

Ab initio study of the infrared spectra of linear C_n clusters (n=6–9)

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The harmonic frequencies, infrared intensities, and isotopic substitution bands of C₆ have been evaluated at the MP2/6-31G* level. They confirm previous assignments of the 1952 and 1197 cm⁻¹ matrix IR bands to C₆. Isotopic substitution spectra at the MP2/6-31G* and HF/4-21G levels, as well as those with a newly developed *ad hoc* modified neglect of diatomic overlap (MNDO) method are shown to be in good agreement with experiment for C₄, C₅, and C₆. On the basis of RHF/4-21G, RHF/6-31G*, MP2/4-21G, MP2/6-31G*, and *ad hoc* MNDO data, including theoretical frequencies, IR intensities, and isotopic substitution spectra, it is shown with virtual certainty that the 2128 and 1893 cm⁻¹ matrix IR bands belong to C₇. A recent assignment of the very intense 1997 cm⁻¹ matrix IR feature to C₈ is contradicted on the same grounds, and an alternative assignment to C₉ put forward.

I. INTRODUCTION

In view of their large interest in astrophysics, materials science, and in combustion processes, among other subjects, carbon clusters have been studied rather extensively over the years: the situation up to April 1989 has been reviewed by Weltner and Van Zee.¹

C₂² and C₃³ are well characterized spectroscopically; IR bands in argon matrix of the higher species have been studied as early as 1971 by Thompson, DeKock, and Weltner (TDW).⁴ On the basis of simple force field arguments, TDW suggested an assignment for these bands involving linear species C₄ to C₉. Except for the actual frequencies, isotopic substitution bands from 95% ¹³C-enriched samples, as well as intensity variation upon thermal annealing, were involved in their assignment. In this context, a later study of the annealing behavior of these bands by Krätschmer and Nachtigall (KN)⁵ should also be mentioned.

It was only eighteen years later, that the TDW assignment for C₄ (2164 cm⁻¹) and C₅ (1544 cm⁻¹) was definitively proven to be wrong by correlated *ab initio* calculations on the force field of C₄ (Refs. 6 and 7) and C₅ (Refs. 8–10). The new assignment, which swapped these frequencies, was experimentally proven by Vala *et al.*,¹¹ Bernath *et al.*,¹² and Heath *et al.*¹³ for C₅, and by Shen and Graham¹⁴ for C₄.

Very recently, the present authors (MFG)¹⁵ developed an *ad hoc* modification of the MNDO (modified neglect of diatomic overlap)¹⁶ method that yields good to excellent results for carbon clusters, especially the harmonic frequencies, which consistently overestimate the available experimental matrix IR frequencies by about 40 cm⁻¹ for the linear species.

In combination with their computed IR intensities and

UHF/6-31G* (unrestricted Hartree–Fock) counterparts of these by Raghavachari,¹⁷ as well as computed isotope shifts, MFG attempted a new assignment, and arrived at the conclusion that the TDW assignment should be completely revised. In particular, they proposed reassignment of the 2128 and 1893 cm⁻¹ pair from C₉ to C₇, of the 1952 cm⁻¹ band from C₅ to C₆, confirmed the assignment of the 1197 cm⁻¹ band to C₆, whereas the very intense 1997 cm⁻¹ feature was reassigned from C₆ to C₉.

After going to press of that work, a preprint by Vala, Chandrasekhar, Szczepanski, and Pellow (VCSP)¹⁸ reached us in which an assignment of 1952 cm⁻¹ to C₆ was proposed on experimental grounds, as well as, “with less certainty,” of 1997 cm⁻¹ to C₈. The former result is in agreement with MFG, the latter is not.

The purpose of the present work is threefold: (a) to seek confirmation for the C₆ assignments; (b) to clarify the situation for C₇, C₈, and C₉ on *ab initio* grounds, and (c) to find out whether the same or different conclusions are reached in the *ad hoc* MNDO study by MFG.

II. METHODS, RESULTS, AND DISCUSSION

A. The C₆ molecule

The harmonic force field was computed numerically from analytical MP2 gradients¹⁹ using the GAUSSIAN 86 program system²⁰ running on an IBM/FPS configuration at the Facultés Universitaires de Namur. The standard 6-31G* basis set^{21,22} was employed. Several bugs in the released FPS version had to be fixed before the calculations could be completed successfully. The final successful calculation, which involved 13 gradient evaluations correlating 36 electrons in 90 orbitals, took about 14 days of CPU time and 800 MB of

disk space. Infrared intensities were obtained by numerical differentiation of the MP2 dipole moment.²³

The stationary point geometry, required for these calculations, was first sought again using analytical gradients. An UHF/6-31G* force constant matrix was employed to initiate the optimization.

As the UHF/6-31G* frequencies or IR intensities for linear C₆ were included neither in the paper of Raghavachari and Binkley (RB)²⁴ nor in the personal communication,¹⁷ we have computed them ourselves using an analytical force constant matrix.¹⁹

Guo and Karplus²⁵ found that MP2/4-21G results for stretching frequencies are on the whole quite acceptable, and that the main influence of polarization functions at this level is found on the geometry and the bending frequencies. As we are basically only interested in the stretching frequencies for the carbon clusters, this result may be useful, since 4-21G (Ref. 26) calculations may still be carried out where MP2/6-31G* would be prohibitive. We have therefore also computed these on the FPS configuration. For comparison,

analytical UHF/4-21G frequencies were computed using GAUSSIAN 88 (Ref. 27) running on a VaxStation 3100 under VMS 5.3.

In order to facilitate comparisons, we have tabulated computed frequencies and IR intensities at all four levels for C₂ to C₅ in Table I. The MP2/6-31G* data are taken from the literature,^{10,6,8} the other values were computed in this work. (The HF/6-31G* frequencies were already published by RB,²⁴ but no IR intensities were given.) Experimental values for C₂ were taken from the Huber and Herzberg compilation,² those for C₃ from the recent work of Hinkle *et al.*²⁸ For C₅, the nearest thing available are the very-high-level calculations of Botschwina and Sebald.⁹ It is evident from Table I that HF/4-21G is definitely no worse, and probably better, than HF/6-31G*. MP2/4-21G leads to false bending distortions, but bending frequencies are only qualitatively reproduced at the other levels as well. Quantitative agreement would not only require anharmonic corrections, but also correlated calculations with basis sets including *f* functions.²⁹ The stretching frequencies, however, are

TABLE I. Computed frequencies (cm⁻¹) for C₂(X¹Σ_g⁺ and a³Π_u), C₃(X¹Σ_g⁺), C₄(X³Σ_g⁻), and C₅(X¹Σ_g⁺). Infrared intensities (km/mol) are given in parentheses for active vibrations.

	HF/4-21G	MP2/4-21G	HF/6-31G*	MP2/6-31G*	<i>ad hoc</i> MNDO ^d	Experiment or high-level <i>ab initio</i>
C ₂ (X ¹ Σ _g ⁺)						
Σ _g	1827	1855	1940	1909	1883	1828 ^e
C ₂ (a ³ Π _u)						
Σ _g	1705	1556	1740	1682	1603	1618 ^e
C ₃						
Σ _u	2324(1182)	2106(419)	2312(1346)	2184(390) ^a	2104(RI 1.0)	2039 ^f
Σ _g	1349	1152	1367	1220 ^a	1301	1224.5 ^f
Π _u	291(0.11×2)	128 <i>i</i>	153(2.1×2)	190(20×2) ^a	383(RI 0.0)	63.4 ^f
C ₄						
Σ _g	2357	2085	2345	2149 ^b	2171	
Σ _u	1648(127)	1437(372)	1740(142)	1586(488) ^b	1541(RI 0.2)	
Σ _g	999	900	1021	951 ^b	965	
Π _g	493	242 <i>i</i>	408	419 ^b	447	
Π _u	198(17×2)	94(13×2)	210(26×2)	187(33×2) ^b	200(RI 0.0)	
C ₅						
Σ _u	2405(5811)	2298(1548)	2344(6550)	2358(1243) ^c	2199(RI 4.2)	2169 ^g
Σ _g	2210	1931	2220	2018 ^c	2015	2008 ^g
Σ _u	1601(93)	1381(63)	1632(83)	1471(64) ^c	1528(RI 0.3)	1498 ^g
Σ _g	856	754	863	786 ^c	813	792 ^g
Π _u	825(65×2)	624 <i>i</i>	648(33×2)	487(1.4×2) ^c	689(RI 0.0)	—
Π _g	301	152 <i>i</i>	222	281 ^c	370	—
Π _u	195(2.7×2)	125(17×2)	111(5.2×2)	130(18×2) ^c	151(RI 0.0)	—

^a L. Adamowicz and J. Kurtz, Chem. Phys. Lett. **162**, 342 (1989).

^b D. Michalska, H. Chojnacki, B. A. Hess, Jr., and L. J. Schaad, Chem. Phys. Lett. **141**, 376 (1987).

^c J. M. L. Martin, J. P. François, and R. Gijbels, J. Chem. Phys. **90**, 3403 (1989).

^d J. M. L. Martin, J. P. François, and R. Gijbels, J. Comp. Chem. (in press).

^e K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).

^f K. H. Hinkle, J. J. Keady, and P. F. Bernath, Science **241**, 1319 (1988).

^g P. Botschwina and P. Sebald, Chem. Phys. Lett. **160**, 485 (1989). These results are anharmonic values derived from a quartic stretching-only CEPA-1/8s4p2d potential, the diagonal force constants being scaled for exact reproduction of the gas-phase value of 2169 cm⁻¹ for the highest active band. Corresponding harmonic values are 2198, 2033, 1494, and 800 cm⁻¹. Harmonic bending frequencies at the CEPA-1/7s3p1d level are 570, 209, and 119 cm⁻¹.

quite good for such a relatively limited theoretical model. Also highlighted is the excellent quality of the *ad hoc* MNDO results, where a substantial part of the remaining error is caused by the harmonic approximation (see, e.g., the results for C_5).

The effect of polarization functions on the computed IR intensities is rather large, as could be expected given their importance for dipole moments.

We have also attempted ROHF/4-21G (restricted open-shell Hartree-Fock) frequency calculations using numerical differentiation of an analytical gradient (since no ROHF analytic second derivatives were available). However, these calculations failed because of symmetry breaking problems that were also encountered for the C_3^+ cation by Grev *et al.*³⁰

The MP2/6-31G* geometry of C_6 is compared in Table II with the available literature data, being those at the UHF/3-21G and UHF/6-31G* levels by Raghavachari *et al.*,³¹ the *ad hoc* MNDO (Ref. 15) values by MFG, and the results of Parasuk and Almlöf³² using a 12/12 complete active space SCF (CASSCF).³³ All levels of theory except *ad hoc* MNDO yield bond distances that contract from the outside in, as was already found for C_5 ^{8,9,10} and C_4 .^{6,7,34,35}

The "effective bond distance," as derived from the computed rotational constant, is also included in Table II, for comparison with experiment. To sketch the accuracy of the MP2/6-31G* results, our MP2/6-31G* geometry for C_5 (Ref. 8) yields an r_{eff} of 1.2846 Å, compared to the experimental value (including zero-point effects) of 1.283 Å,¹³ and the "best theoretical estimate" by Botschwina and Sebald of 1.284 Å. In considering the *ad hoc* MNDO results, it should be remarked that the parametrization was based on an older value of 1.287 Å for the r_e of C_3 ,³⁶ compared to a more recent determination of 1.297 Å.²⁸ Applying the difference as a correction term, *ad hoc* MNDO leads to an r_{eff} value for C_5 of 1.284 Å, in excellent agreement with available data. As far as C_6 is concerned, both the MP2/6-31G* and *ad hoc* MNDO values appear to be reasonable; our best estimate is to bracket the experimental value between these.

The MP2/4-21G bond distances, especially the outer one, are apparently seriously overestimated, as would be expected.²⁵

The harmonic frequencies are presented in Table III,

together with the UHF/3-21G (Ref. 31) and *ad hoc* MNDO values from the literature. For the IR active vibrations, intensities in km/mol are given in parentheses; for the *ad hoc* MNDO results, the intensities are relative to the 2039 cm^{-1} band of linear C_3 .

Taking the customary scaling by 0.89 (Ref. 37) into account for the UHF/3-21G, UHF/4-21G, and UHF/6-31G* values, all levels of theory predict an intense IR band around 2000 cm^{-1} , and a less intense band around 1200 cm^{-1} . But whereas the HF calculations predict low intensities for the latter, it is found to have a quite appreciable intensity at the MP2/6-31G* level. Scaling the MP2/6-31G* frequencies by the ratio between the observed C_4 frequency of 1543.4 cm^{-1} (Ref. 14) and the calculated MP2/6-31G* value⁶ of 1586 cm^{-1} , we find frequencies of 1955 and 1210 cm^{-1} , in near-perfect agreement with the proposed 1952 and 1197 cm^{-1} bands. Incidentally, our UHF/4-21G frequencies, scaled by 0.89, are also in good agreement with these band origins. As our reference molecule, linear C_4 , also has significant spin contamination, the effects hereof are at least partially absorbed in the scaling; they will tend to lower computed frequencies,³⁸ which is one of the reasons why the generic scaling factor of 0.93 (Refs. 8 and 39) for MP2/6-31G* frequencies produces too low values, both for C_4 and C_6 .

Although MP2/4-21G produces two false imaginary frequencies for the bendings, stretching frequencies, as well as the associated intensity pattern, appear to be quite reasonable. The frequencies are even in excellent agreement with experiment, due to a fortunate error compensation.

Bernath *et al.*¹² derived a column density of C_5 in the circumstellar shell of the carbon star IRC + 10216 from our computed MP2/6-31G* intensity and an accurate literature value⁴⁰ for the IR intensity of the 2039 cm^{-1} band of C_3 . Botschwina and Sebald⁹ noted later that the absolute value of the IR intensity is in error by about a factor of three, and presented a revised estimate based on their CE-PA1/[8s4p2d] results. However, the relative intensity compared to the MP2/6-31G* value for the 2039 cm^{-1} band of C_3 (Ref. 10) is in fairly good agreement with the value proposed in Ref. 9. For C_6 , we thus find a relative intensity of 3.74 with respect to C_3 : this value should be more reliable for the evaluation of column densities.

TABLE II. Computed bond distances (Å) for linear C_6 .

	MP2/6-31G*	UHF/6-31G*	UHF/4-21G	UHF/3-21G	MP2/4-21G	CASSCF	<i>ad hoc</i> MNDO
R_o^a	1.3007	1.293 ^b	1.2986	1.297 ^b	1.3192	1.298 ^c	1.299 ^d
R_m^a	1.2940	1.275 ^b	1.2672	1.266 ^b	1.2938	1.280 ^c	1.266 ^d
R_i^a	1.2812	1.269 ^b	1.2660	1.265 ^b	1.2857	1.265 ^c	1.272 ^d
R_{eff}^a	1.293	1.279	1.276	1.275	1.299	1.281	1.277

^a R_o , R_m , and R_i designate the bond distances from the outside in. R_{eff} is defined as $\{[(R_i/2)^2 + (R_i/2 + R_m)^2 + (R_i/2 + R_m + R_o)^2]/(35/4)\}^{1/2}$.

^b K. Raghavachari, R. A. Whiteside, and J. A. Pople, *J. Chem. Phys.* **85**, 6623 (1986).

^c V. Parasuk and J. Almlöf, *J. Chem. Phys.* **91**, 1137 (1989).

^d J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

TABLE III. Theoretical frequencies (unscaled, cm^{-1}) and infrared intensities (km/mol) for C_6 .

	MP2/6-31G*	UHF/6-31G*	UHF/4-21G	MP2/4-21G	UHF/3-21G ^a	<i>ad hoc</i> MNDO ^b
Σ_g	2167	2418	2455	2137	2459 ^a	2245 ^b
Σ_u	2009(1457)	2190(1221)	2179(1377)	1942(1008)	2184 ^a	1999(RI 1.6) ^b
Σ_g	1759	1845	1795	1654	1801 ^a	1694 ^b
Σ_u	1244(332)	1327(17)	1284(25)	1162(330)	1289 ^a	1240(RI 0.2) ^b
Σ_g	673	721	718	651	715 ^a	677 ^b
Π_g	551	134i	845	964i	866 ^a	540 ^b
Π_u	432(0.3×2)	368(4.3×2)	487(0.3×2)	223i(4.8)	494 ^a	453 ^b
Π_g	223	264	223	41	228 ^a	248 ^b
Π_u	108(11×2)	117(16×2)	104(11×2)	128(223×2)	105 ^a	105 ^b

^a K. Raghavachari, R. A. Whiteside, and J. A. Pople, *J. Chem. Phys.* **85**, 6623 (1986).

^b J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

The spectra in both TDW and KN reveal a relatively constant intensity behavior for both the 1952 and 1197 cm^{-1} bands: any observed variation appears to be correlated. So our assignment of both bands to the same molecule appears to be sound.

A final check can be made by comparing the isotope shifts. In order to assess the accuracy of these first, we compare the calculated shifts at the MP2/6-31G*, UHF/6-31G*, UHF/4-21G*, and *ad hoc* MNDO levels with the available experimental data for C_4 (Ref. 14) and C_5 (Ref. 11).

It is perhaps the place to point out that the methodological requirements for an accurate prediction of isotope shifts are quite different from those for the prediction of actual frequencies. As a meaningful comparison is only possible by scaling the computed bands so that the computed and experimental unsubstituted bands match, any systematic overestimate of *all* frequencies is immaterial: what matters is that the relative magnitudes for the force constants are reasonably well predicted. Consequently, if a method predicts an exaggerated difference between two harmonic frequencies, isotope shifts should be taken with great caution.

Table IV tabulates the computed and experimental isotope shifts for C_4 . It can be seen that the agreement is excellent, except for an obvious misassignment by Shen and Graham: the 1511.6 cm^{-1} line clearly comes from the 13-13-12-12 species rather than the 13-12-12-13 species, the band of which accidentally coincides with the 13-12-13-12 and 12-13-13-12 bands at 1513.8 cm^{-1} . As all levels of theory produce virtually identical isotope bands that are furthermore all in excellent agreement with experiment, there is little to choose between them.

The cluster of doubly substituted isotopic bands around 1513 cm^{-1} is the $\Delta = 30$ band seen by TDW and erroneously interpreted as a primary isotopic band with weight one (i.e., the central band for an odd-numbered chain). The two singly substituted bands nearly coincide, leading to the TDW $\Delta = 15$ band.

Table IV also presents the same analysis for C_5 , the resolution of the experimental spectrum being much smaller

here. Somewhat surprisingly, MP2/6-31G*, *ad hoc* MNDO, and RHF/4-21G (restricted Hartree-Fock) all hold their own very well, whereas RHF/6-31G* finds several exaggerated shifts. The band assignment by Vala *et al.* appears to be entirely correct. Regarding the TDW data, the 13-13-13-13-12 peak apparently was absorbed in the parent $^{13}C_5$ peak (which, upon inspection of Fig. 4 in TDW, is seen to have a shoulder on the high-frequency side). The 2105 cm^{-1} band comes from the 13-13-13-12-13 species, whereas the 2118 cm^{-1} band they dismissed as a shoulder to another band is actually caused by 13-13-12-13-13.

For C_6 now, we may compare the various computed isotope spectra to that obtained for the 1952 cm^{-1} band by VCSP. According to the Teller-Redlich rule, the ratio between the $^{13}C_n$ and $^{12}C_n$ frequencies should be $(12.000\ 00/13.003\ 35)^{1/2} = 0.9606$; the actual experimental ratio is slightly higher because of anharmonicity. In order to facilitate comparison with the computed (harmonic) isotope shifts, the latter have been subjected to a linear transformation, enforcing the $^{12}C_6$ and $^{13}C_6$ bands to coincide with their experimental counterparts. The resulting 36 isotopic frequencies are tabulated in Table V, together with the 35 experimental bands reported by VCSP.

We have not attempted an assignment of individual experimental isotopic bands. In the 1952–1920 cm^{-1} range, the bands overlap with isotopic substitutions from the 1997 cm^{-1} feature; below 1893 cm^{-1} , they overlap with those of the 1893 cm^{-1} band. Despite the ingenious procedure involving observation of thermal annealing behavior employed by VCSP, some errors in the assignment are simply unavoidable. Two immediate examples are 1878.3 cm^{-1} (whose isotopic shift is unrealistically low) and 1886.3 (which is too low in intensity and appears to be “superfluous” in that range). Also, at least one actual peak will be obscured by the $^{12}C_n$ parent of the 1893 cm^{-1} band.

It is, however, obvious that the observed spectrum is unmistakably that of linear C_6 .

Turning to the TDW data, their $\Delta = 6$ appears to correspond to a merger of the 13-13-13-13-13-12 and 13-13-13-13-

TABLE IV. Computed and experimental isotope shifts for the 1544 and 2164 cm^{-1} bands of C_4 and C_5 , respectively.

Species	HF/4-21G	HF/6-31G*	MP2/6-31G*	<i>ad hoc</i> MNDO	Experiment
C_4					
12-12-12-12	1543.4	1543.4	1543.4	1543.4	1543.4 ^a
13-12-12-12	1528.6	1528.6	1528.6	1528.7	1528.8 ^a
12-13-12-12	1527.4	1527.3	1527.3	1527.5	1527.5 ^a
13-13-12-12	1511.6	1511.2	1511.2	1511.5	—
13-12-13-12	1513.4	1513.4	1513.5	1513.7	1513.8 ^a
13-12-12-13	1513.3	1513.3	1513.3	1513.5	1511.6(??) ^a
12-13-13-12	1513.3	1513.3	1513.3	1513.4	1513.8 ^a
13-13-13-12	1498.2	1498.2	1498.1	1498.4	1498.8 ^a
13-13-12-13	1496.9	1496.9	1497.0	1497.2	1497.7 ^a
13-13-13-13	1482.7	1482.7	1482.7	1482.9	—
C_5					
12-12-12-12-12	2164.0	2164.0	2164.0	2164.0	2164 ^b
13-12-12-12-12	2161.2	2161.1	2161.4	2161.8	2161 ^b
13-12-12-12-13	2158.2	2157.7	2158.6	2159.5	2158 ^b
12-13-12-12-12	2145.6	2147.0	2144.2	2146.0	2146 ^b
12-12-12-13-13	2144.0	2145.9	2142.3	2144.9	2144 ^b
13-12-12-13-12	2141.5	2141.8	2141.0	2142.8	2142 ^b
13-13-12-12-13	2139.7	2140.4	2138.9	2141.5	2140 ^b
12-12-13-12-12	2130.3	2131.6	2129.2	2127.8	2129 ^b
13-12-13-12-12	2127.2	2128.3	2126.2	2125.2	2128 ^b
13-12-13-12-13	2123.6	2124.2	2123.1	2122.2	2126 ^b
12-13-12-13-12	2120.5	2120.0	2121.0	2122.2	2122 ^b
13-13-12-13-12	2117.9	2117.2	2118.4	2120.3	2120 ^b
13-13-12-13-13	2115.1	2114.1	2115.8	2118.2	2117.5 ^b
12-13-13-12-12	2112.0	2115.7	2109.1	2109.8	2111 ^b
13-13-13-12-12	2110.4	2114.8	2108.7	2108.6	2109 ^b
13-12-13-13-12	2106.7	2109.0	2105.3	2105.6	2106.5 ^b
13-13-13-12-13	2105.1	2107.6	2103.0	2104.2	2104.4 ^b
12-13-13-13-12	2085.2	2085.9	2084.7	2084.2	2086 ^b
13-13-13-13-12	2082.2	2082.7	2081.8	2081.2	2083 ^b
13-13-13-13-13	2078.8	2078.8	2078.8	2079.1	2079.5 ^b

^aL. N. Shen and W. R. M. Graham, *J. Chem. Phys.* **91**, 5115 (1989).

^bM. Vala, T. M. Chandrasekhar, J. Szczepanski, R. J. Van Zee, and W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).

12-13 bands (hence the abnormally high intensity), whereas the $\Delta = 22$ peak corresponds to the 13-13-13-12-13-13 band. Their $\Delta = 38$, a weak satellite of the very intense parent peak of the original 1997 cm^{-1} feature, may correspond to a cluster of multiply substituted peaks, which is seen both in our theoretical data and in the experimental VCSP spectrum.

For the 1197 cm^{-1} band, all theoretical methods predict primary substitution peaks for $^{13}C_6$ to lie at $\Delta \sim 10$ (13-13-13-12-13-13) and $\Delta \sim 12.5$ (13-13-13-13-13-12) cm^{-1} , whereas the 13-13-13-13-12-13 cm^{-1} peak coincides with the parent. This is in excellent agreement with TDW's finding of two equally intense peaks at $\Delta = 10$ and $\Delta = 12$. Furthermore, several doubly substituted peaks cluster around these, leading to the "smeared" appearance of the double peak. To facilitate future experimental work, we have listed the computed peaks at the various levels considered in Table VI.

The fact that a theoretical method as simple as HF/4-21G is apparently quite capable of reproducing experimental isotope spectra rather well is reassuring, in the light of what follows.

B. Higher clusters

With the present hardware and software, MP2/6-31G* analytical gradients for C_7 (42 electrons in 105 orbitals, 15 gradients required for harmonic force field) are simply out of the question. We have therefore adopted a different approach at the expense of the infrared intensities: the harmonic force constant matrix for just the stretching frequencies was set up by double numerical differentiation (stepsize 0.01 Å) of the MP2 energy, the latter being evaluated by the fast in-core algorithm (L903 of the Gaussian series) which avoids the separate integral transformation as well as reduces dead I/O time to virtually nil.

The geometry was first optimized at the same level using the energy-only variant⁴¹ of the Fletcher–Powell method.⁴² Together, these calculations took about two weeks on a Vax-Station 3100.

Near-degeneracy effects lead to MO coefficients in excess of 100, which may affect the numerical precision of the MP2 energies. Whereas the amounts involved will still be negligible for an energy calculation, they will introduce con-

TABLE V. Computed and experimental isotope shifts for the 1952 cm⁻¹ band of C₆.

Species	MP2/6-31G*	Experiment*	UHF/6-31G*	UHF/4-21G	<i>ad hoc</i> MNDO
12-12-12-12-12-12	1952.5	1952.5	1952.5	1952.5	1952.5
13-12-12-12-12-12	1948.0	1947.5	1948.3	1948.9	1948.7
12-12-13-12-12-12	1943.7	1942.5	1943.4	1942.6	1943.2
13-12-12-12-12-13	1943.3	1938.5	1943.8	1945.2	1944.7
13-12-12-13-12-12	1939.95	1937	1939.7	1939.4	1939.8
13-12-13-12-12-12	1937.9	1936.4	1938.3	1938.3	1938.4
12-12-13-13-12-12	1937.4	1932.4	1936.6	1934.8	1935.6
13-12-13-12-12-13	1934.1	1931.5	1934.4	1935.0	1935.0
13-12-13-13-12-12	1932.5	1929.2	1932.0	1931.0	1931.4
12-13-12-12-12-12	1927.6	1926.5	1927.8	1928.0	1927.8
13-12-13-13-12-13	1927.5	1923.3	1927.4	1927.0	1927.1
13-13-12-12-12-12	1923.7	1922.5	1924.1	1924.8	1924.4
12-13-12-13-12-12	1922.9	1918.2	1921.9	1921.0	1921.6
13-12-12-12-13-12	1922.5	1917.5	1923.1	1924.1	1923.6
13-13-12-13-12-12	1919.5	1916.5	1918.6	1918.1	1918.6
13-13-12-12-12-13	1918.4	1913.5	1919.2	1920.7	1920.1
13-12-13-12-13-12	1916.8	1912.3	1916.5	1916.5	1916.6
12-13-13-12-12-12	1913.6	1910.3	1914.7	1914.5	1914.6
13-12-13-12-13-13	1913.2	1908.0	1912.9	1913.4	1913.4
12-13-13-13-12-12	1911.0	1906.5	1910.9	1909.6	1910.0
13-12-12-13-13-12	1909.6	1905.2	1910.5	1911.0	1910.9
13-13-13-12-12-12	1908.4	1904.7	1910.0	1910.6	1910.2
13-13-13-13-12-12	1906.3	1901.9	1906.7	1905.9	1906.1
13-12-13-13-13-12	1906.1	1899.7	1906.2	1905.5	1905.7
13-12-12-13-13-13	1904.1	1894.3	1905.7	1906.9	1906.4
12-13-12-12-13-12	1902.9	1892	1903.0	1903.4	1903.3
13-12-13-13-13-13	1901.2	1891	1901.7	1901.7	1901.2
13-13-12-12-13-12	1898.4	1890.2	1898.8	1899.8	1899.4
12-13-13-12-13-12	1893.8	1889.5	1893.6	1893.2	1893.6
13-13-12-12-13-13	1893.5	1888.2	1894.3	1896.1	1895.5
13-13-12-13-13-12	1890.0	1886.3	1889.8	1889.9	1890.3
13-13-13-12-13-12	1888.1	1883.7	1888.6	1888.9	1888.9
12-13-13-13-13-12	1887.3	1883	1886.5	1885.1	1885.8
13-13-12-13-13-13	1884.1	1878.3	1884.6	1885.5	1885.4
12-13-13-13-13-13	1882.3	1877.2	1882.0	1881.2	1881.5
13-13-13-13-13-13	1877.2		1877.2	1877.2	1877.2

* M. Vala, T. M. Chandrasekhar, J. Szczepanski, and R. Pellow, in *Materials Chemistry at High Temperatures*, edited by J. Hastie (Humana, Clifton, NJ, 1990), Vol. II.

siderable noise in the potential energy surface, so that force constants may be seriously affected. This should be kept in mind when considering the accuracy of the reported MP2/6-31G* frequencies.

The geometry is reported in Table VII, together with MP2/4-21G and RHF/4-21G results, as well as *ad hoc* MNDO and RHF/6-31G* values from literature. A progressive inward contraction of the bonds is again found at the RHF/4-21G, MP2/4-21G, and MP2/6-31G* levels—as well as, this time, at the *ad hoc* MNDO level—but not at the RHF/6-31G* level. We have again included the r_{eff} values for comparison with experiment: again we propose the MP2/6-31G* value as an upper bound and the *ad hoc* MNDO value as a lower bound.

The previous elimination of the 2164 and 1952 cm⁻¹ bands makes the task of vibrational assignment relatively easy even at the Hartree-Fock level, at least when intensities are also included in the interpretation. Although quantitative agreement at this level of theory is probably illusory for these, it is well known that the prime qualitative features are

quite well reproduced even for unusual or highly strained molecules.⁴³

Table VIII lists computed frequencies and IR intensities at the *ad hoc* MNDO, RHF/4-21G and RHF/6-31G* levels, as well as computed frequencies at the MP2/4-21G level and MP2/6-31G* stretching frequencies. Two very intense bands, the upper more intense than the lower, of comparable intensity and about 250 cm⁻¹ apart, are predicted at the Hartree-Fock and *ad hoc* MNDO levels. Two such bands exist at 2128 and 1893 cm⁻¹. TDW already noted that their intensity variations are so closely correlated that they probably belong to the same molecule, which they thought was C₉ (but which has a quite different intensity pattern—*vide infra*). Incidentally, the RHF/4-21G band origins scaled by 0.89 are in quite good agreement with these frequencies. TDW also suggested a band at 1447 cm⁻¹ to belong to the same molecule: however, the data of KN do not show any significant intensity correlation between that band and the 1893–2128 twins, which are indeed very closely correlated in their spectra. Our calculations furthermore find no such

TABLE VI. Computed isotope shifts for the 1197 cm^{-1} band of linear C_6 .

Species	MP2/6-31G*	UHF/6-31G*	UHF/4-21G	<i>ad hoc</i> MNDO
12-12-12-12-12	1197.0	1197.0	1197.0	1197.0
12-13-12-12-12	1196.9	1196.9	1196.7	1196.7
12-13-12-12-13	1196.8	1196.8	1196.5	1196.6
12-12-13-12-12	1185.5	1185.8	1186.4	1186.1
12-13-13-12-12	1185.5	1185.7	1186.2	1186.0
12-13-12-13-12	1185.5	1185.7	1186.2	1186.0
12-13-13-12-13	1185.5	1185.6	1186.1	1185.9
13-12-12-12-12	1184.2	1184.0	1183.6	1183.7
13-12-12-12-13	1184.1	1184.0	1183.4	1183.6
13-13-12-12-12	1183.9	1183.7	1183.1	1183.2
13-13-12-12-13	1183.9	1183.6	1182.9	1183.1
12-12-13-13-12	1175.1	1175.5	1176.7	1176.2
12-13-13-13-12	1175.1	1175.5	1176.5	1176.1
12-13-13-13-13	1175.1	1175.4	1176.4	1176.1
13-12-12-13-12	1173.3	1173.4	1173.6	1173.5
13-12-12-13-13	1173.3	1173.4	1173.5	1173.4
13-13-12-13-12	1173.1	1173.1	1173.2	1173.1
13-13-12-13-13	1173.1	1173.1	1173.1	1173.1
13-12-13-12-12	1172.4	1172.5	1172.7	1172.5
13-12-13-12-13	1172.4	1172.5	1172.6	1172.4
13-13-13-12-12	1172.3	1172.3	1172.3	1172.1
13-13-13-12-13	1172.3	1172.2	1172.2	1172.1
13-12-12-12-12-13	1171.5	1171.1	1170.3	1170.6
13-13-12-12-12-13	1171.3	1170.9	1169.9	1170.2
13-13-12-12-13-13	1171.1	1170.7	1169.5	1169.9
13-12-13-13-12-12	1162.5	1162.8	1163.5	1163.2
13-12-13-13-13-12	1162.5	1162.8	1163.4	1163.1
13-13-13-13-12-12	1162.4	1162.6	1163.2	1162.9
13-13-13-13-13-12	1162.4	1162.6	1163.1	1162.9
13-12-13-12-12-13	1160.3	1160.2	1159.9	1160.0
13-13-13-12-12-13	1160.2	1160.0	1159.6	1159.7
13-13-12-13-12-13	1160.2	1160.0	1159.6	1159.7
13-13-13-12-13-13	1160.0	1159.9	1159.3	1159.5
13-12-13-13-12-13	1150.0	1150.1	1150.3	1150.2
13-13-13-13-12-13	1150.0	1150.0	1150.1	1150.1
13-13-13-13-13-13	1149.9	1149.9	1149.9	1149.9

band in the C_7 spectrum, which again supports our interpretation.

The MP2 results also predict two IR active frequencies in that region, but their separation appears to be exaggerated; furthermore, the ordering of the highest Σ_g and Σ_u bands is interchanged. Because of this, predicted isotope shifts will be particularly unreliable. Nevertheless, the deviation between computed and experimental frequencies is still not unusual. The bending part of the potential is again ill reproduced at the MP2/4-21G level, as expected.

A final check is provided by the primary isotope shifts. At the RHF/4-21G level, we predict for the 2128 cm^{-1} band (substituting with ^{12}C from the outside in) $\Delta = 0, 1, 12, 32$, and for the 1893 cm^{-1} band $9, 21, 0, 8$. Experimentally, TDW found for the 2128 cm^{-1} band a single $\Delta = 13$, as well as a weak shoulder to the parent of the C_5 band at $\Delta = 29$, which is in excellent agreement with our data; for the 1893 cm^{-1} band, they saw a pair of bands at $\Delta = 9$ and 11 , again in good agreement (the missing band may have been obscured by various contaminants in the spectrum).

TABLE VII. Computed bond distances (\AA) for linear C_7 .

	MP2/6-31G*	RHF/6-31G*	RHF/4-21G	MP2/4-21G	<i>ad hoc</i> MNDO
R_0^a	1.3012	1.270 ^b	1.2735	1.3174	1.279 ^c
R_m^a	1.2953	1.280 ^b	1.2728	1.2973	1.271 ^c
R_i^a	1.2814	1.264 ^b	1.2591	1.2825	1.258 ^c
R_{eff}^a	1.291	1.271	1.267	1.2953	1.267

^a R_0 , R_m , and R_i designate the bond distances from the outside in. R_{eff} is defined as $\{[R_i^2 + (R_i + R_m)^2 + (R_i + R_m + R_0)^2]/14\}^{1/2}$.

^b K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).

^c J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

TABLE VIII. Theoretical frequencies (cm⁻¹) and infrared intensities (km/mol) for linear C₇.

	RHF/6-31G*	RHF/4-21G	MP2/4-21G	MP2/6-31G*	<i>ad hoc</i> MNDO ^c
Σ _g	2376 ^a	2401	2159	2216	2202
Σ _u	2281 ^a (11 604 ^b)	2364(12 984)	2338(2934)	2405	2193(RI 4.1)
Σ _u	2132 ^a (7169 ^b)	2131(3803)	1880(613)	1962	1939(RI 3.3)
Σ _g	1745 ^a	1717	1490	1576	1631
Σ _u	1206 ^a (0.14 ^b)	1188(1.26)	1038(9)	1098	1135
Π _u	710 ^a (51×2 ^b)	1405(93×2)	1400 <i>i</i>		670
Σ _g	631 ^a	629	562	580	594
Π _g	598 ^a	812	480 <i>i</i>		602
Π _u	240 ^a (0.7×2 ^b)	357(1.25×2)	144 <i>i</i>		357
Π _g	157 ^a	157	155		212
Π _u	73 ^a (5.8×2 ^b)	77(5.0×2)	79		80

^aK. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).

^bK. Raghavachari (private communication).

^cJ. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

Summarizing, we may be quite confident of the assignment. As the table of isotope shifts would be long and not very interesting to read, we have tabulated the symmetry-unique Cartesian force constants in Table IX: any interested reader may then easily derive any desired frequency by setting up the secular problem.

We now turn to the famous very intense feature at 1997 cm⁻¹. VCSP *et al.* reassigned it from TDW's original C₆ to C₈. However, we feel uncomfortable with this assignment for a number of reasons: (a) because of odd-even alternation in stability discussed at length in Ref. 24, C₉ will be much more stable than C₈; (b) as seen by comparing Tables X and

XI, all levels of theory predict an extremely intense band for C₉, whereas the intensities for the strongest band of C₈ are an order of magnitude lower; (c) the growth of the 1997 cm⁻¹ feature is strongly correlated with the shrinking of the 2039 cm⁻¹ band of C₃, which already led TDW to believe that C₃ was the "building block" for the species at 1997 cm⁻¹. Brown *et al.*⁴⁴ also pointed out that reactions with C₃ are the most exergonic way to grow for each cluster. As, according to mass spectrometric measurements,⁴⁵ the initial carbon vapor consists for about 75, 20, and 5 % each of C₃, C, and C₂, the following mechanism seems more logical to us:

TABLE IX. HF/4-21G Cartesian force constants (atomic units) required to obtain isotope shifts for linear C₇, C₈, and C₉. The atoms are numbered from end to end. To obtain frequencies in cm⁻¹, multiply isotope masses by 1880.860 (number of electron masses in an amu) and frequencies obtained by 219 474.8 (twice the Rydberg constant).

C ₇ , RHF/4-21G			
<i>k</i> 11 = 0.809 117	<i>k</i> 12 = -0.778 091	<i>k</i> 13 = -0.063 660 9	<i>k</i> 14 = 0.053 288 8
<i>k</i> 15 = -0.038 833 0	<i>k</i> 16 = 0.028 555 0	<i>k</i> 17 = -0.010 376 0	<i>k</i> 22 = 1.546 210
<i>k</i> 23 = -0.666 597	<i>k</i> 24 = -0.157 402	<i>k</i> 25 = 0.108 609	<i>k</i> 26 = -0.081 286 2
<i>k</i> 33 = 1.526 59	<i>k</i> 34 = -0.703 169	<i>k</i> 35 = -0.162 939	<i>k</i> 44 = 1.614 57
C ₈ UHF/4-21G			
<i>k</i> 11 = 0.664 453	<i>k</i> 12 = -0.628 233	<i>k</i> 13 = -0.051 816 7	<i>k</i> 14 = 0.023 813 1
<i>k</i> 15 = -0.007 039 62	<i>k</i> 16 = -0.005 498 74	<i>k</i> 17 = 0.013 927 1	<i>k</i> 18 = -0.009 604 50
<i>k</i> 22 = 1.404 77	<i>k</i> 23 = -0.710 519	<i>k</i> 24 = -0.092 684 0	<i>k</i> 25 = 0.038 464 2
<i>k</i> 26 = -0.002 069 85	<i>k</i> 27 = -0.023 651 9	<i>k</i> 33 = 1.554 50	<i>k</i> 34 = -0.717 761
<i>k</i> 35 = -0.106 996	<i>k</i> 36 = 0.0401 157 5	<i>k</i> 44 = 1.580 65	<i>k</i> 45 = -0.718 448
C ₉ , RHF/4-21G			
<i>k</i> 11 = 0.808 073	<i>k</i> 12 = -0.774 357	<i>k</i> 13 = -0.068 529	<i>k</i> 14 = 0.057 784 4
<i>k</i> 15 = -0.043 386 0	<i>k</i> 16 = 0.034 930 7	<i>k</i> 17 = -0.028 822 0	<i>k</i> 18 = 0.023 084 1
<i>k</i> 19 = -0.008 777 68	<i>k</i> 22 = 1.523 09	<i>k</i> 23 = -0.641 840	<i>k</i> 24 = -0.170 535
<i>k</i> 25 = 0.122 323	<i>k</i> 26 = -0.094 910 6	<i>k</i> 27 = 0.074 754 4	<i>k</i> 28 = -0.061 605 4
<i>k</i> 33 = 1.505 02	<i>k</i> 34 = -0.690 410	<i>k</i> 35 = -0.183 405	<i>k</i> 36 = 0.131 352
<i>k</i> 37 = -0.098 120 7	<i>k</i> 44 = 1.579 22	<i>k</i> 45 = -0.656 446	<i>k</i> 46 = -0.190 985
<i>k</i> 55 = 1.521 83			

TABLE X. Theoretical frequencies (cm^{-1}) and infrared intensities (km/mol) for linear C_9 .

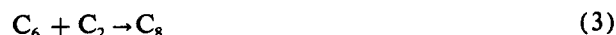
	UHF/6-31G*	UHF/4-21G	<i>Ad hoc</i> MNDO ^b
Σ_g	2393 ^a	2435	2233
Σ_u	2330(3193) ^a	2345(4073)	2128(RI 4.6)
Σ_g	2161 ^a	2160	2005
Σ_u	1867(909) ^a	1828(1032)	1715(RI 1.3)
Σ_g	1495 ^a	1461	1410
Σ_u	1049(9) ^a	1027(4)	984
Σ_g	552 ^a	549	518
Π_g	355 ^a	528	429
Π_u	293(5.6×2) ^a	264(3.2×2)	533
Π_u	225(4.5×2) ^a	888(2.9×2)	277
Π_g	170 ^a	147	162
Π_u	67(10×2) ^a	66(8×2)	63
Π_g	819 ^a	1570	557

^aK. Raghavachari (private communication).

^bJ. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).



In such a mechanism, the C_6 concentration would remain relatively constant during depletion of C_3 and creation of C_9 , which agrees with the observed behavior of the bands. Reactions such as



will be much less important.

What can be said from the harmonic frequencies? The RHF/4-21G band origin for C_9 is in good agreement with the observed 1997 cm^{-1} , whereas that for C_8 is on the high side. Furthermore, this last frequency is itself lowered by spin contamination effects, making the actual value perhaps

TABLE XI. Theoretical frequencies (cm^{-1}) and infrared intensities (km/mol) for linear C_9 .

	RHF/4-21G	RHF/6-31G*	<i>Ad hoc</i> MNDO ^c
Σ_g	2465	2415 ^a	2266
Σ_u	2373(2945)	2338 ^a (433 ^b)	2196(RI 4.4)
Π_u	2239(100×2)	783 ^a (63×2 ^b)	657(RI 0.1)
Σ_u	2188(33883)	2084 ^a (40408 ^b)	2042(RI 22.9)
Σ_g	2122	2134 ^a	1938
Σ_u	1780(681)	1803 ^a (867 ^b)	1676(RI 1.5)
Σ_g	1375	1393 ^a	1312
Π_g	1293	658 ^a	628
Σ_u	949(12.5)	960 ^a (30 ^b)	905
Π_u	821(19×2)	567 ^a (2.7×2 ^b)	543
Σ_g	495	496 ^a	467
Π_g	426	252 ^a	350
Π_u	198(0.2×2)	187 ^a (2.2×2 ^b)	248
Π_g	117	114 ^a	132
Π_u	53(5×2)	49 ^a (5.2×2 ^b)	49

^aK. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).

^bK. Raghavachari (private communication).

^cJ. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).

still higher. In order to give this reasoning a more firm basis, we apply here a little statistics.

Doing a linear regression with the available experimental values on the abscissa and the 4-21G values on the ordinate, for the two lowest-lying states of C_2 and the lowest linear states of C_3 – C_7 , and eliminating the $X^1\Sigma_g^+$ state of C_2 as a clear outlier, we find (with 9 data points)

$$y = 1.1851x + 143.0, \quad r = 0.9961. \quad (4)$$

For the 1997 cm^{-1} band, this leads to a “predicted” 4-21G frequency of 2223.8 cm^{-1} . Standard statistical techniques lead to

$$y - 2223.8 = 16.9\sqrt{2F_p(2,7)}, \quad (5)$$

where F represents the well-known Fisher–Snedecor variance ratio distribution. Its P-value for C_9 is 17.66%, that for C_8 only 0.06%. A similar analysis of the *ad hoc* MNDO data (where there is no outlier) leads to $P = 99.83$ and 0.03%, respectively. The frequency data alone are thus already sufficient for assignment to C_9 .

A more likely candidate for linear C_8 would appear to us to be a band at $\sim 2075 \text{ cm}^{-1}$, which enters the spectra of KN upon strong annealing. For this to be linear C_8 , a companion band of about one-third that intensity should grow in $\sim 1650 \text{ cm}^{-1}$: there is one present at 1589 cm^{-1} . As far as the predicted companion bands (around 2200 cm^{-1} and 1600 cm^{-1}) of C_9 go, there is a band with the right behavior and intensity at 1601 cm^{-1} , as well as a pile-up of features (upon stronger annealing) beginning at 2200 cm^{-1} . These latter assignments are tentative, however, as we do not have experimental isotope shift data at our disposal.

Then come the TDW isotope shift data (as the VCSP spectrum with 50:50 isotope ratios results in an undecipherable plethora of peaks). TDW found a single relatively sharp $\Delta = 14$, with a shoulder on the high frequency side, as well as a very wide (about 10 cm^{-1}) parent peak with again a high-frequency shoulder. Computed primary shifts at the HF/4-21G level are $\Delta = 3, 15, 16, 7, \text{ and } 1 \text{ cm}^{-1}$ from the outside in for C_9 , compared to $\Delta = 1, 13, 18, 4$ for C_8 . Given the

large width of the parent peak, $\Delta = 7$ is still acceptable for the shoulder, whereas the 15 and 16 cm^{-1} peaks are in good agreement with the sharp peak-cum-shoulder at 14 cm^{-1} shift. The C_8 data are less easy to fit in, as they would certainly imply a double isotope peak.

The following point is the intensity reduction of the parent peak upon isotopic 50:50 dilution. Given the fact that the parent peak is near the baseline, the intensity ratio can only be used to say that the cluster contains at least eight atoms, not to discriminate between C_8 and C_9 .

The issue of band density is another one. The predicted band densities for C_8 and C_9 by VCSP are based upon two implicit assumptions: (a) the resolution of the spectrum is small enough to discern all individual peaks; (b) there is little or no coincidence between peaks.

The first is definitely not the case: VCSP quote a resolution of about 0.25 cm^{-1} . We have then computed isotopic substitution bands for C_8 and C_9 from the HF/4-21G force constant matrices (symmetry-unique Cartesian force constants again being given in Table IX), and found the second assumption not to hold at all: especially for C_9 , bands often cluster so closely that even the instruments with the highest resolution would not be able to resolve them. Furthermore, if any atoms have zero travel in a given normal vibration (which is nearly the case for the third and sixth atoms in C_9), all possible combinations of isotopes for these atoms will give rise to exactly or nearly exactly the same frequency.

Using these data and an estimated mean full width at half maximum (FWHM) of 0.25 cm^{-1} (from Fig. 5 of VCSP), we have simulated the spectra assuming Gaussian line shapes. The simulated spectra for C_8 and C_9 are depicted in Figs. 1 and 2, respectively. The cluttering of bands is especially obvious in Fig. 2. Even at sight, both spectra are quite different: the C_8 spectrum contains several relatively wide "gaps," none of which (except a small one around 1940

cm^{-1} also seen in Fig. 2) is present in the experimental spectrum (Fig. 5 of VCSP). The "smear" of bands in several areas of the experimental spectrum (especially around 1960 cm^{-1}) is well reproduced in Fig. 2, but not in Fig. 1. The behavior near the $^{12}C_n$ peak, where contamination is relatively absent, is relatively well reproduced in Fig. 2, but not in Fig. 1. Finally, the locations of several high peaks appear to be better reproduced in Fig. 2 than in Fig. 1.

The peak density was subsequently determined by counting the peaks in each spectrum manually. In Fig. 1, 90 peaks are detected in 78.3 cm^{-1} (which corresponds to a smaller area in the experimental spectrum of about 77 cm^{-1} due to anharmonicity), which leads to an approximate band density of $90/77 = 1.169$ per cm^{-1} . For C_9 , 109 distinct peaks and 7 "borderline cases" (that might get lost in the noise of an actual spectrum) are counted, leading to a density between 1.416 and 1.506 per cm^{-1} , in excellent agreement with the experimental value of about 1.4 per cm^{-1} . A larger FWHM would decrease both densities, as well as the difference.

Summing up, we would be highly surprised if the 1997 cm^{-1} peak turned out to be C_8 rather than C_9 . A high-resolution rotational fine structure such as recorded for C_5 by Heath *et al.*¹³ could settle the issue: assuming a comparable effective bond length, the predicted rotational constant would be about one-quarter that of C_5 for C_8 , and one-sixth for C_9 . Another possibility is a high-resolution isotope spectrum with 95:5 $^{12}C:^{13}C$ ratio: then primary isotope peaks could be observed in more detail than by TDW, in a range where comparatively little interference from other bands exists.

It was very recently shown,⁴⁶ that the intensity variation of the 1997 cm^{-1} feature is strongly correlated with that of a band at 307.5 nm in the UV spectrum. This latter band may consequently also be assigned to C_9 , as may a band

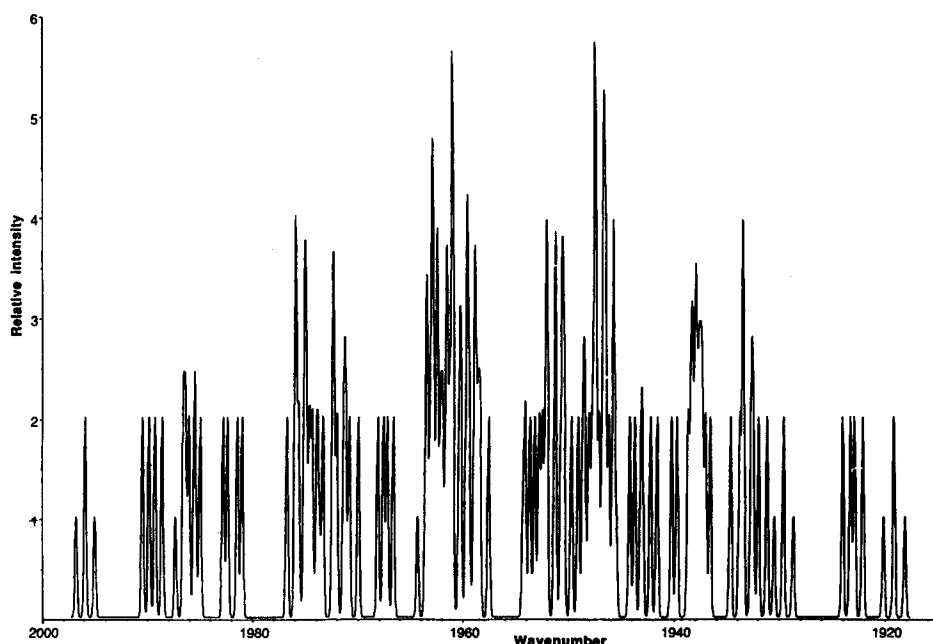


FIG. 1. Simulated isotopic substitution spectrum for the 1997 cm^{-1} band from the UHF/4-21 force constant matrix for linear C_8 .

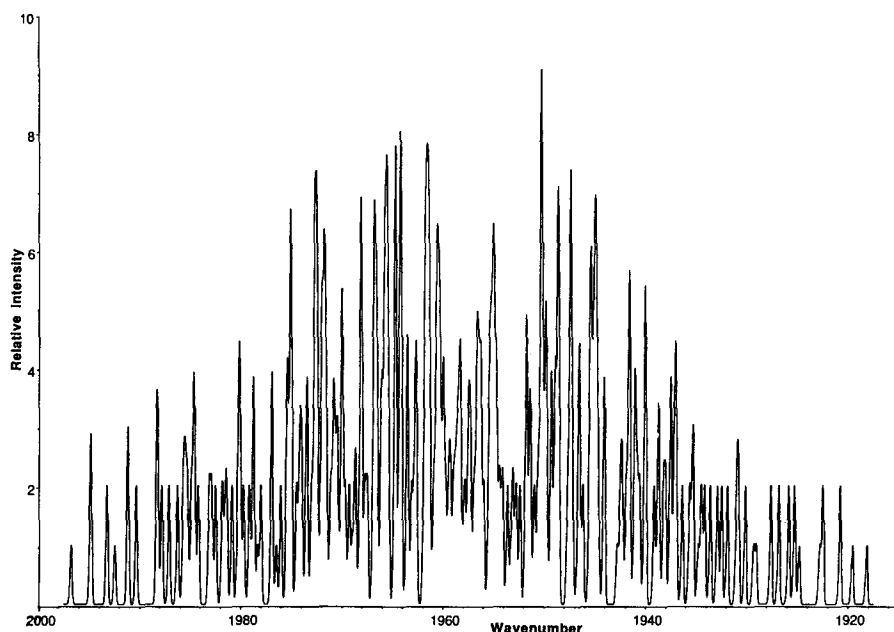


FIG. 2. Simulated isotopic substitution spectrum for the 1997 cm^{-1} band from the RHF/4-21 force constant matrix for linear C_9 .

around 246.5 nm be assigned to linear C_6 because of its strong correlation with the 1952 cm^{-1} line.

Assignments of the bands around 1700 and 1800 cm^{-1} is more speculative: as discussed by MFG, the most likely candidate for the features around 1700 cm^{-1} is cyclic C_6 , whereas the features between 1800 and 1850 cm^{-1} are probably caused by cyclic C_8 and C_{10} . As shown by RB, cyclic and linear structures will be nearly isoenergetic for C_4 , C_6 , and C_8 , whereas C_{10} has a distinct cyclic structure. However, the presence of still higher species cannot be ruled out, like C_{11} which is a "magic number" cluster in mass spectra of graphite.⁴⁷ Concerning the 1447 cm^{-1} band, the only conclusion is negative: the isotope shift pattern completely contradicts assignment to cyclic C_4 as well as linear C_5 , which are about the only species considered that have an IR active band of some intensity in that region. The 1284 cm^{-1} band may be caused by the cyclic form of C_4 (no experimental isotope data are available): a very-high level study of linear and cyclic C_4 , which may give conclusive evidence, is presently near completion in our laboratory. As discussed in MFG, the fact that the growth of the band is not correlated with that of the linear C_4 band may be explained on thermodynamic and kinetic grounds. Another possible candidate would be the lower bending frequency of cyclic C_6 (computed by RB at 1286 cm^{-1} , HF/6-31G*); its IR intensity is on the low side, however.

III. CONCLUSIONS

The harmonic frequencies, infrared intensities, and isotopic substitution bands of C_6 have been evaluated at the MP2/6-31G* level. They confirm previous assignments of the 1952 and 1197 cm^{-1} matrix IR bands to C_6 . Isotopic substitution spectra at the MP2/6-31G* and HF/4-21G level, as well as those with a newly developed *ad hoc* MNDO

method are shown to be in good agreement with experiment for C_4 , C_5 , and C_6 . On the basis of RHF/4-21G, RHF/6-31G*, MP2/4-21G, MP2/6-31G*, and *ad hoc* MNDO data, including theoretical frequencies, IR intensities, and isotopic substitution spectra, it is shown with virtual certainty that the 2128 and 1893 cm^{-1} matrix IR bands belong to C_7 . A recent assignment of the very intense 1997 cm^{-1} matrix IR feature to C_8 is contradicted on the same grounds, and an alternative assignment to C_9 put forward.

Note added in proof: After going to press of this paper, the Berkeley group has succeeded in recording spectra with Doppler-limited resolution of the 2128 cm^{-1} [J. R. Heath, R. A. Sheeks, A. L. Cooksy, and R. J. Saykally, *Science* **249**, 895 (1990); J. R. Heath *et al.*, *Science* (in press)] and 1998 cm^{-1} [J. R. Heath *et al.*, *J. Chem. Phys.* (in press)] bands. The results unambiguously confirm our assignment of the 2128 cm^{-1} band to C_7 and of the 1998 cm^{-1} band to C_9 .

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- ¹ W. Weltner, Jr. and R. J. Van Zee, *Chem. Rev.* **89**, 1713 (1989).
- ² K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ³ L. Gausset, G. Herzberg, A. Lagerqvist, and B. Rosen, *Astrophys. J.* **142**, 45 (1965).
- ⁴ K. R. Thompson, R. L. DeKock, and W. Weltner, Jr., *J. Am. Chem. Soc.* **93**, 4688 (1971).
- ⁵ W. Krätschmer and K. Nachtigall, in *Polycyclic Aromatic Hydrocarbons and Astrophysics*, edited by A. Léger *et al.* (Reidel, Dordrecht, 1987), p. 75.
- ⁶ D. Michalska, H. Chojnacki, B. A. Hess, Jr., and L. J. Schaad, *Chem. Phys. Lett.* **141**, 376 (1987).
- ⁷ D. E. Bernholdt, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.* **89**, 3612 (1988).
- ⁸ J. M. L. Martin, J. P. François, and R. Gijbels, *J. Chem. Phys.* **90**, 3403 (1989).
- ⁹ P. Botschwina and P. Sebal, *Chem. Phys. Lett.* **160**, 485 (1989).
- ¹⁰ L. Adamowicz and J. Kurtz, *Chem. Phys. Lett.* **162**, 342 (1989).
- ¹¹ M. Vala, T. M. Chandrasekhar, J. Szczepanski, R. J. Van Zee, and W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).
- ¹² P. F. Bernath, K. H. Hinkle, and J. J. Keady, *Science* **244**, 562 (1989).
- ¹³ J. R. Heath, A. L. Cooksy, M. H. W. Gruebele, C. A. Schmuttenmaer, and R. J. Saykally, *Science* **244**, 564 (1989).
- ¹⁴ L. N. Shen and W. R. M. Graham, *J. Chem. Phys.* **91**, 5115 (1989).
- ¹⁵ J. M. L. Martin, J. P. François, and R. Gijbels, *J. Comp. Chem.* (in press).
- ¹⁶ M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
- ¹⁷ K. Raghavachari, private communication. The unpublished data comprise: (a) UHF/6-31G* IR intensities and Raman activities for linear C₇, C₈, and C₉, as well as cyclic C₈; (b) UHF/6-31G* frequencies for linear C₈.
- ¹⁸ M. Vala, T. M. Chandrasekhar, J. Szczepanski, and R. Pellow, in *Materials Chemistry at High Temperatures*, edited by J. Hastie (Humana, Clifton, NJ, 1990), Vol. II.
- ¹⁹ J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem. Symp.* **13**, 225 (1979).
- ²⁰ M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, GAUSSIAN 86 Release C (Carnegie-Mellon University, Pittsburgh, PA, 1987).
- ²¹ R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* **54**, 724 (1971).
- ²² P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973); *Chem. Phys. Lett.* **16**, 217 (1972).
- ²³ Y. Yamaguchi, M. J. Frisch, J. Gaw, H. F. Schaefer III, and J. S. Binkley, *J. Chem. Phys.* **84**, 2262 (1986).
- ²⁴ K. Raghavachari and J. S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
- ²⁵ H. Guo and M. Karplus, *J. Chem. Phys.* **91**, 1719 (1989).
- ²⁶ P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.* **101**, 2550 (1979).
- ²⁷ M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, GAUSSIAN 88 Release C (Gaussian, Inc., Pittsburgh, PA, 1989).
- ²⁸ K. H. Hinkle, J. J. Keady, and P. F. Bernath, *Science* **241**, 1319 (1988).
- ²⁹ E. D. Simandiras, J. E. Rice, T. J. Lee, R. D. Amos, and N. C. Handy, *J. Chem. Phys.* **88**, 3187 (1988).
- ³⁰ R. S. Grev, I. L. Alberts, and H. F. Schaefer III, *J. Phys. Chem.* **94**, 3379 (1990).
- ³¹ K. Raghavachari, R. A. Whiteside, and J. A. Pople, *J. Chem. Phys.* **85**, 6623 (1986).
- ³² V. Parasuk and J. Almlöf, *J. Chem. Phys.* **91**, 1137 (1989).
- ³³ B. O. Roos, *Int. J. Quantum Chem. Symp.* **14**, 175 (1980); B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, *Chem. Phys.* **48**, 157 (1980); B. O. Roos, *Adv. Chem. Phys.* **69**, 399 (1987).
- ³⁴ D. H. Magers, R. J. Harrison, and R. J. Bartlett, *J. Chem. Phys.* **84**, 3284 (1986).
- ³⁵ J. P. Ritchie, H. F. King, and W. S. Young, *J. Chem. Phys.* **85**, 5175 (1986).
- ³⁶ C. F. Hansen, B. J. Henderson, and W. E. Pearson, *J. Chem. Phys.* **60**, 754 (1974).
- ³⁷ J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem. Symp.* **15**, 269 (1981).
- ³⁸ J. M. L. Martin, J. P. François, and R. Gijbels, *Chem. Phys. Lett.* **166**, 238 (1989).
- ³⁹ R. F. Hout, Jr., B. A. Levi, and W. J. Hehre, *J. Comp. Chem.* **3**, 234 (1982).
- ⁴⁰ W. P. Kraemer, P. R. Bunker, and M. Yoshimine, *J. Mol. Spectrosc.* **107**, 191 (1984).
- ⁴¹ J. B. Collins, P. von Ragué Schleyer, J. S. Binkley, and J. A. Pople, *J. Chem. Phys.* **64**, 5142 (1976), see Appendix there.
- ⁴² R. Fletcher and M. J. D. Powell, *Computer Journal* **6**, 163 (1963).
- ⁴³ B. A. Hess, Jr., L. J. Schaad, P. Čársky, and R. Zahradník, *Chem. Rev.* **86**, 709 (1986).
- ⁴⁴ W. L. Brown, R. R. Freeman, K. Raghavachari, and M. Schlüter, *Science* **235**, 860 (1987).
- ⁴⁵ P. D. Zavitsanos and G. A. Carlson, *J. Chem. Phys.* **59**, 2966 (1973).
- ⁴⁶ J. Kurtz and D. R. Huffmann, *J. Chem. Phys.* **92**, 30 (1990).
- ⁴⁷ J. A. Van Vechten and D. A. Keszler, *Phys. Rev. B* **36**, 4570 (1987), and references therein.