***Ab initio* calculations of the structure and dynamics of C₆₀ and C₆₀^{3−}**

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[Received 17 December 1991† and accepted 16 March 1992]

ABSTRACT

A local density functional cluster method is used to calculate the structure and vibrational modes of C₆₀. We find C-C lengths in good agreement with observed values. The effect of doping the molecule with three extra electrons is investigated and shown to result in a surprising *shortening* of the longer bonds. The second derivatives of the energy are evaluated and enabled, for the first time, *all* the normal modes of the molecule to be found. We find these to be in fair agreement with the available experimental results.

The discovery (Hebard *et al.*, 1991) of superconductivity in alkali-metal doped C₆₀ has created intense interest in the structure of the molecule and its vibratory modes. We calculate these using an *ab initio* local density functional pseudopotential method (Jones and Sayyash, 1986; Jones, 1988) with a Gaussian basis set of *s*- and *p*-orbitals. The pseudopotential is taken from (Bachelet *et al.*, 1982) and obviates the need to describe the C 1*s*-orbital. The exchange and correlation potentials of Ceperley and Alder (1980) are utilised. The Hartree and exchange-correlation energies are evaluated by performing an intermediate fit to the charge density also using Gaussian functions.

We used a basis of two independent *s*- and *p*-Gaussian orbitals per atom. Thus all atoms are treated symmetrically. Relaxing this cluster gave bond lengths of 1.40 and 1.48 Å, in reasonably good agreement with values of 1.40, 1.45 and 1.388, 1.45 Å deduced by nuclear magnetic resonance (Yannoni *et al.*, 1991) and X-ray work (Hawkins *et al.*, 1991) respectively. The energy gap found was 2.01 eV and compares well with 1.9 eV found by Saito and Oshiyama (1991). This represents the difference in one-electron energy levels between the highest occupied level (*h*) and the lowest unoccupied level (*t*).

We then added three electrons to the cluster: occupying each of the three degenerate states of the *t*-level above. This would correspond to the doping configuration M₃C₆₀ where M is an alkali metal atom. Now, occupying these orbitals results in extra forces on the C atoms. We have evaluated these forces and re-relaxed the cluster. The short

†Received in final form 9 March 1992.

Figure 1: The displacements caused by the charging the buckyball are shown as projections almost normal to the molecular surface.

Table 1: Parameters for Musgrave-Pople Potential for C_{60} ($r_0 = 1.428 \text{ \AA}$).

k_r (eV/ $\text{\AA}^2$)	k_θ (eV/ $\text{\AA}^2$)	$k_{r\theta}$ (eV/ $\text{\AA}^2$)	k_{rr} (eV/ $\text{\AA}^2$)	$k_{\theta\theta}$ (eV/ $\text{\AA}^2$)
38.11	6.37	2.78	3.74	2.74

bonds were unaffected but the long bonds *decreased* in length to $1.466 \text{ \AA}$. This effect can be understood by saying that the wave-functions of the unoccupied t -levels, which are largely composed of p orbitals normal to the ball, have a degree of bonding character along the pentagonal sides: it is simply not possible to have purely anti-bonding p -orbitals on all pairs of vertices connected by edges of the pentagons. Another way of putting it is that the charge density is high in the inter-hexagonal (double) bonds and thus the extra electrons reside in the pentagonal bonds which are regions of reduced electron density.

We now wish to investigate which vibratory modes will couple most strongly to this distortion. This will be important in the application of the Bardeen-Cooper-Schrieffer theory of superconductivity. The technique adopted here (Jones and Sayyash, 1986; Jones, 1988), is to generate the dynamical matrix of the molecule from that of a small patch of four atoms on the surface of the molecule (fig. 1) which is treated with a very large basis set and the remaining atoms with a much smaller basis. The atoms in the patch and their neighbours are then allowed to move until the forces on them vanish.

We now use a wave-function basis consisting of four s - and p -Gaussian functions with independent exponents (i.e. 16 orbitals per atom) on the central four atoms of the patch. The remaining atoms were treated with a fixed linear combination of these four functions with the coefficients of the fit determined from the free atom. The charge density was fitted to Gaussian s -like functions with five independent exponents per atom. In addition, bond centred s - and p -Gaussian orbitals were placed at the centres

Table 2: Frequencies for C_{60} : MP, use of Musgrave Pople potential.

Mode	Frequency (cm^{-1})			
	<i>Ab initio</i>	MP	MNDO ¹	Empirical ²
A_g	1416	1472	1667	1830
	582	538	610	510
T_{1g}	1253	1350	1410	1662
	820	955	865	1045
	661	700	627	513
T_{3g}	1310	1386	1483	1900
	1129	1104	919	951
	803	857	784	724
	514	633	591	615
G_g	1466	1449	1650	2006
	1326	1392	1404	1813
	1094	1188	1235	1327
	977	970	856	657
	517	601	579	593
	454	489	491	433
H_g	1516	1446	1722	2085
	1395	1412	1596	1910
	1193	1261	1407	1575
	1106	1145	1261	1292
	829	825	924	828
	787	818	771	526
	437	471	447	413
	288	276	263	274
A_u	991	1138	972	1243
T_{1u}	1403	1445	1628	1868
	1127	1232	1353	1462
	647	656	719	618
	614	632	577	478
T_{3u}	1494	1433	1687	1954
	1164	1319	1314	1543
	1009	1062	1134	1122
	850	844	776	526
	363	370	348	358
G_u	1408	1427	1587	2004
	1286	1354	1436	1845
	1115	1102	1110	1086
	936	990	914	876
	749	804	750	663
	374	384	362	360
H_u	1507	1449	1709	2086
	1317	1395	1467	1797
	1203	1195	1344	1464
	909	914	822	849
	634	762	706	569
	510	542	546	470
	303	404	403	405

^aStanton and Newton (1988).^bNewton and Stanton (1986).

Table 3: Raman-active frequencies of C₆₀: MP, use of Musgrave-Pople potential.

Mode	Raman-active frequency (cm ⁻¹)					
	Experimental ^a	<i>ab initio</i>	MP	Calculated ^b	Calculated ^c	MNDO ^d
<i>A_g</i>	1470	1416	1472	1368	1680	1667
	496	582	438	454	537	610
<i>H_g</i>	1575	1516	1446	1500	1726	1722
	1428	1395	1412	1314	1624	1596
	1250	1193	1261	1110	1453	1407
	1099	1106	1145		1209	1261
	774	829	825		845	924
	710	787	818	688	681	771
	437	437	471	405	413	447
	273	288	276	246	249	263

^aBethune *et al.* (1990)^bFeuston *et al.* (1991)^cAdams *et al.* (1991)^dStanton and Newton (1988)

of nine innermost bonds.

Tests with larger bases showed little change to the structure found below. The starting structure possessed bond lengths of 1.42 Å. The forces on the inner nine atoms were evaluated and these atoms moved by a conjugate gradient scheme until they vanished. The bond lengths of the central atom were then 1.37 and 1.43 Å –slightly smaller than those deduced above.

The second derivatives of the energy were then evaluated between the inner four atoms. These were used in two ways: firstly, we fitted them to the derivatives of a Musgrave-Pople potential (Musgrave and Pople, 1962) where the potential for atom *i* is

$$\begin{aligned}
 V_i = & \quad 1/4 \sum_j k_r^{(i)} (\Delta r_{ij})^2 + r_0^2/2 \sum_{j>k} k_\theta^{(i)} (\Delta \theta_{jik})^2 + r_0 \sum_{k>j} k_{r\theta}^{(i)} (\Delta r_{ij} + \Delta r_{ik}) \Delta \theta_{jik} \\
 & + \sum_{k>j} k_{rr}^{(i)} \Delta r_{ij} \Delta r_{ik} + r_0^2 \sum_{l>k>j} k_{\theta\theta}^{(i)} \Delta \theta_{jik} \Delta \theta_{kil}.
 \end{aligned} \tag{1}$$

Here Δr_{ij} and $\Delta \theta_{jik}$ are the changes in the length of the *i* – *j* bond and angle between the *i* – *j* and *i* – *k* bond, respectively. The sum is over the nearest neighbour atoms only. Table 1 gives the coefficients $k_r^{(i)}$, $k_\theta^{(i)}$, $k_{r\theta}^{(i)}$, $k_{rr}^{(i)}$ and $k_{\theta\theta}^{(i)}$. This potential was used to generate the dynamical matrix of C₆₀ and the resulting 174 non-zero modes are given in table 2.

Secondly, we used the symmetry of the icosahedral molecule to generate all the derivatives from a set calculated by the *ab initio* method. These involved the derivative on the central atom, between it and two nearest neighbours and between two pairs of next-nearest neighbours. These were used directly to determine the modes also given in table 2. The symmetries of the normal modes were assigned by comparing with the normal modes given by Weeks and Harter (1989).

(a)

(b)

Figure 2: The normal coordinates corresponding to (a) the lowest and (b) the highest A_g modes.

Table 4: Infrared-active frequencies of C₆₀: MP, use of the Musgrave-Pople potential.

Mode	Infrared-active frequency (cm ⁻¹)							
	Experimental ^a	Experimental ^b	Experimental ^c	<i>Ab initio</i>	MP	Calculated ^d	Calculated ^e	MNDO ^f
T_u	1428	1428.9	1406.9	1403	1445	1345	1641	1628
	1183	1181.2	1169.1	1127	1232	1105	1358	1353
	577	576.3	570.3	647	656	555	643	719
	527	527.3	527.1	614	632	530	494	577

^aBethune *et al.* (1990)^bCox *et al.* (1986)^cFrum *et al.* (1991)^dFeuston *et al.* (1991)^eAdams *et al.* (1991)^fStanton and Newton (1988)

In tables 3 and 4 we compare the calculated modes with experiment and other *ab initio* density functional calculations (Adams *et al.*, 1991; Feuston *et al.*, 1991). The greatest error in the Raman modes is nearly 90 cm^{-1} and it occurs for the lowest A_g mode. In the calculation of Feuston *et al.* (1991) there was a problem in determining the higher H_g modes. It is clear that our errors are somewhat less than these.

The infra-red modes are given in table 4. Again our error is less than about 90 cm^{-1} compared with 80 for Feuston *et al.* (1991) and 200 cm^{-1} for Adams *et al.* (1991). It is interesting that the Musgrave-Pople potential is able to account for almost all the modes with a similar error.

We then projected the forces deduced from the addition of three electrons to the ball onto each normal mode coordinate calculated using the Musgrave Pople potential above. The most significant overlap occurs with the lowest A_g mode at 580 cm^{-1} and to a lesser extent the upper A_g mode. The normal coordinates of these modes are shown in fig. 2. Clearly the lower frequency one involves a breathing mode of the molecule and the higher a tangential displacement field. Thus the electron-phonon coupling will be strongest for these modes. The high values of the superconducting transition temperature may then be related to these high frequencies.

In conclusion, we have shown that the addition of three electrons to the molecule results in the shortening of the pentagonal bonds. We have evaluated, for the first time, all the dynamical modes by an *ab initio* method and shown that this distortion is strongly coupled with the lowest vibratory A_g mode.

ACKNOWLEDGEMENTS

VJBT acknowledges the British Council and Instituto Nacional de Investigação Científica for financial support permitting a visit to Exeter. SÖ thanks SuperDator-Centrum Norr in Sweden for computer time on the IBM 3090-600 J/VF in Skellefteå. SKE was supported by grant D-1126 from the Robert A. Welch Foundation in Houston.

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