On the vibrational spectrum of C_9, C_{11} and C_{13}

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Abstract

The harmonic frequencies and infrared intensities of C_9, C_{11} and C_{13} have been calculated using SCF and complete active space SCF (CASSCF) methods. The ordering of the harmonic frequencies in C_9 is predicted wrongly unless at least the π HOMO and LUMO are included in the active space. Infrared intensities depend crucially on the size of the active space. For linear odd-numbered clusters C_{13} and larger, the computed SCF spectrum is qualitatively wrong. The recent observation of a band near 1809 cm^{-1} in the gas phase is explained using our CASSCF results on C_{13}.

1. Introduction

Small carbon clusters have been the subject of many extensive theoretical and experimental studies (see Refs. [1,2] and the introduction to Ref. [3] for reviews), even before the development of fullerene chemistry. The diatomic C_2 has been studied extensively [4], while the linear clusters C_n (n = 3–7,9) have been characterized by high-resolution infrared spectroscopy. Very recently, high-level ab initio frequency calculations [5] presented convincing evidence for the existence of cyclic C_6, C_8, and C_{10} in matrix infrared spectra of trapped carbon vapor [6,7], while the assignment of a band at 1284 cm^{-1} to cyclic C_4 [8] was confirmed with virtual certainty in a large-basis set calculation of the quartic force field of C_4 [9]. Further, accurate ab initio heats of formation are available for C_3 through C_{10} inclusive [10].

Very little is known about clusters larger than C_{10} but still below the fullerene regime in size, except that there appears to be a consensus in the literature that they are cyclic. However, very recently, a pa-

per by Giesen et al. (denoted GOHFPS) [11] appeared which reports high-resolution infrared spectra for a band at 1808.96399(7) cm^{-1} that, from the rotational fine structure, unambiguously belonged to a linear C_{13} molecule with average bond distance r_{eff} = 1.2770(5) Å. The nearest band in the matrix infrared spectra [6,7] is one at 1804 cm^{-1}: however, not only is the intensity variation upon annealing of this band strongly correlated with another band at 1844 cm^{-1} (no corresponding band to which is found by GOHFPS), but previous studies indicate [12] a linear relationship between cluster size and matrix red-shift, from which the observed *matrix band* of linear C_{13} would be predicted between 1780 and 1795 cm^{-1}. No such band is found in the matrix IR spectra, which suggests that linear C_{13} is not present in the matrix experiments. Hence linear C_{13} is presumably thermodynamically metastable. GOHFPS explain that, at the high temperatures involved in laser vaporization, linear structures are strongly favored by entropy, while the fast cooling down in supersonic expansion may

never give these high-energy structures the chance to relax to more stable cyclic isomers. Moreover, high barriers towards isomerization may exist, as demonstrated by Von Helden et al. [13,14] in their experimental and theoretical study on C_7.

While Hartree–Fock level frequency calculations on the smaller clusters [15] had been instrumental in the experimental identification of several smaller species, such as C_4 [16], C_5 [17], C_6 [18,19], C_7 [20] and C_9 [21], SCF-level calculations by one of the authors [22] on C_{11} through C_{19} did not exhibit any calculated band for C_{13} that could plausibly correspond to the observations of GOHFPS. Second-order perturbation theory (MP2) calculations on the smaller clusters [23] yield results that differ increasingly from nature as the cluster size increases, with qualitatively incorrect results being predicted for C_9. One plausible explanation might be that nondynamical correlation increases steadily with chain length: under such circumstances, a Hartree–Fock treatment might benefit from a cancellation of errors between neglect of dynamical and nondynamical correlation, whereas a low-order perturbation theory treatment will not benefit from such a cancellation since dynamical correlation is treated explicitly. However, such a cancellation of errors in Hartree–Fock must also eventually break down.

The present Letter reports attempts to perform more refined ab initio frequency calculations for C_{11} and C_{13}. Since extensive material is available for C_9 [5], this molecule will be used as a gauge for the reliability of our calculations.

2. Computational methods

All calculations were performed using Dunning's correlation consistent polarized valence double zeta (cc-pVDZ) basis set [24], which is a [3s2p1d] contraction of a (9s4p1d) primitive set. Experience suggests [25,26] that this basis set is generally much more reliable for correlated frequency calculations than the commonly used Huzinaga–Dunning [27,28] double-zeta plus polarization (DZP) basis set.

Because of the size of the largest system, C_{13}, coupled-cluster frequency calculations, which would have been our approach of choice, are virtually out of the question even in this modest basis set. Since

our main interest here is to treat nondynamical correlation adequately, the best alternative for a system this size is CASSCF (complete active space SCF) [29]. The calculations were carried out on the CRAY C90 computer at the San Diego Supercomputer Center using the SIRIUS/ABACUS [30] program system. Hartree–Fock level frequency calculations were carried out using TURBOMOLE [31] on an IBM RS/6000 model 350 workstation at SDSC. In both cases, analytical second derivatives were used, and infrared intensities were determined within the double-harmonic approximation. We may note that the cc-pVDZ basis set would not necessarily be expected to yield reliable IR intensities even at the SCF or CASSCF level without some augmentation with diffuse functions. However, the intensities computed here are used primarily for comparisons, and the cc-pVDZ set is adequate for this purpose.

Active spaces for the CASSCF calculations were determined from natural orbital occupations at the MP2 level. The obvious candidate would be an active space consisting of the HOMO ($\pi_{g/u}$) and LUMO ($\pi^*_{u/g}$) orbitals, which leads to a 4-electron in 4-orbital, or CASSCF(4/4), active space. However, the MP2 calculations suggested that the natural orbital occupations of π HOMO-1 and LUMO$+1$ deviated significantly from their Hartree–Fock values of four and zero, respectively, as well, suggesting further calculations involving a CASSCF(8/8) wave function.

3. Results and discussion

Table 1 contains calculated results for C_9, together with CCSD(T)/cc-pVDZ [5], MP2/6-31G* [23], density functional [3], and ad hoc MNDO [32] results from the literature.

We immediately see that all methods predict the same ordering of the stretching frequencies, except for HF/cc-pVDZ and MP2/6-31G*. At the HF/cc-pVDZ level, the second highest σ_g and σ_u frequencies are interchanged, while at the MP2/6-31G* level, the top σ_g and σ_u frequencies are interchanged. Of the results presented, it was shown amply in Ref. [5] that the CCSD(T)/cc-pVDZ ones should be the most reliable. It is striking how both the density functional results of Hütter et al. [3] and the MNDO (modified neglect of diatomic overlap [33]) calculations with parameters

Table 1
Computed frequencies (cm^{-1}) and IR intensities (km/mol) for C_9

	SCF /cc-pVDZ this work		CASSCF(4/4) /cc-pVDZ this work		CASSCF(8/8) /cc-pVDZ this work		CCSD(T) /cc-pVDZ Ref. [5]	MP2/6-31G* Ref. [23]		Density functional Ref. [3]		Ad hoc MNDO Ref. [32]	
	freq.	inten.	freq.	inten.	freq.	inten.	freq.	freq.	inten.	freq.	inten.	freq.	inten.
σ_g	2419	0	2421	0	2340	0	2212	2287	0	2209	0	2266	0
σ_u	2340	572	2267	589	2276	8014	2148	2426	2628	2182	2324	2196	RI=4.4
σ_u	2087	41784	2165	28607	2174	2578	2061	2133	824	2073	3030	2042	RI=22.9
σ_g	2131	0	2115	0	2093	0	1898	1930	0	1903	0	1938	0
σ_u	1800	1050	1797	85	1775	780	1607	1635	190	1624	377	1676	RI=1.5
σ_g	1390	0	1390	0	1382	0	1247	1267	0	1247	0	1312	0
σ_u	958	32	955	33	960	4	864	879	0.4	905	12	905	RI small
π_u	740	56	739	29	737	12				496	111	657	RI=0.1
π_g	657	0	652	0	651	0				500	0	628	0
σ_g	495	0	495	0	495	0	449	457	0	458	0	467	0
π_u	568	1	546	4	551	0				442	13	543	RI small
π_g	495	0	290	0	335	0				255	0	350	0
π_u	206	3	210	2	253	8				184	435	248	RI small
π_g	121	0	129	0	143	0				116	0	132	0
π_u	49	5	54	6	55	6				49	161	49	RI small

RI denotes the relative intensity with respect to the 2039 cm^{-1} band of C_3 (RI= 1.0).

specifically optimized for carbon clusters [32] are in very good agreement with the CCSD(T)/cc-pVDZ values. Both levels of theory suggest two very intense bands in the 2000–2150 cm^{-1} range: the lower of the two bands is known to correspond to the 1998 cm^{-1} matrix IR feature which becomes extremely intense upon strong annealing, while it was shown in Ref. [5] that the upper one is almost certainly a component of a broad, convoluted, feature stretched out between 2080 and 2095 cm^{-1}. In addition, the third lowest IR active band was assigned to features around 1600 cm^{-1} in Ref. [5].

At the SCF level, the band corresponding to the 1998 cm^{-1} matrix feature has an anomalously high intensity (41784 km/mol) that is certainly unphysical, while the upper band, observed in accurate studies to be of the same order of magnitude as the lower one, is found here to be almost two orders of magnitude less intense. We can say with some certainty that these intensities are not realistic.

Going to a CASSCF(4/4) calculation very significantly affects the frequencies of the two highest σ_u bands, but leaves the other stretches virtually untouched. However, the intensity problem is not resolved, while the third IR band becomes almost

invisible by comparison to the two others. At the CASSCF(8/8) level, the two uppermost σ_g modes become affected (especially the top one), and, to a lesser extent, the third σ_u mode. The intensity problem appears to be less acute, in that now at least all bands have physically plausible intensities. Examination of natural orbital occupation numbers suggests that the CASSCF(8/8) treatment accounts for most of the nondynamical correlation effects, and any further expansion of the active space would really correspond to describing dynamical correlation, for which CASSCF is not an effective treatment. Increasing the active space further in any balanced way would also probably require inclusion of σ orbitals, which would anyway lead to calculations too large to be feasible. Thus CASSCF(8/8) seems to be an appropriate and economic level of treatment.

We can now turn to C_{13}. The HF/cc-pVDZ frequencies are dominated by an anomalously intense band at 1720 cm^{-1}. Going to CASSCF(8/8) drastically changes not only the frequencies of the third and fourth highest σ_u bands, but also the intensity behavior. Now we have extremely intense bands calculated at 1843 and 2003 cm^{-1}; with more account for external correlation, either band could come close enough

Table 2
Computed frequencies (cm^{-1}) and infrared intensities (km/mol) for linear C_{13}

	SCF/cc-pVDZ		CASSCF(8/8)/cc-pVDZ	
σ_u	2419	703	2409	136
σ_g	2390	0	2346	0
σ_g	2333	0	2318	0
σ_u	2245	72	2227	200
σ_g	2099	0	2083	0
σ_u	1874	3616	2003	84067
σ_u	1720	$> 10^5$	1843	13738
σ_g	1587	0	1573	0
σ_u	1300	1	1294	88
σ_g	996	0	987	0
π_u	804	71	793	46
π_g	725	0	722	0
σ_u	677	253	678	69
π_u	656	6	649	9
π_g	591	0	587	0
π_u	534	0	511	0
σ_g	340	0	341	0
π_g	275	0	295	0
π_u	239	2	244	2
π_g	183	0	192	0
π_u	119	4	124	3
π_g	65	0	68	0
π_u	25	4	27	5

Table 3
Computed frequencies (cm^{-1}) and infrared intensities (km/mol) for linear C_{11}

	SCF/cc-pVDZ		CASSCF(8/8)/cc-pVDZ	
σ_g	2408	0	2407	0
σ_u	2400	80	2387	1
σ_g	2269	0	2236	0
σ_u	2126	2400	2075	1378
σ_u	1913	81231	1895	93266
σ_g	1842	0	1804	0
σ_u	1507	147	1478	130
σ_g	1162	0	1144	0
σ_u	795	107	787	253
π_u	771	65	779	60
π_g	694	0	697	0
π_u	617	3	620	0
π_g	547	0	550	0
σ_g	406	0	406	0
π_u	269	1	276	7
π_g	226	0	241	0
π_u	156	4	162	9
π_g	87	0	87	0
π_u	34	4	34	6

to 1809 cm^{-1} to correspond to the feature seen by GO-HFPS. Hence we are clearly dealing with a situation here where nondynamical correlation effects essentially preclude any useful prediction at the SCF level, as well as (of course) from low-order perturbation theory. The anomalously high intensities still suggest that an even higher-level calculation would be desirable, however, it is hard to see what more sophisticated calculation would be technically feasible at present.

Having discussed C_9 and C_{13}, we may look at results for C_{11}. These are given in Table 3. Interestingly, here intensity patterns of the SCF and CASSCF(8/8) frequencies are quite similar, while the effect on the actual frequencies is also relatively small (the second through fourth σ_g and σ_u modes, counting from the top, are affected significantly). Still, we see one band with an anomalously high intensity, which might take on a somewhat more physically plausible value if the active space were enlarged (which is presently beyond the realm of the computationally feasible). Qualitatively, however, the computed spectrum is in agreement with the HF/6-31G* values presented previously

by Martin et al. [34].

It should be remarked that in all cases, the APT population analysis [35], which is based on the dipole gradient tensor, produces populations which are qualitatively at odds with conventional expectations (such as carbon atom populations exceeding ± 4). This is indicative of very large charge movement along the molecular axis and a rapidly changing (with geometry) ionic contribution to the wave function. Also noteworthy are the very large polarizabilities along the molecular axis: 131.5 Å^3 for C_{11}, 172.5 Å^3 for C_{13}. All these results suggest that carbon fiber materials could have interesting nonlinear optical properties.

4. Conclusions

We are in a position to state that:
– as the length of linear carbon clusters C_{2n+1}, and especially C_{4n+1}, increases, nondynamical correlation effects on the harmonic frequencies and intensities become noticeable;
– at the CASSCF(8/8)/cc-pVDZ level a band corresponding to the observed transition for C_{13} is found, with a very high computed intensity;

– for C_9, at least a CASSCF(4/4) is required to reproduce the ordering of the frequencies correctly;

– the computed infrared intensities change qualitatively with the size of the active space.

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