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**QUANTUM-CHEMICAL INVESTIGATION
OF FRANCK-CONDON AND JAHN-TELLER ACTIVITY
IN THE ELECTRONIC SPECTRA OF BUCKMINSTERFULLERENE**

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Quantum-chemical results are reported which indicate that the absorption, fluorescence and phosphorescence spectra of Buckminsterfullerene are governed by a $^1T_{1u} \leftarrow ^1A_g$, $^1T_{2g} \rightarrow ^1A_g$ and $^3T_{2g} \rightarrow ^1A_g$ transition, respectively. Normal modes are calculated and their Franck-Condon and Jahn-Teller activity in these spectra are evaluated, along with the Jahn-Teller distortion of the radical anion. Vibrational progressions are expected to be short. A high phosphorescence quantum yield is predicted.

1. Introduction

An impressive experimental [1–12] and theoretical [13–29] effort has been made to investigate clusters of carbon atoms. Recently clusters of 60 carbon atoms have been detected in unusual abundance in time-of-flight mass spectra of graphite vaporized by a laser beam and have been suggested to have a structure belonging to the I_h icosahedral group closely resembling a soccerball [1]; as a tribute to R. Buckminster Fuller, it has been named Buckminsterfullerene (BF). Very recently a striking proof of the existence of a quasi-spherical structure for carbon clusters has been found in electron micrographs of graphitized carbon [12]. These carbon clusters are beginning to be studied spectroscopically and quite recently an absorption experiment has been reported on BF [6].

Prompted by this study we have undertaken a quantum-chemical study of BF in the states governing the absorption, the fluorescence and the phos-

phorescence spectrum. Because of the high symmetry of BF, excited states will be degenerate and subject to Jahn-Teller (JT) distortion. This would give rise to the appearance of JT-active modes along with Franck-Condon- (FC) active modes in the spectra. JT distortion may also occur in the mass-spectroscopically detected anion BF^- . To investigate these properties we use the QCFF/PI method [30–32] which has been shown to predict them reliably in several conjugated and aromatic systems [33–40].

2. Results and discussion

The ground state equilibrium geometry of BF is a regular truncated icosahedral, a structure limited by 32 faces, 12 regular pentagons and 20 hexagons (fig. 1). The computed length of the CC bonds forming the pentagons is 1.471 Å while the length of the CC bonds common to two hexagons is 1.411 Å. These bond lengths are comparable with those previously obtained, viz. 1.465 and 1.376 Å by STO/3G [18], 1.474 and 1.400 Å by MNDO [23] and 1.453 and 1.369 Å by a double-zeta basis set [26]. Note that

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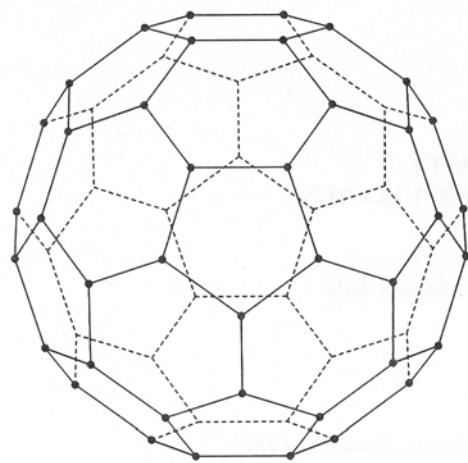


Fig. 1. BF in its regular truncated icosahedral geometry.

all these theoretical methods produce essentially the same difference (0.07–0.09 Å) between the two types of bonds, suggesting that bond alternation is a characteristic feature of the BF structure.

The calculated SCF energies of the last three HOMO and of the first four LUMO levels at the equilibrium geometry are: –9.29 eV (g_g), –8.94 eV (h_g) and –8.12 eV (h_u); and –1.52 eV (t_{1u}), –0.88 eV (t_{1g}), 1.20 eV (h_g), 1.60 eV (t_{2u}) and 2.12 eV (h_u). The energy of the HOMO, –8.12 eV, is in reasonable agreement with the experimental ionization threshold found to be above 6.42 eV and below 7.87 eV and compares well with the result of previous calculations, viz. –9.1 [23], –8.24 [26] and –7.55 eV [29], although it is at variance with the energy of –4.5 eV [25] obtained by a PRDDO calculation.

The energies of the lowest singlet excited states and the oscillator strength for their transition to the ground state are shown in table 1. The CI treatment comprises 266 singly excited (SE) configurations arising from the above HOMOs and LUMOs. In the CI matrix, the size of the off-diagonal elements between configurations arising from $h_g \rightarrow t_{1u} + t_{1g} + h_g + t_{2u} + h_u$ excitations and configurations arising from $g_g \rightarrow t_{1u} + t_{1g} + h_g + t_{2u} + h_u$ excitations amounts roughly to 20% of the size of the other interactions. This reflects the fact that h_g and g_g MOs originate from spherical orbitals with the same angular momentum quantum number $L=4$ and are degenerate under spherical symmetry.

Table 1
Electronic energies (in eV) and oscillator strength (f) for the lowest singlet and triplet states of BF computed by QCFF/PI and CI of 196 SE

Type	E	f	Type	E
1 $^1T_{2g}$	2.58	–	1 $^3T_{2g}$	2.06
1 $^1T_{1g}$	2.61	–	1 $^3T_{1g}$	2.40
1 1G_g	2.70	–	1 3G_u	2.58
1 $^1T_{2u}$	2.89	–	1 3H_g	2.59
1 1H_u	3.15	–	1 $^3T_{2u}$	2.59
1 1H_g	3.15	–	1 $^3T_{1u}$	2.61
1 1G_u	3.21	–	1 3G_g	2.66
2 1H_u	3.89	–	1 3H_u	2.98
2 1G_u	3.90	–	2 $^3T_{2u}$	3.66
1 $^1T_{1u}$	4.08	0.61	2 3H_u	3.81
2 $^1T_{2u}$	4.12	–	2 3G_u	3.84
3 1G_u	4.37	–	2 3G_g	4.26
3 1H_u	4.39	–	2 3H_g	4.28
2 $^1T_{2g}$	4.41	–	3 3G_u	4.29
2 $^1T_{1u}$	4.53	0.41	2 $^3T_{2g}$	4.32
–	–	–	3 3H_u	4.32
3 $^1T_{1u}$	6.19	4.84	3 $^3T_{1u}$	4.34

The singlet excited states are very densely packed and the lowest of them, belonging to the T_{2g} species, lies at 2.58 eV. The second excited singlet state, 1 $^1T_{1g}$, is only 0.03 eV above 1 $^1T_{2g}$; nevertheless, the latter state was found to remain the lowest also changing the size of the CI matrix. The lowest allowed transition is to a $^1T_{1u}$ state at 4.08 eV and has an oscillator strength (f) of 0.61. The wavefunction of 1 $^1T_{1u}$ is dominated by the $h_u \rightarrow t_{1g}$ configuration, while the wavefunction of 2 $^1T_{1u}$, computed at 4.53 eV, is dominated by the $h_g \rightarrow t_{1u}$ configuration. The $^1T_{1u}$ state with the largest oscillator strength is found at higher energy (6.19 eV). A very recent Pariser-Pople calculation [22] reports generally similar energies for the excited states. However, the energy of the most intense $^1T_{1u}$ state is at variance with our result. We have checked that these differences are due to the smaller size (<150) of the CI matrix used in ref. [22].

In table 1 are shown also the energies of the lowest triplet states. The two lowest triplets (1 $^3T_{2g}$ and 1 $^3T_{1g}$) are of the same symmetry type as the two lowest singlets. The energy difference between 1 $^1T_{2g}$ and 1 $^3T_{2g}$ is relatively small, ≈0.5 eV.

A CNDO/S CI calculation based on a similar number (250) of SE configurations [29] finds 1 $^1T_{1u}$ at

3.6 eV. Our higher value of the 1^1T_{1u} energy may be due to the lack of $\sigma\pi^*$ configurations which in this non-planar system can mix with $\pi\pi^*$ configurations. Experimentally, the absorption spectrum of BF reveals a single band at 3860 Å (3.21 eV) [6] that has been attributed to the $1^1T_{1u} \leftarrow 1^1A_g$ transition. Since the observed band lies at an energy lower than the 1^1T_{1u} energy found by both the QCFF/PI and CNDO/S methods, it might at this stage be attributed also to a forbidden transition, induced by vibronic coupling to a state with an energy closer to 3.21 eV.

The fluorescence transition, which originates from the lowest singlet state, 1^1T_{2g} , is symmetry forbidden and is induced vibronically by g_u and h_u modes. Also the phosphorescence transition, $1^3T_{2g} \rightarrow 1^1A_{1g}$, is symmetry forbidden and is induced by vibronic and spin-orbit perturbations. The active modes in phosphorescence are t_{1u} , t_{2u} , g_u and h_u .

In table 2 we show the vibrational frequencies computed by the QCFF/PI method together with those obtained in ref. [28] on the basis of an empirical force field partly derived from MNDO calculations. On average the two sets of frequencies are

similar, except that the CC stretch frequencies of ref. [28] ($\approx 1800 \text{ cm}^{-1}$) are higher than ours ($\approx 1600 \text{ cm}^{-1}$). This difference is not surprising since it reflects the tendency of MNDO to overestimate CC stretch frequencies. Also, in agreement with ref. [17], we find 4 modes of type t_{2g} and 3 of type t_{1g} , instead of 5 modes t_{2g} and 2 modes t_{1g} as reported in ref. [28]; hence we have chosen to correlate the t_{2g} mode of 1464 cm^{-1} [28] with our t_{1g} mode of 1398 cm^{-1} . The IR spectrum of BF is expected to be very simple, namely composed of only 4 bands located at 1437 cm^{-1} , 1212 cm^{-1} , 607 cm^{-1} and 544 cm^{-1} . The Raman spectrum, due to a_g and h_g vibrations, is expected to show 10 bands.

Upon excitation and ionization this highly symmetric molecule distorts both along the a_g coordinates and the JT-active coordinates. We are interested in the excited states 1^1T_{1u} , 1^1T_{2g} and 1^3T_{2g} , which are likely to govern the absorption, fluorescence and phosphorescence spectra, respectively. Furthermore, we consider the ground state of BF^- , which is 1^2T_{1u} . Thus the JT-active coordinates are of the type h_g . A measure of the distortion along a_g and h_g coordinates caused by excitation or ionization is given by the di-

Table 2
Computed ground state vibrational frequencies (in cm^{-1}); in parentheses the frequencies of ref. [28]

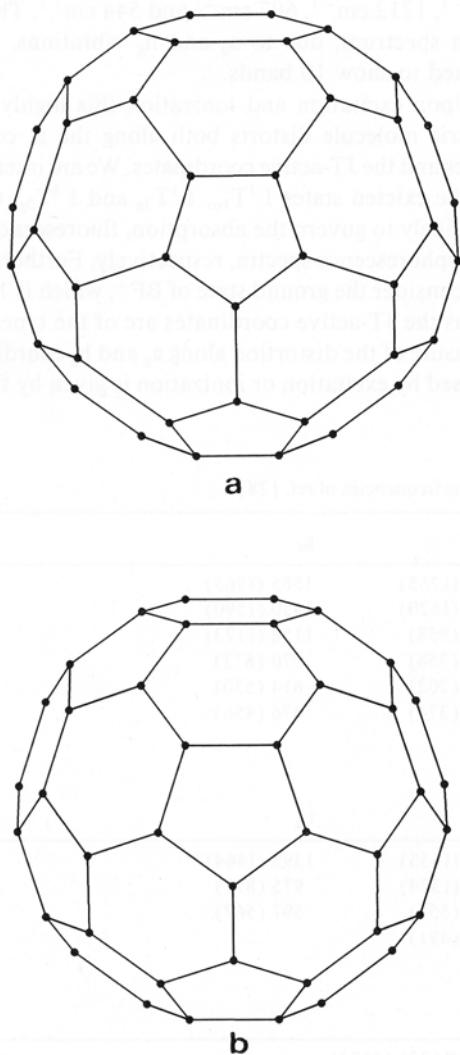
h_u	h_g	g_u	g_g
1646 (1830)	1644 (1830)	1546 (1765)	1585 (1765)
1469 (1578)	1465 (1688)	1401 (1620)	1450 (1590)
1269 (1290)	1265 (1398)	1007 (958)	1158 (1173)
812 (770)	1154 (1160)	832 (756)	770 (673)
724 (578)	801 (780)	816 (702)	614 (530)
531 (492)	691 (552)	358 (374)	476 (456)
403 (354)	440 (428)		
	258 (272)		
t_{2u}	t_{2g}	t_{1u}	t_{1g}
1558 (1720)	1470 (1665)	1437 (1655)	1398 (1464) ^{b)}
1241 (1309)	890 (927)	1212 (1374)	975 (811)
999 (1019)	834 (726)	637 (551)	597 (567)
690 (627)	637 (525)	544 (491)	
350 (362)			
a_u		a_g	
1206 (1084) 973 ^{a)}		1442 (1627) 1667 ^{a)}	
		513 (548) 611 ^{a)}	

^{a)} From ref. [23]. ^{b)} See text.

Table 3

Main displacement components B_i in the excited states 1^1T_{2g} , 1^1T_{1u} and 1^3T_{2g} , and the anion BF^-

		$B_i(1^1T_{2g})$	$B_i(1^1T_{1u})$	$B_i(1^3T_{2g})$	$B_i(BF^-)$
a_g	1442	0.47	0.47	0.47	0.43
	513	0.10	0.13	0.11	0.21
h_g	1644	0.50	-	0.26	0.30
	1465	0.37	-	0.17	0.24
	801	0.35	-	0.18	0.22
	257	1.13	0.17	0.64	0.56

Fig. 2. Representation of a_g modes: BF distorted along the (a) 1442 cm^{-1} and (b) 513 cm^{-1} coordinates.

dimensionless displacement parameters B_i . These are proportional to the projection onto normal coordinates Q_i of the change of equilibrium coordinates due to excitation or ionization. The vector \mathbf{B} of displacement parameters is thus given by

$$\mathbf{B} = 0.176 \Omega^{1/2} [\mathbf{x}(\text{New}) - \mathbf{x}(1^1A_g)] \mathbf{M}^{1/2} \mathbf{L}(1^1A_g), \quad (1)$$

where Ω is the vector of the $3N-6$ vibrational frequencies in cm^{-1} , $\mathbf{x}(\Gamma)$ is the $3N$ -dimensional vector of the equilibrium Cartesian coordinates in the Γ electronic state, \mathbf{M} is the $3N \times 3N$ diagonal matrix of the atomic masses (amu) and \mathbf{L} is the $3N \times (3N-6)$ matrix describing normal coordinates in terms of mass-weighted Cartesian coordinates (\AA amu $^{1/2}$). The equilibrium geometries in 1^1T_{2g} , 1^1T_{1u} , 1^3T_{2g} and in 1^2T_{1u} have been computed by the QCFF/PI method. The largest components of the \mathbf{B} vectors are listed in table 3 and corresponding a_g and g_g normal coordinates are depicted in figs. 2 and 3. The $513 \text{ cm}^{-1} a_g$ mode, corresponding to the breathing mode, has smaller displacements than the $1442 \text{ cm}^{-1} a_g$ mode, in which the two different types of bonds vibrate with opposite phases, in the three excited states and in the anion. The parameter $\gamma = 1/2B^2$, which measures the Stokes shift in units of frequency, amounts to 0.1 for the 1442 cm^{-1} mode. Since QCFF/PI calculations underestimate γ , we estimate $\gamma(1442 \text{ cm}^{-1})$ to be ≈ 0.2 . This value corresponds to a very short progression for the most active a_g mode, the 0-0 band being strongly dominant. The very small value of γ (513 cm^{-1}) indicates negligible FC activity of this mode.

The JT distortion is negligible in the state 1^1T_{1u} , hence no h_g mode is expected to contribute to the vibrational structure of the absorption spectrum $1^1T_{1u} \leftarrow 1^1A_g$. Thus this spectrum is predicted to

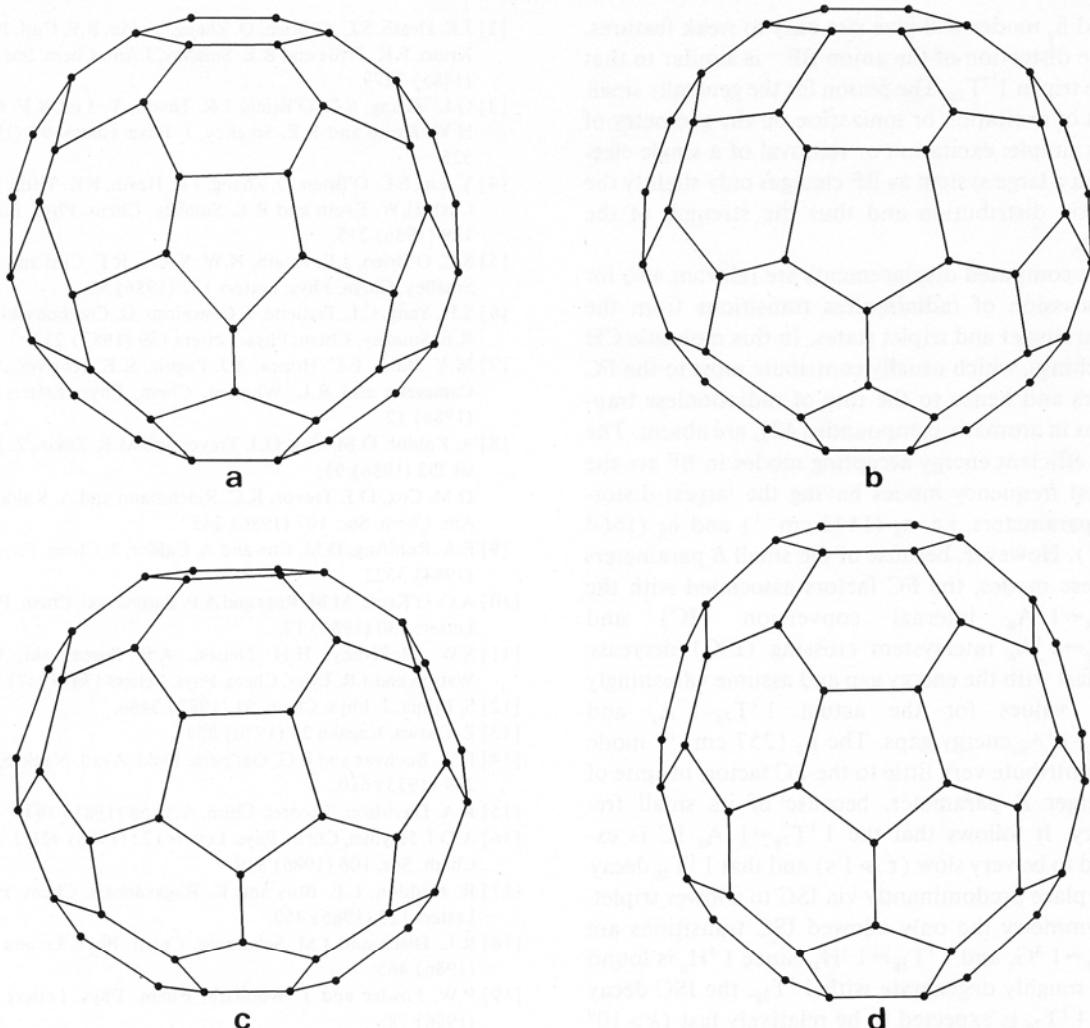


Fig. 3. Representation of the JT-active modes: BF distorted along the (a) 1664 cm^{-1} , (b) 1465 cm^{-1} , (c) 801 cm^{-1} and (d) 257 cm^{-1} h_g coordinates.

consist of a single strong band, i.e. the 0–0 band. The absorption spectrum to states of symmetry different than $^1T_{1u}$ is vibronically induced. Hence it is based in general on a number of bands, each corresponding to a false origin, even in the absence of combination bands involving a_g or h_g modes. The observed spectrum [41], consisting of a single band at 3860 \AA , is in agreement with the predicted structure of the $1\text{ }^1T_{1u}\leftarrow 1\text{ }^1A_g$ spectrum but it is unlikely to correspond to a forbidden transition.

The JT distortion is larger in the lowest excited state 1 ^1T_{2g} and it is significant especially for the 257 cm^{-1} mode which has a parameter $B=1.13$. The vibrational structure contributed by h_g modes in the fluorescence $1\text{ }^1T_{2g}\rightarrow 1\text{ }^1A_g$ spectrum is expected to show a few strong bands of the 257 cm^{-1} mode and only weak features of the 1664 cm^{-1} mode. This vibrational structure is superimposed on each false origin.

The distortion in the lowest triplet state along the a_g coordinates is similar to that of the corresponding singlet 1 ^1T_{2g} , but JT distortions are about half as large. Hence the phosphorescence spectrum is predicted to be dominated by the false origins, while the

a_g and h_g modes will give rise only to weak features.

The distortion of the anion BF^- is similar to that of the triplet $^3T_{2g}$. The reason for the generally small effect of excitation or ionization on the geometry of BF is simple: excitation or removal of a single electron in a large system as BF changes only slightly the electron distribution and thus the strength of the bonds.

The computed displacements are relevant also for a discussion of radiationless transitions from the lowest singlet and triplet states. In this molecule CH stretchings, which usually contribute most to the FC factors and hence to the rate of radiationless transitions in aromatic compounds [42], are absent. The most efficient energy accepting modes in BF are the highest frequency modes having the largest distortion parameters, i.e. a_g (1442 cm^{-1}) and h_g (1664 cm^{-1}). However, because of the small B parameters of these modes, the FC factors associated with the $^1T_{2g} \rightsquigarrow ^1A_g$ internal conversion (IC) and $^3T_{2g} \rightsquigarrow ^1A_g$ intersystem crossing (ISC) decrease very fast with the energy gap and assume vanishingly small values for the actual $^1T_{2g}-^1A_g$ and $^3T_{2g}-^1A_g$ energy gaps. The h_g (257 cm^{-1}) mode can contribute very little to the FC factor, in spite of its larger B parameter, because of its small frequency. It follows that the $^1T_{2g} \rightsquigarrow ^1A_g$ IC is expected to be very slow ($\tau \gg 1\text{ s}$) and that $^1T_{2g}$ decay takes place predominantly via ISC to a lower triplet. By symmetry the only allowed ISC transitions are $^1T_{2g} \rightsquigarrow ^1^3G_g$ and $^1T_{2g} \rightsquigarrow ^1^3H_g$. Since $^1^3H_g$ is found to be roughly degenerate with $^1T_{2g}$, the ISC decay from $^1T_{2g}$ is expected to be relatively fast ($k > 10^9\text{ s}^{-1}$).

On the basis of the small FC factor, a very low rate ($\tau \gg 1\text{ s}$) is predicted also for the ISC $^3T_{2g} \rightsquigarrow ^1A_g$. Furthermore, this process is symmetry forbidden and it is induced by a spin-vibronic mechanism based on h_g vibrations; this is an additional reason for its inefficiency.

Thus we predict that emission of BF is predominantly due to phosphorescence and that it occurs with high quantum yield.

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