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Vibrational properties of C_{20} isomers, a semi-empirical study[1]

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Abstract

Self-consisent field Hartree–Fock calculations using MNDO, AM1 and PM3 hamiltonians were carried out for the vibrational spectra of the geometrical isomers of the smallest fullerene cluster, C_{20}. Comparisons with a recent density functional approach brought out similarities and differences among the methods and were in accord with earlier first principles stability ordering of the three ground state isomers: the planar cyclic form (the ring), the corannulene form (the bowl), and the closed cage fullerene form. Complete vibrational symmetry assignments are given for the fullerene and the bowl forms and an approximate grouping is presented for the ring isomer. The distribution of all vibrational levels is compared among the three forms and the density functional results for the PM3 method, and schematic infrared spectra are calculated for the three C_{20} forms.

1. Introduction

The smallest closed cage fullerene molecule, C_{20}, is composed of twelve pentagonal faces and is assumed to exist [1]. There have been a number of studies of the stability of its topologically possible structural isomers; the planar monocyclic ring, the bowl-shaped corannulene form and the closed fullerene cage [2–8]. These three structures correspond to closed shell ground state configurations, as there is a non-zero HOMO–LUMO gap between the electronic levels. Fowler et al. [8] claim that in the fullerene series the smallest cage that has a properly closed shell is C_{60}, defined by having a fully occupied bonding HOMO separated from a nonbonding or antibonding LUMO. The fourth possible geometrical isomer, the linear chain, is an open shell triplet excited state arrangement. Fig. 1 shows a space-filling model of the three isomers.

Recent fullerene cluster formation observations showed the presence of ionic forms $C_{20}{}^{+}$ and $C_{20}{}^{-}$ that are monocyclic planar rings [9,10]. No experimental evidence is available so far for the fullerene cage and corannulene structures, neutral or ionic. This cannot, however, be taken as evidence regarding the existence of these C_{20} forms, as it is not yet clear whether under conditions more close to thermodynamic equilibrium the bowl and the fullerene cage may not be observable.

So far, the problem of stability ordering among the three C_{20} forms has met with various suggestions. There is a disagreement among semi-empirical and ab initio calculations as to stability ordering,and recent density functional [6] and coupled cluster [11] calculations were aimed at

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[1] Dedicated to Professor James E. Boggs on the occasion of his 75th birthday.

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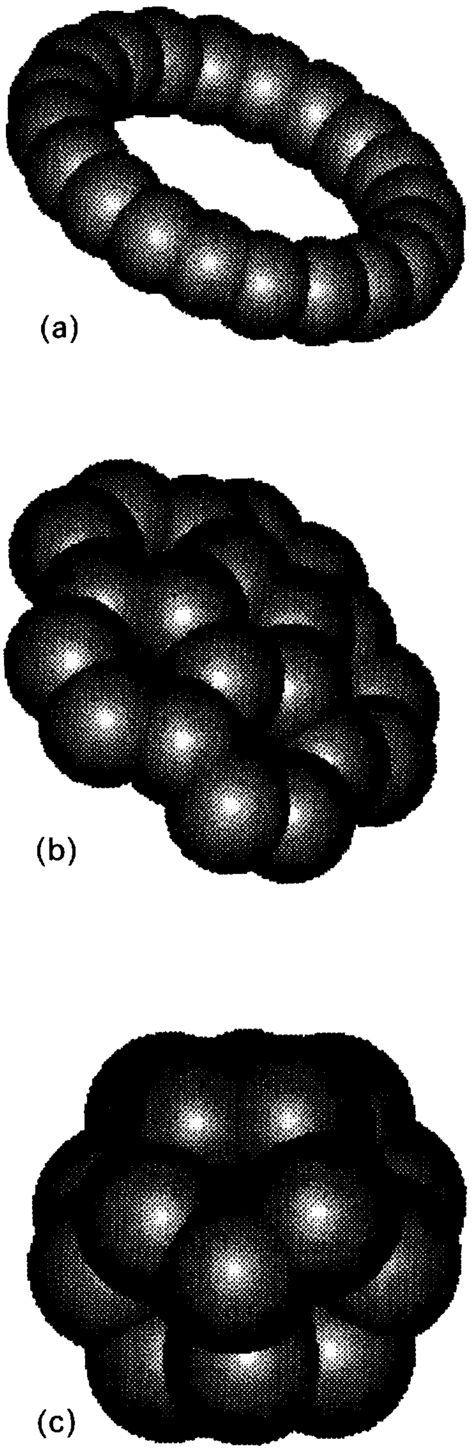

Fig. 1. Molecular models for the C_{20} isomers: (a) the ring, (b) the bowl and (c) the cage.

Table 1
Semi-empirically calculated C–C bond length parameters for the C_{20} isomers (Å)

Isomer and geom. sym.	MNDO	AM1	PM3
C_{20} (cage), D_2	1.403	1.408	1.397
	1.413	1.414	1.406
C_{20} (bowl), C_{5v}	1.248	1.249	1.244
	1.407	1.397	1.404
	1.456	1.446	1.442
C_{20} (ring) D_{10h}	1.278	1.272	–
C_{10h}	–	–	1.363
			1.204

resolving the dilemma. Early ab initio Hartree–Fock (HF) calculations [2] led to the ring form being identified as the most stable (in apparent agreement with formation experiments [9,10]), but second-order perturbative calculations by the same authors [2] favored the cage isomer. In recent work using gradient-corrected density functional theory [6], support is provided for earlier semi-empirical approaches [5], and the ring is shown to be the most stable isomer. However, Taylor et al. [11], in their recent coupled-cluster calculations in the singlet spin state with CCSD(T) excitation and Dunning's cc-pVDZ basis set arrived at the conclusion that the fullerene cage form has the lowest energy, very nearly degenerate with the bowl form. These calculations were carried out at the San Diego Supercomputer Center and were near the capability limit of the CRAY C90 supercomputer.

We present here inexpensively obtained semi-empirical results which are not expected to contribute to the solution of this intriguing stability problem. However, it is interesting that our results conform to gradient corrected density functional conclusions. Our main purpose was to carry out a vibrational analysis on a good semi-empirical basis for the three ground state isomers that may be expected to help the search for their spectra in the infrared region.

2. Semi-empirical methods and results

RHF self-consistent field calculations in a singlet spin state on the 40 doubly occupied levels of the three isomers using the MOPAC6.1 program package

Table 2
Heats of formation and total energy of C_{20} isomers from semi-empirical calculations

Isomer	Heat of formation (eV per atom)			Total energy (eV)		
	MNDO	AM1	PM3	MNDO	AM1	PM3
Cage	1.79	1.90	1.63	−2522.4352	−2526.5342	−2340.2779
Bowl	1.49	1.57	1.40	−2528.4067	−2533.0897	−2344.8602
Ring	1.33	1.43	1.24	−2531.5796	−2535.8747	−2347.9091

were done with MNDO [12], AM1 [13] and PM3 [14] parametrization. Starting from maximal geometrical symmetry, structural optimization of all internal coordinates was carried out first (without any symmetry constraints), and force constants and normal coordinates were calculated using the FORCE option of the package. No configuration interaction calculations were attempted.

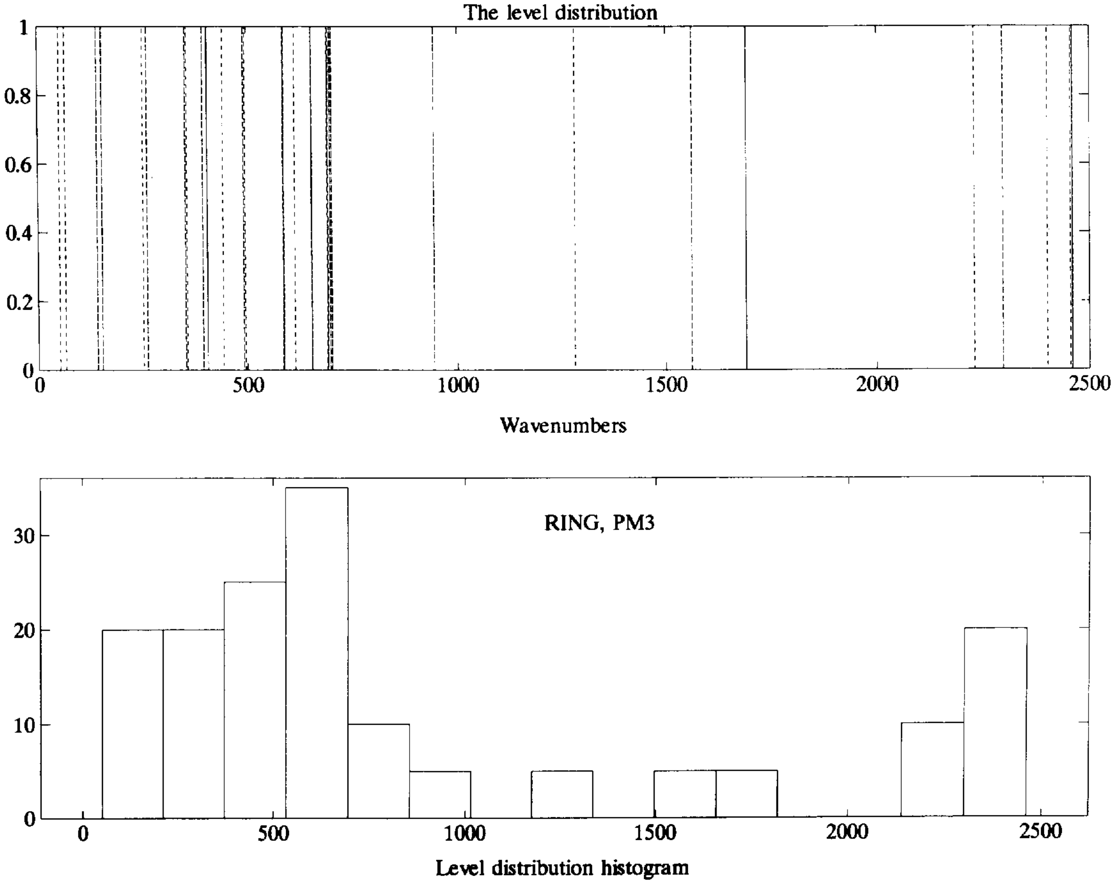

Fig. 2. Distribution of vibrations for the ring isomer from PM3 calculations.

Table 3
Ionization potential and zero-point vibrational energy of C_{20} isomers

Isomer	Ionization potential (eV)			Zero-point energy (cm^{-1})		
	MNDO	AM1	PM3	MNDO	AM1	PM3
Cage	8.850	9.143	8.797	28027	29098	28404
Bowl	9.593	10.164	9.930	26326	27053	26957
Ring	7.533	7.887	9.034	24074	23986	24654

Table 1 contains the converged bond length parameters for the three isomers with the final, converged symmetry indicated. This was D_{10h} for the ring structure when MNDO and AM1 hamiltonians were used, but the application of PM3 reduced the symmetry to C_{10h}. Also, although the initial geometry for the fullerene cage was icosahedral (I_h) in the course of structure optimization, it was reduced to D_2 for all three semi-empirical hamiltonians.

Table 2 summarizes the heats of formation and total energies, and Table 3 lists ionization and zero-point vibrational energies.

Predicted vibrational wavenumbers are presented in Tables 4, 5 and 6 according to the

Table 4
Symmetry sorted vibrational wavenumbers for the cage isomer of C_{20} (D_2) by PM3 (cm^{-1})

Symmetry			
A	B1	B2	B3
488	497	514	464
518	642	621	630
642	676	640	664
652	761	762	825
676	785	813	833
827	812	854	849
1013	1107	1085	1104
1169	1213	1174	1214
1261	1242	1277	1224
1270	1278	1315	1269
1318	1363	1325	1516
1380	1598	1551	1584
1454	1619	1603	1604
1591			
1629			

Table 5
Symmetry sorted vibrational wavenumbers for the bowl isomer of C_{20} (C_{5v}) by PM3 (cm^{-1})

Symmetry			
A_1	A_2	E_1	E_2
163	554	362	157
683	610	491	313
756	865	509	431
1089	1789	651	564
1636		724	620
2128		1010	713
		1240	856
		1567	1157
		1737	1451
		2114	1485
			1629
			2032

Table 6
Vibrational wavenumbers for the ring isomer of C_{20} (C_{10h}) by PM3 (cm^{-1}), sorted into non-degenerate and degenerate species

Symmetry	
A + B	E
353	51
357	65
395	140
406	152
443	251
697	261
701	492
1690	496
2229	586
2455	588
	614
	653
	654
	690
	692
	944
	1281
	1561
	2297
	2401
	2458
	2460

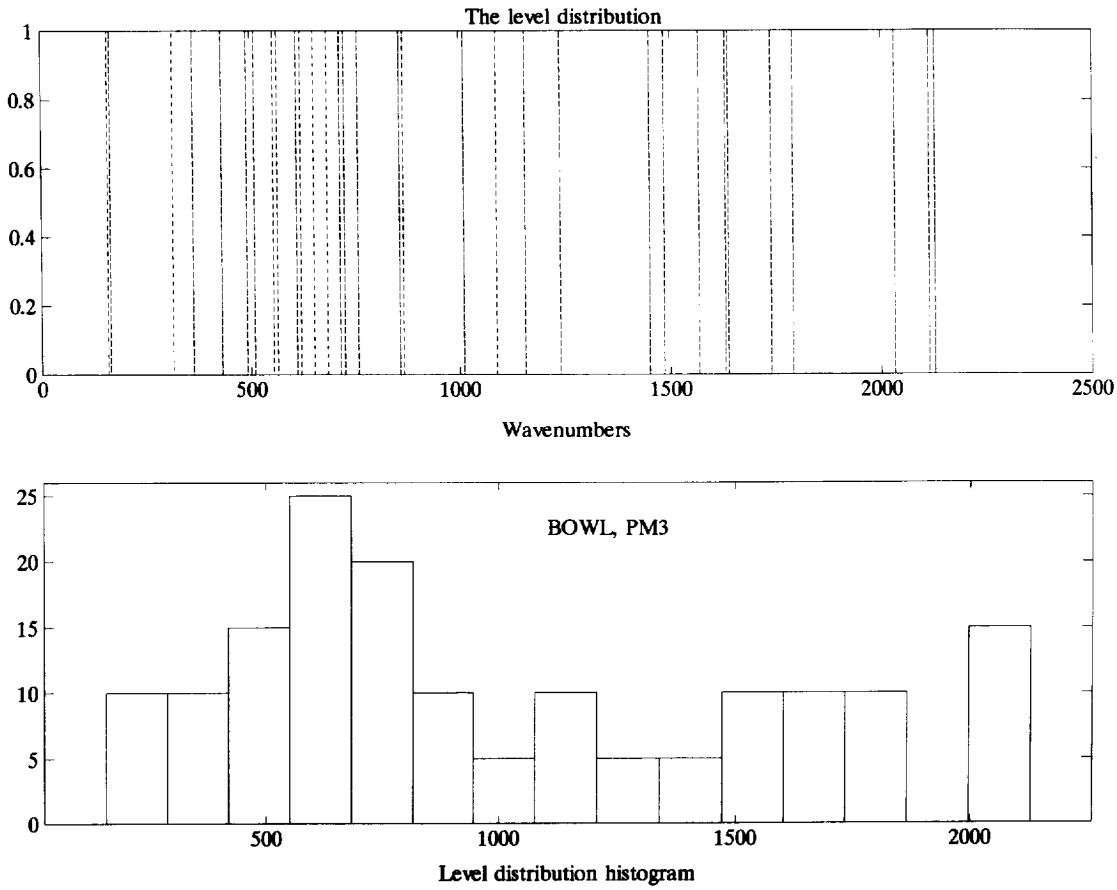

Fig. 3. Distribution of vibrations for the bowl isomer from PM3 calculations.

converged symmetries, but only for the PM3 method in order to save space.

The distribution of normal modes among the group species is

$$\Gamma_Q(D_2) = 15\mathrm{A} + 13\mathrm{B}_1 + 13\mathrm{B}_2 + 13\mathrm{B}_3$$
$$\Gamma_Q(C_{5v}) = 6\mathrm{A}_1 + 4\mathrm{A}_2 + 10\mathrm{E}_1 + 12\mathrm{E}_2$$
$$\Gamma_Q(C_{10h}) = 10(\mathrm{A},\mathrm{B}) + 22\mathrm{E} \qquad (1)$$

The point group C_{10h} should contain the species A, B, E_1, E_2, E_3 and E_4 for "g" and "u" modes, but to our knowledge its character table is not available. So we have classified the ring C_{20} vibrations in the approximate way indicated in Eq. (1).

The vibrational symmetries in Tables 4, 5 and 6 were arrived at in two steps. In the first step, near degeneracies of the calculated frequencies were sought in order to localize E modes, and in the second step a careful, computer-aided analysis of the transformation properties of normal coordinate atomic amplitudes from MOPAC calculations towards point group symmetry elements was carried out. For the ring isomer only the first step could be taken.

The distribution of vibrational transitions calculated in the PM3 model is shown in Figs. 2, 3 and 4 for the three isomers. The upper part of each figure shows the actual transitions, and the lower part presents a large bin size histogram for easier grouping. Figs. 5, 6 and 7 give the corresponding distributions from the density functional work of Raghavachari et al. [6].

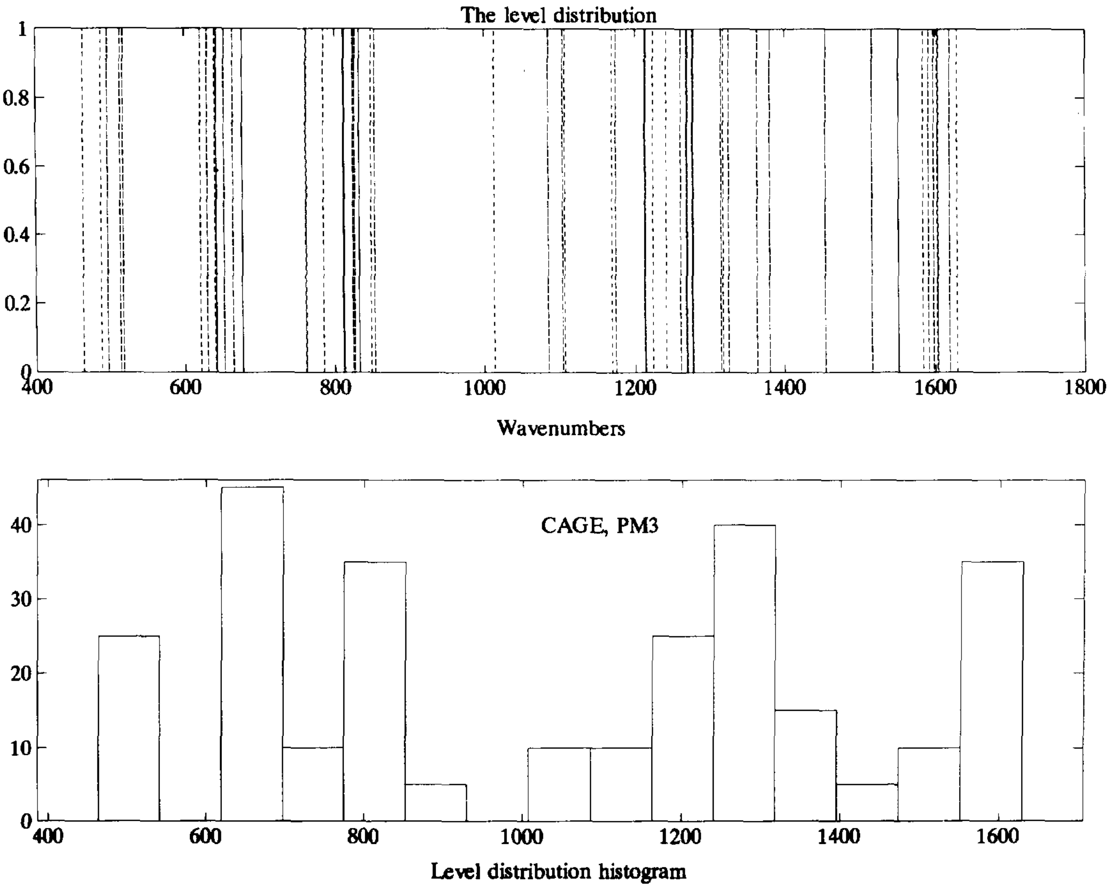

Fig. 4. Distribution of vibrations for the cage isomer from PM3 calculations.

Vibrational transition dipoles from MOPAC were squared, binned, interpolated and plotted to obtain a rough approximation for the infrared spectra. Figures 8, 9 and 10 depict the results for the PM3 hamiltonian.

Although the squared transition moments are only proportional to vibrational band intensities and may have systematic errors from MOPAC6.1, Figs. 8–10 provide some ideas of the expected vibrational spectra.

3. Discussion

The presence of five-fold symmetry and degenerate electronic states in the icosahedral C_{20} isomer induces Jahn–Teller interaction with the similarly degenerate vibrational states [15]. Such a (static or dynamic) effect may lead to spontaneous symmetry reduction to non-degenerate point groups. In the field of icosahedral fullerenes, first of all for C_{60}, these effects have already been studied [16,17]. In our calculation we have not applied symmetry constraints in the course of MOPAC runs, but a spontaneous reduction occurred for all three isomers. For the fullerene cage symmetry, reduction proceeded only to D_2. For the ring isomer this reduction ended up with a C_{10h} symmetry. Symmetry lowering was observed also for the corannulene structure; starting from the planar D_{5h} group, a reduction occurred to C_{5v}. In the case of the closed cage isomer, Taylor et al. [11] note that whereas

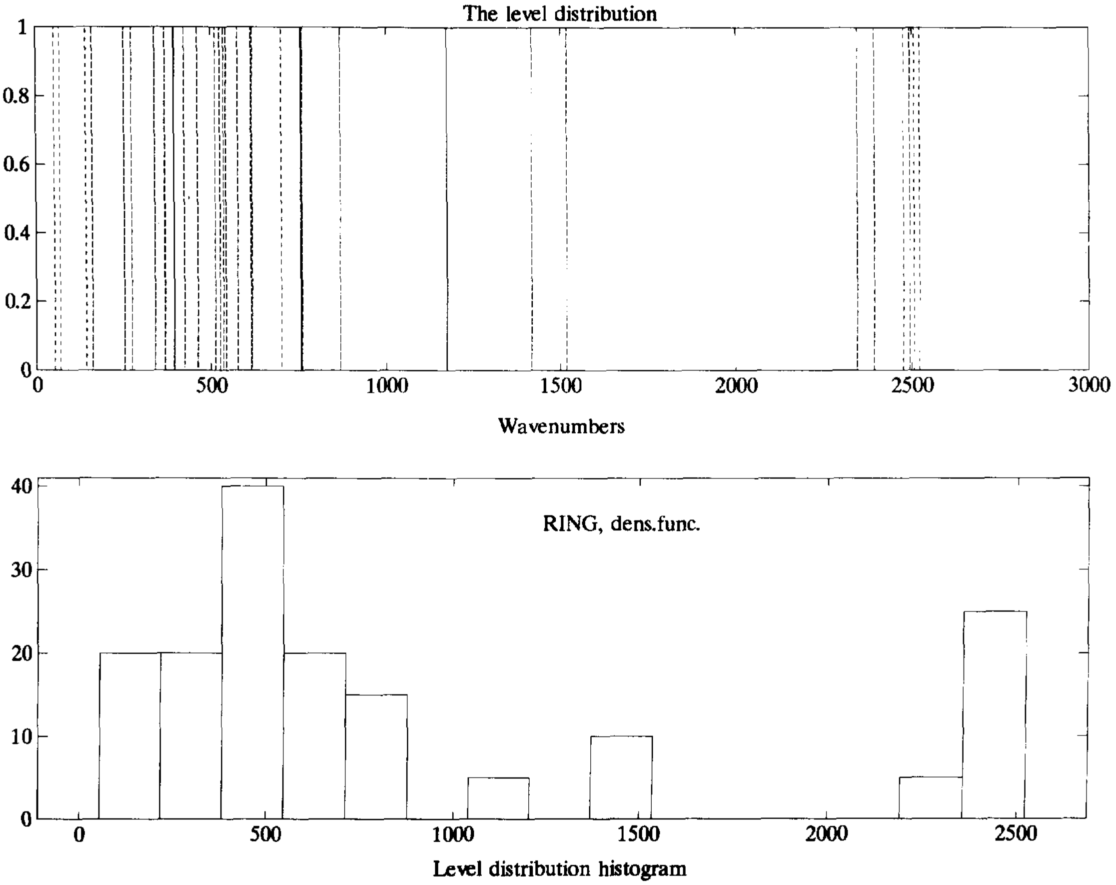

Fig. 5. Distribution of ring isomer vibrations from density functional calculations [6].

previous SCF optimizations led to a final C_2 symmetry, the application of local density theory [18] yielded C_i symmetry.

The comparison of the semi-empirical vibrational transition (or level) distributions given here with those of Raghavachari et al. [6] shows that, for the PM3 parametrization, differences are relatively small for the ring and bowl isomers, at least in the low energy region, whereas for the fullerene cage differences are large, also at the low wavenumber end. We believe that such level distribution studies might be meaningful for complicated molecular systems, such as fullerenes, in searching for systematic corrections to bring the calculated frequencies closer to experimental ones. From our result it appears that the semi-empirical PM3 hamiltonian might yield distributions similar to those produced computationally expensively using ab initio density functional techniques.

A large fraction of the vibrational modes remains inaccessible for optical studies in the icosahedral group, owing to high fullerene symmetry, but in all the converged symmetries here the number of infrared active modes is large (with the possible exception of the C_{10h} group of the ring isomer). Optically inactive modes can be determined from, e.g., inelastic neutron diffraction experiments. The sparsity of strong infrared transition dipoles, as obtained from our semi-empirical results, is striking, as can be seen from a comparison of Figs. 2, 3 and 4 with Figs. 8, 9 and 10,

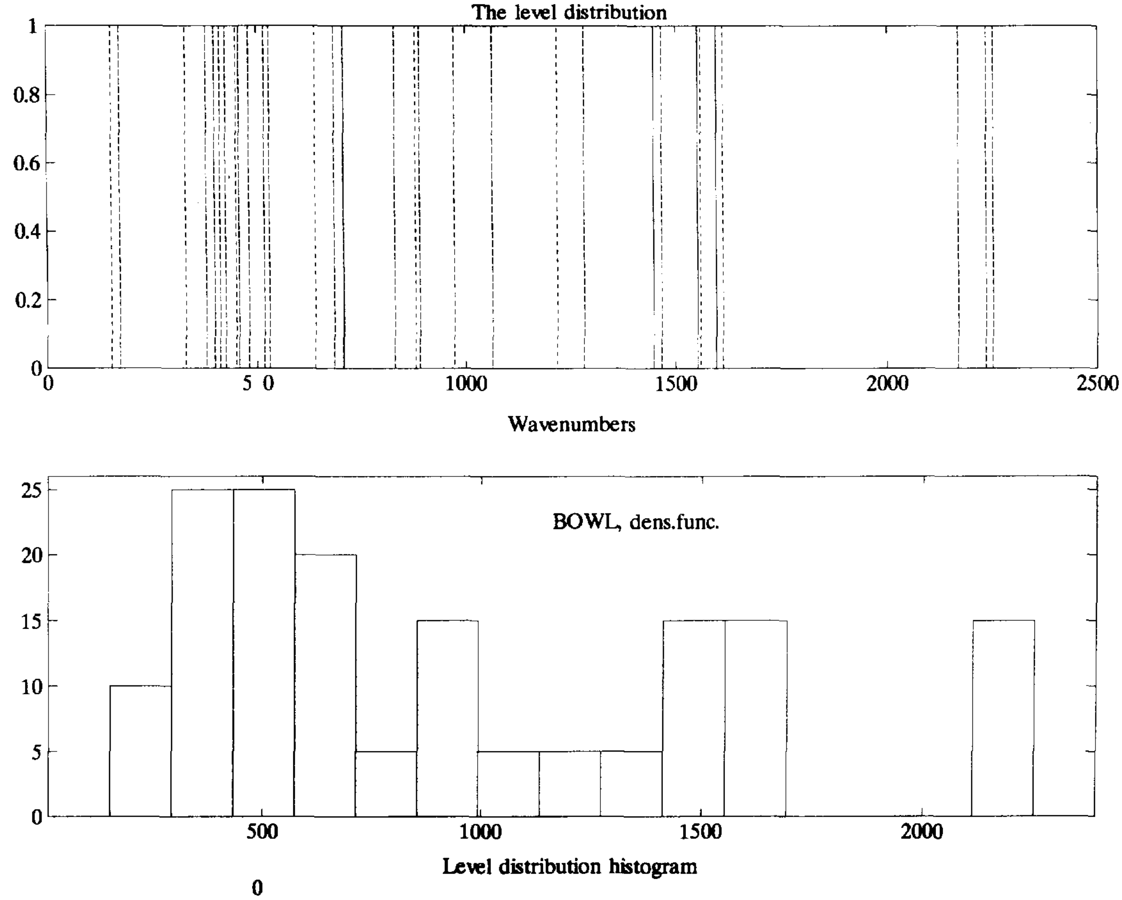

Fig. 6. Distribution of bowl isomer vibrations from density functional calculations [6].

especially for the ring isomer. Raman scattering and depolarization experiments might be more useful for the ring.

As to the relative stability of the three C_{20} isomers, heats of formation and total energy data in Table 2 appear to be in agreement with [6], even though the coupled-cluster calculations of Taylor et al. [11] may render such comparisons unimportant. The cage and the bowl have energies of 7.63 and 3.05 eV relative to the ring isomer. Another entropy factor possibly contributing to the stability of the ring is that its zero-point energy is lower by 3750 and 2300 cm^{-1} than those of the cage and the bowl form, respectively. In other words, the ring is vibrationally softer than the other forms. The main reason for this is the presence of low frequency modes. Taylor et al. [11] acknowledge the magnitude of vibrational entropy as being important in stability problems, but maintain that the fullerene cage form is still the most stable according to their calculations. They also believe the the dramatic effect of gradient corrections in the work of Raghavachari et al. [6], which induced those authors to claim the ring as the most stable form, may be due to an error ensuing from such corrections.

Obviously the C_{20} stability problem will finally be decided by experiments that might also allow infrared spectra to be taken for these structures. The schematic spectra produced here by semi-empirical methods will obviously change upon

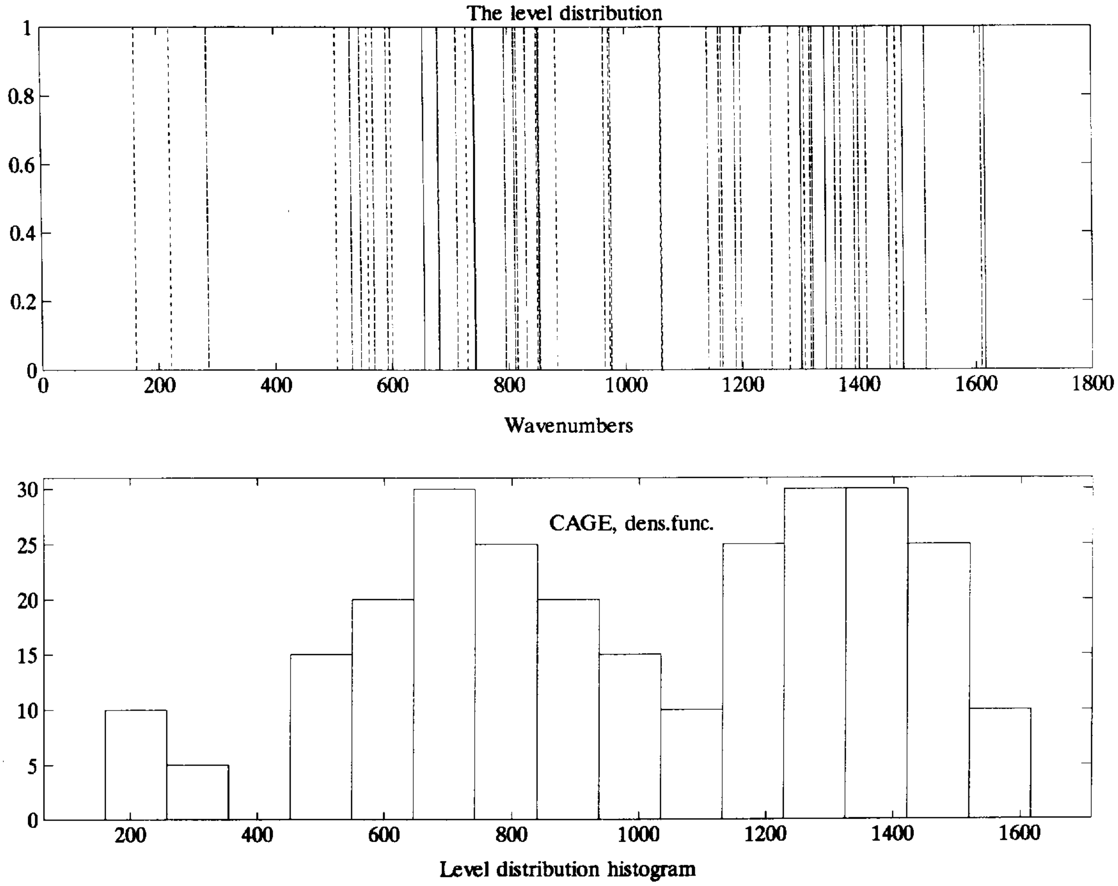

Fig. 7. Distribution of cage isomer vibrations from density functional calculations [6].

going to a higher level in theory. However, we believe that the very large difference between the ring spectrum and the spectra of the other two isomers will not change qualitatively upon theoretical upgrading. Thus, a very simple infrared spectrum is expected for the ring isomer in any case. When very low temperature gas-phase vibration–rotation spectra become available in the future for the C_{20} isomers (from molecular beam studies, perhaps), the perfect symmetric top geometry of the cyclic planar ring form should also contribute to the strikingly simple appearance of its infrared vibration–rotation bands. The fullerene cage form, on the other hand, has a complex vibrational structure and is a strongly asymmetric oblate rotor. These two factors will produce a complicated spectrum for the fullerene cage even at molecular beam temperatures.

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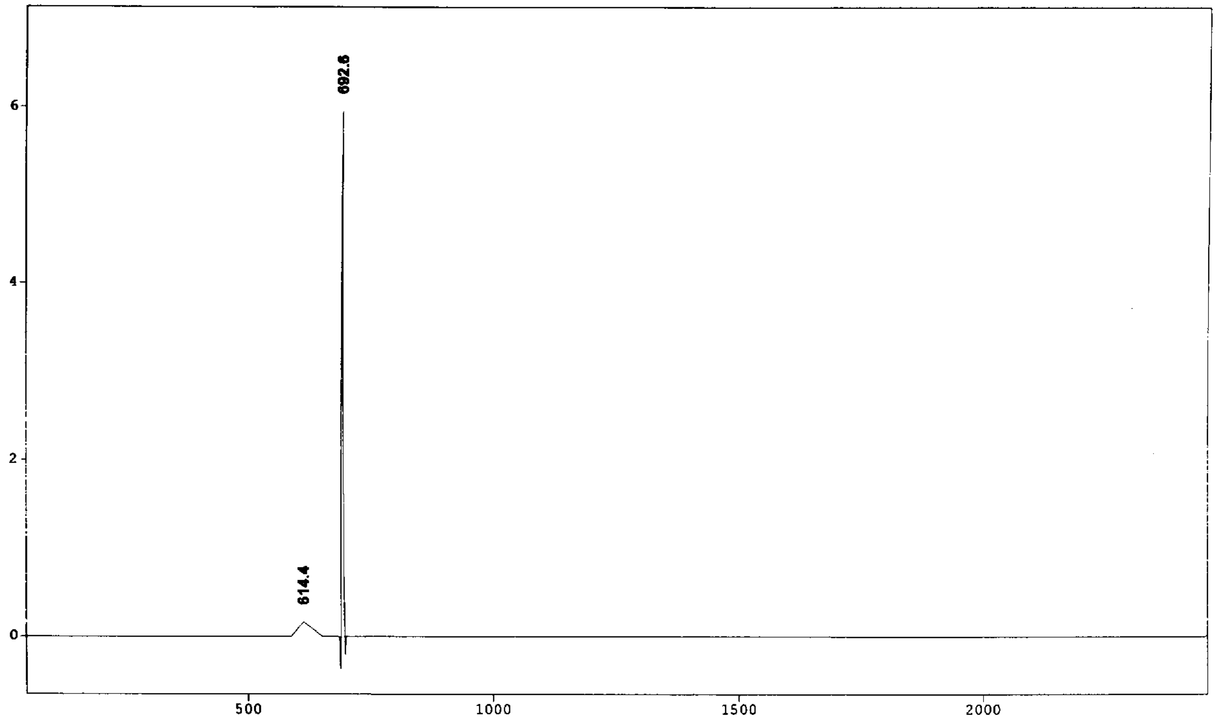

Fig. 8. Schematic infrared spectrum for the ring isomer from PM3 calculations.

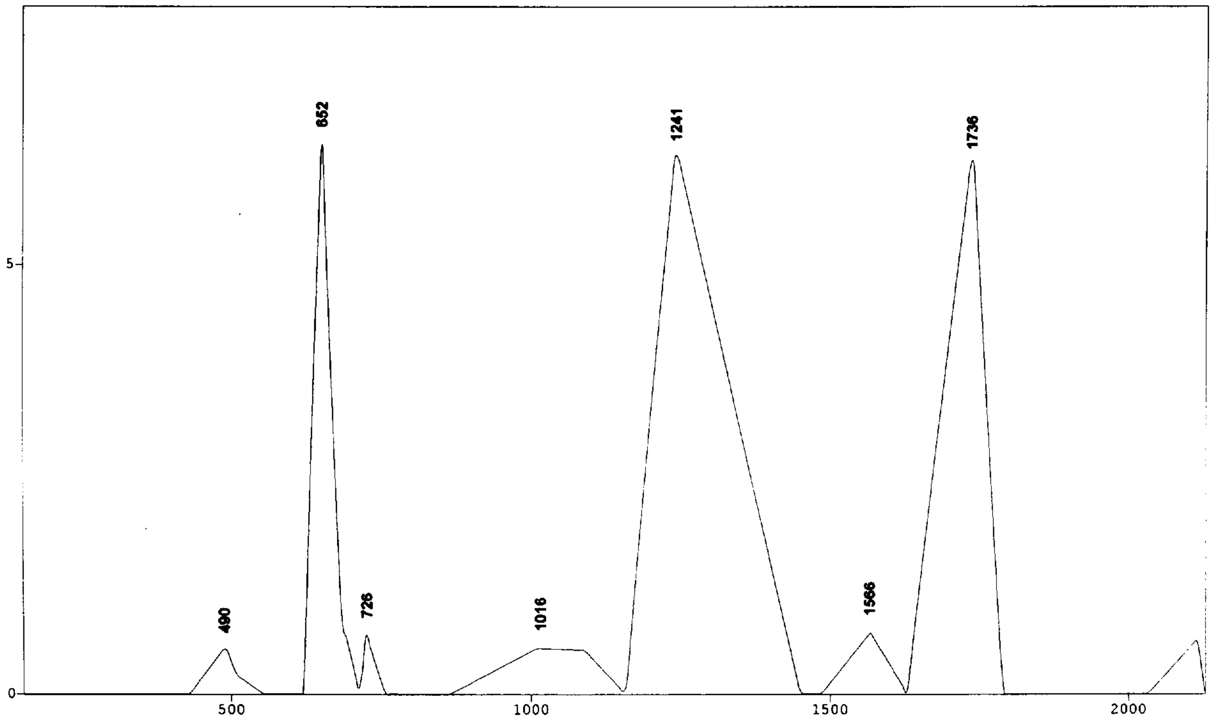

Fig. 9. Schematic infrared spectrum for the bowl isomer from PM3 calculations.

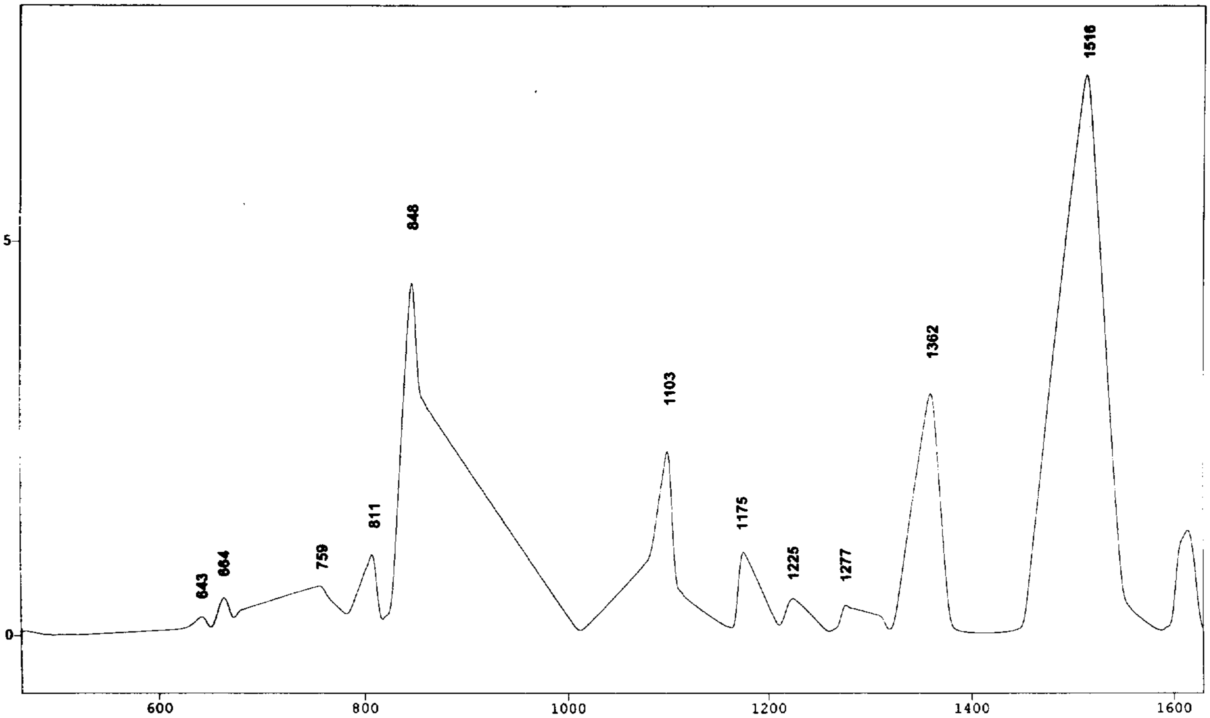

Fig. 10. Schematic infrared spectrum for the cage isomer from PM3 calculations.

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