}. The fourth Σ_u^+ frequency is calculated to lie near 800 cm^{-1}, beyond our limit of investigation.

Discussion

Probably the most reliably identified molecule in this investigation is C$_6$. It is rapidly and dominantly formed during the diffusion process, its growth correlating well with the decrease in intensity of C$_3$. Its mixed-isotope molecules yield distinctive shifts, and the final fit of a reasonable set of force constants is more than satisfactory (see Table V). An attempt was made to generalize the force field, but the computation diverged and no progress was made beyond the results given in Table V. However, alternating carbon-bond force constants of 11.9 and 8.06 for C$_6$ are about what one would expect when extrapolating from its smaller even-membered chain, C$_4$. Using these force constants, the Raman-active Σ_g^+ vibrational frequencies were calculated and are given in Table V. The Σ_g^+ frequencies are poorly determined in all of these molecules because they depend principally upon force constants which are relatively insensitive to the observed Σ_u^+ frequencies.

The mixed-isotope species and their shift in frequency relative to ^{13}C$_4$ were critical in identification of the Σ_u^+ ^{12}C$_4$ frequency at 2164 cm^{-1}. This is a surprisingly high frequency and indicates that the outer bond is a strong C≡C with $f_R \cong 16.6$. This is slightly stronger than the corresponding bond in diacetylene[18] (perhaps as high as 16.2) or acetylene[19] (15.80). This force constant, or rather $f_R - f_{RR}$ (f_{RR} is expected to be small[20]), is exactly determined by this frequency, but the other force constants in the molecule are very insensitive to the mixed-isotope frequencies and cannot be determined. Raman data, providing Σ_g^+ frequencies, are required to improve the computation. The force constant found here is in agreement with the theoretical model ·C≡C—C≡C· proposed by Strickler and Pitzer[9] and supported by Hoffmann's calculations.[10] It does not support the completely double-bonded molecule suggested by the calculations of Clementi and Clementi.[9]

Similar difficulties in the calculation of force constants also occur in C$_5$, as is shown in Table IV. The values of $f_R = 10.95$ and $f_{Rr} = 2.10$ are rather reliably calculated, as indicated by the low values of the dispersion for these two parameters; however, f_r, the inner-bond constant, and f_{rr} are quite insensitive to the data supplied. The fit is good, but then setting $f_R = f_r = 10.88$ and $f_{Rr} = f_{rr} = 2.12$ provides almost as good a fit. However, the force constants that are obtained are reasonable and in essential agreement with those expected from C$_3$O$_2$.[14]

One might expect that there will be a gradual equalization of the carbon bonds as these chain molecules become longer and a gradual approach to some asymptotic force constant. If our assignment of C$_9$ is correct, the asymptote would lie near 8.6. Hoffmann's calculations[10] on long-chain C$_n$ molecules, out to C$_{17}$, do not support such a picture for this assumed bonding in C$_9$. He finds that there should still be a large bond alternation in C$_9$ with a large "end effect." Unfortunately, our data do not allow a test of his theory.

Now that the stretching frequencies of these molecules have been identified, attention should be turned to the establishment of their bending frequencies. These will be more difficult to observe and identify since some are quite low. Sanborn[12] has recently discussed the

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(18) S. M. Ferigle and A. Weber, *J. Chem. Phys.*, 21, 722 (1953).
(19) Reference 15, p 180.
(20) Reference 15, p 189.

correlation of the bending frequencies among similar linear molecules and has proposed a set of frequencies for C_4, C_5, and C_6.

It should be mentioned here that some electronic transitions of these carbon molecules were observed in the region of 5500–2500 Å, but the identification of the molecules producing the bands is difficult. This is an area worthy of more experimental and theoretical research, since the spectra of these molecules might be observable in stars or comets.

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Structure and Conformation of Thorium(IV) Complexes of Diethylenetriaminepentaacetic Acid in Aqueous Solution[1]

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Abstract: The aqueous (D_2O) infrared and proton nmr spectra of the 1:1 complexes of thorium(IV)–diethylenetriaminepentaacetic acid (DTPA) have been studied as a function of "*a*" value (*a* = moles of base added/mole of metal ion). On the basis of ir and nmr data, plausible solution structures are proposed and compared with proposed structures from previous potentiometric studies. Unlike the 10^{-3} *M* potentiometric study of Th(IV)–DTPA at *a* = 0, the 0.10 *M* ir and nmr spectra at *a* = 0 confirm the presence of a 1:1 complex in which the ligand is pentadentate. A structure is proposed for the 1:1 DTPA complex at *a* = 5 (pD 5.3) on the basis of the nmr spectra. Infrared and nmr data for the complex at *a* = 6 (pD 10.24 indicate that the monohydroxo chelate is nine-coordinate.

The detection of the formation of mononuclear and polynuclear chelates of multidentate ligands of Th(IV) ion in aqueous solution and determination of equilibrium constants for their formation, hydrolysis, and polymerization reactions have led to the need for further information about the structure and conformation of the molecular species in solution. The development of fundamental understanding of the nature of these chelate compounds requires microscopic information about the specific metal–donor bonds formed, relative coordinate bond strengths, and their steric configuration with respect to both the coordination sphere of the metal ion and the multidentate structure of the ligand. The combination of potentiometric data of these chelates with the corresponding infrared and proton magnetic resonance spectra under varying solution conditions provides the method for obtaining microscopic information about substances in solution. The nmr spectra are of particular importance because they can provide information about stoichiometry, structures, and certain bonding features of the complexes.

The basic principles of the application of proton nmr to the elucidation of bonding in labile metal chelates of aminopolycarboxylic acids have been described by Reilley[3] and Sawyer.[4] The proton nmr spectra of the ethylenediaminetetraacetic acid complexes of zirconium(IV), hafnium(IV), and palladium(II) in aqueous solution have been described by Aochi and Sawyer.[5] Recently Smith and Betts[6] have isolated a cobalt(III)–DTPA complex and proposed a solution structure using proton nmr spectroscopy. A particularly successful example of structure determination of complexes in solution by nmr has recently been reported for Al(III) chelates of vitamin B_6 Schiff bases by Abbott and Martell.[7]

Nakamoto[8] and coworkers have explained the structures of the predominant species in solution of various aminopolycarboxylic acid chelates at various pH values by combining the results of infrared studies with those of potentiometric titrations. The following antisymmetric carboxylate stretching frequencies were found:[9] type A, un-ionized carboxyl (R_2N–CH_2COOH), 1730–1700 cm^{-1}; type B, α-ammonium carboxylate (R_2N^+H-CH_2COO^-), 1630–1620 cm^{-1}; type C, α-amino carboxylate (R_2N–CH_2COO^-), 1595–1575 cm^{-1}. In these investigations they also establish that coordinated carboxyl groups absorb between 1650 and 1590 cm^{-1}, the exact frequency depending on the nature of the metal. This technique was later extended to various complexes containing amide carbonyl groups by Kim and Martell. This work was recently summarized.[10]

Previous potentiometric studies of the interaction of Th(IV) ion with ethylenediaminetetraacetic acid

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