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Electronic and vibrational properties of C_{60} at finite temperature from *ab initio* molecular dynamics

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A Car-Parrinello molecular-dynamics study of C_{60} in the fullerene structure has been performed. The ground-state properties were calculated and found to be in agreement with other theoretical estimates. The finite-temperature properties of such clusters are computed. These can be directly compared to experiments performed at finite temperature. The comparison is very favorable for structural, vibrational, and electronic properties.

The carbon cluster C_{60} was found only a few years ago to be exceptionally abundant in the mass spectrum of laser-evaporated graphite.[1] This has spurred a great interest in its structural and electronic properties.[2] The very recent discovery of an inexpensive way of producing macroscopic amounts of C_{60} (Refs. 3 and 4) has further enhanced the interest in this fascinating system, leading to the possibility of creating artificial two-dimensional (2D) and 3D structures, the building blocks of which are C_{60} clusters. Such structures are expected to find applications as lubricant materials and to exhibit novel properties. C_{60} has also been found to be a component of carbon soot[3-6] and is expected by some to be a component of interstellar dust.

In order to justify the extraordinary stability of C_{60}, a remarkable structure has been proposed,[1,7] usually called the fullerene structure. This consists of a truncated icosahedron with 12 pentagons and 20 hexagons. This structure implies that all the atoms are equivalent and are threefold coordinated with an alternation in the hexagons of single and double bonds, characteristic of aromatic molecules. Rapidly accumulating experimental evidence confirms this picture.[8] Nuclear-magnetic resonance[6,9] (NMR) has very convincingly demonstrated the equivalence of all the atomic positions in the structure. Extended-x-ray-absorption-fine-structure (EXAFS) data[6] indicate an average first-neighbor distance of 1.42 Å. Raman[8,10] and infrared (IR)[3,6,8,11] spectroscopy confirm that the C_{60} symmetry is that of the fullerene structure. Numerous theoretical models exist for f-C_{60}, ranging from *ab initio* calculations of the structural and/or electronic properties of the neutral and ionized clusters [Hartree Fock[12-14] (HF) and density-functional theory in the local-density approximation[15] (LDA)] to Hückel molecular-orbital descriptions of the chemical bonding,[16,17] to various empirical models of structural parameters and vibrational frequencies,[18-21] to classical molecular-dynamics (MD) simulations.[22]

In this paper, we present the results of an *ab initio* MD approach, carried out with the Car-Parrinello method.[23] This has been proven to be a powerful tool for the study of structural, electronic, and dynamical properties of a variety of microclusters[24] and also provides a rather accurate description of carbon in a variety of aggregation states.[25] This kind of simulation is unique in that it not only gives information on the ground-state properties but also allows ionic and electronic properties at finite temperature to be studied.

We optimize the structure by starting from the fullerene configuration. The resulting structure and electronic properties are in good agreement with experimental data. We have also equilibrated the system at about 450 K and from an analysis of the atomic trajectories, we obtain finite-*T* properties and the optically active modes. We also calculate the time-averaged electronic density of states which gives information on the vibrational broadening of the electronic states. The agreement with experimental data is very good.

The Car-Parrinello method has been described in a number of papers, to which we refer the reader.[26] In particular, a recent publication on carbon microclusters (C_4 and C_{10}) (Ref. 27) contains the input of this calculation, i.e., the parameters of the LDA angular-momentum-dependent pseudopotential used to describe the valence-core interaction as well as several tests of the accuracy of the computational scheme. Both bond lengths and vibrational frequencies turned out to agree with more sophisticated configuration interaction calculations and with experimental data (when available) within a few percent. The unit cell of our face-centered-cubic (fcc) periodic array has an edge of 17.464 Å. This is much larger than the diameter of the C_{60} fullerene structure (~ 7 Å). Therefore our calculation is aimed at describing an isolated cluster. The energy cutoff in the expansion of the Kohn-Sham (KS) orbitals in plane waves is 35 Ry which implies the use of ~ 32000 plane waves. With the time step 0.7×10^{-16} s used in the MD runs the electron states lie on the Born-Oppenheimer surface within 10^{-4} Hartree.

The first step of the calculations was the optimization of the C_{60} structure, done by a combined ionic and electronic steepest descent method. Subsequent MD runs confirmed that the resulting structure was a local minimum of the potential-energy surface. The equilibrium structure is spherical in the sense that all atoms are equidistant from the center of mass. The nearest-neighbor distances split into two long r_l pentagon edges and one short r_s hexagon edge. We find $r_s = 1.39$ Å and $r_l = 1.45$ Å, which compare very well with recent NMR data:[28] $r_s = 1.40 \pm 0.015$ Å and $r_l = 1.45 \pm 0.015$ Å. Previous theoretical estimates are also similar. In particular, we quote here the results of the self-consistent field (SCF) calculation performed with the largest basis set: $r_s = 1.370$ Å and $r_l = 1.447$ Å.[14]

In a further step, we heated the cluster to ~850 K, and found that the cluster was stable in the fullerene structure. We then gradually reduced the kinetic energy of the cluster and subsequently let the system evolve freely under the action of the forces. The cluster kinetic energy then fluctuated around 450 K. The average structure turned out to be only slightly distorted, average structural parameters being changed by ~0.01 Å at most. At finite temperature, the structure can be quantitatively described in terms of correlation functions. The usual $g(r)$ definition of pair correlation used in bulk systems is not very meaningful in the cluster. For this reason, we use instead the function $j(r)$, which is such that $j(r)dr$ gives the average number of particles whose distance from a given particle is between r and $r+dr$. This is shown in Fig. 1 together with the running coordination number $N(r) = \int_0^r j(r')dr'$. Both $j(r)$ and $N(r)$ functions clearly reflect the fullerene structure. Owing to thermal broadening, closely spaced shells of neighbors merge. Most noticeably, the splitting in the first-neighbor distances can only barely be seen as a shoulder. Similar and even smaller effects can be seen in the second peak, where two distances (the diagonal of the pentagon and the short diagonals of the hexagon) merge. EXAFS experiments[6] performed at finite temperature are not able to distinguish these splittings either. In Table I we compare our calculated peak positions (at finite T and at $T=0$) with those deduced from the EXAFS data. The agreement is very good, except for the second and fourth peaks where some significant differences can be seen. The origin of these discrepancies is not well understood. It must be mentioned that the second- and fourth-peak positions in the EXAFS data are not consistent with the otherwise well-established fullerene structure.

TABLE I. Structural parameters of C_{60} at finite temperature: positions of the first peaks of $j(r)$ (in Å) (Fig. 1) calculated at ~450 K compared to EXAFS data (Ref. 6). For comparison, our results at $T=0$ as well as NMR data (Ref. 28) are also reported.

	This work		
EXAFS	450 K	0 K	NMR
1.42	1.43	1.39,1.45	1.40,1.45
2.2	2.42	2.34,2.46	
2.9	2.84	2.84	
3.46	~3.61	3.56,3.68	
4.1	~4.1	4.1	

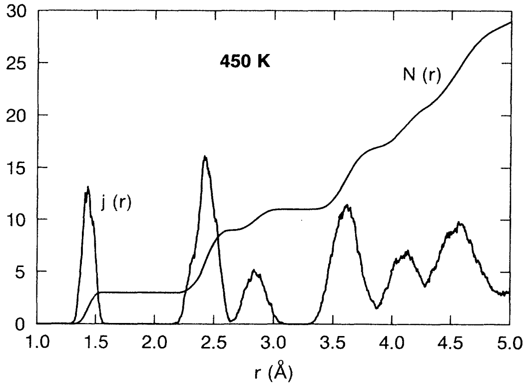

FIG. 1. Interatomic distances distribution and current coordination number (see text) calculated at ~450 K.

From the atomic trajectories it is, in principle, possible to extract the vibrational spectrum by computing the Fourier transform of the velocity-velocity autocorrelation function. However, such a procedure can only yield limited information since the frequency resolution is limited by the time span of the MD run. In our case, this is insufficient to resolve many of the modes and to single out those modes that are Raman or IR active. C_{60} has icosahedral symmetry which is the largest amongst the point groups. This leads to large degeneracy in the spectrum, having only 46 independent modes out of the possible 174. Of these modes, four with T_{1u} symmetry are IR active, while ten are Raman active. The Raman-active modes can be classified into two A_g (or totally symmetric) and eight H_g modes. We focus our attention here only on these measured vibrations but other modes could also have been obtained with the same procedure. In order to separate modes of different symmetry, we have used the symmetry-adapted coordinates defined in Ref. 29 and computed the correlation functions between the time derivatives of those coordinates. The resolution has then been enhanced by using a signal processing technique already successfully employed in another context.[30] With this methodology, we have been able to extract all four of the T_{1u} IR frequencies, the two A_g and six out of the eight H_g frequencies. The remaining two H_g modes were very difficult to identify, since the signal analysis did not produce a stable answer, in contrast to all the modes reported here. In Tables II and III, we compare our results with experimental data for the solid and, when available, for the gaseous phase as well as with the only available SCF estimate for the A_g modes.[13] The agreement between theory and experiments is very satisfactory, giving confidence in our predictions. In certain cases our analysis also allows us to assign the eigenmodes, shown in Tables II and III. These are particularly simple to describe in the case of the two A_g modes which, as already pointed out, correspond to the uniform breathing and to the out-of-phase motions of the pentagons and hexagons. Also rather simple to describe is the lowest H_g mode, which is a d-like "squashing" mode.

We examine now the electronic properties of our system at $T=0$ and at finite temperature. At $T=0$ the KS eigenvalues can be classified according to the irreducible representation of the icosahedral point group. It is to be noted,

TABLE II. IR modes: frequencies in cm^{-1}.

Expt.[a]	Expt.[b]	Expt.[c]	This work	Eigenvector[d]
527	527.3	527.1	530	$S_{T_{1u},a_4}(\tau)$
577	576.3	570.3	555	$\sqrt{3}/2S_{T_{1u},a_3}(d)+1/2S_{T_{1u},a_1}(r)$
1183	1181.2	1169.1	1105	$S_{T_{1u},a_2}(\tau)$
1428	1428.9	1406.9	1345	$-1/2S_{T_{1u},a_3}(d)+\sqrt{3}/2S_{T_{1u},a_1}(r)$

[a] Solid C_{60}, Ref. 8.

[b] Solid C_{60}, Ref. 6.

[c] Gas phase, Ref. 11.

[d] We use the notation of Ref. 29. r, d, and τ denote linear combinations of the stretching coordinates of the hexagons, of the stretching coordinates of the pentagons, and of the "boat" torsion angles, respectively. At variance with Ref. 29, the S's are normalized.

however, that for the lowest 64 states an approximated classification in terms of the angular momentum can be made, from $l=0$ to $l=7$. This reflects the fact that these states are rather diffuse and see an approximate spherical potential. This is not true for the higher states in which the icosahedral symmetry of the atomic field disrupts the spherical symmetry. We notice that, compared to previous SCF calculations,[14] the sequence of the first 64 states is the same and only after that can some inversion of levels be observed. The same is true (although to a lesser extent) when we compare our KS eigenvalues to the one-electron energies of a very recent HF calculation made with the same atomic structure that we have obtained here.[31] In all three calculations the highest occupied molecular orbital (HOMO) has H_u symmetry, i.e., it corresponds to a fully occupied fivefold degenerate state. This guarantees that C_{60} is a closed-shell system, in agreement with experimental data.[32]

Unique to the Car-Parrinello method is the possibility of studying electronic properties at finite temperature in a consistent way. Thus we can calculate the time-averaged electronic density of states (DOS) and obtain information on the thermally induced broadening. This can be directly compared with very recent photoelectron spectroscopic (PES) data[33] as shown in Fig. 2. The agreement is excel-

TABLE III. Raman-active modes: frequencies in cm^{-1}.

Expt.[a]	This work	SCF[b]	Eigenvector[c]
	(i) Symmetry:	A_g	
496	454	570	$\frac{1}{\sqrt{2}}[S_{A_{g_2}}(d)-S_{A_{g_1}}(r)]$
1470	1368	1770	$S_{A_{g_1}}(r)$
	(ii) Symmetry:	H_g	
	246		$\sum_i X_i Y_i$[e]
273			
	405		$S_{H_g,b_7}(\tau)$
437			
	688		$S_{H_g,a_8}(\tau)$
710			
774			
1099[d]			
	1110		
1250[d]			
	1314		$\sim S_{H_g,a_1}(\tau)$
1428			
	1500		
1575			

[a] Solid C_{60}, Ref. 10.

[b] From Ref. 13.

[c] Same as in Table II.

[d] Tentative assignment.

[e] This mode is more conveniently expressed in terms of the vector distances of the atoms from the center of the cluster.

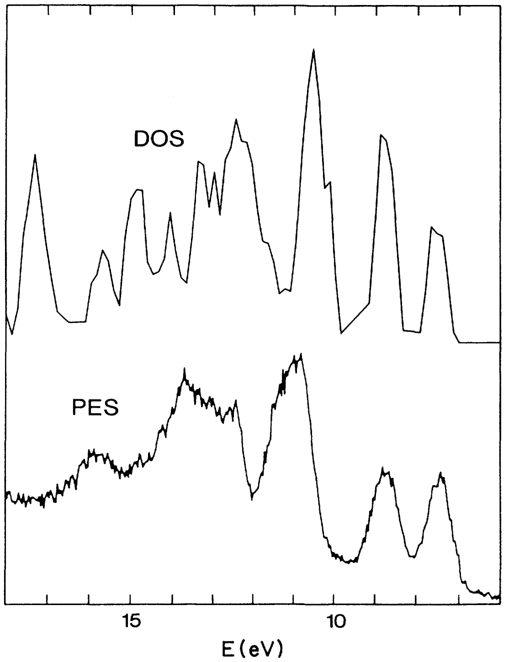

FIG. 2. (a) Average density of states (DOS) calculated at ~450 K; (b) Photoelectron spectrum (PES) from Ref. 33. The zero of the energy in (a) is adjusted such that the position of the first peak (which corresponds to the HOMO) coincides with that in (b).

lent, especially if one bears in mind that matrix element, electronic relaxation, and finite lifetime change the shape and position of the peaks in the PES.[34] These effects are mostly relevant for the lower ionization states. Instead the low-energy side of the PES more closely reflects the underlying electronic DOS. It is seen from Fig. 2 that indeed in this energy region our DOS closely reproduces relative peak distances and peak widths.

In conclusion, we have shown here that the *ab initio* MD method can provide accurate information on the ground-state properties of such a complex cluster as C_{60}. Furthermore, at variance with more conventional methods, it can include the effect of temperature. The comparison with experiments is very favorable.

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[1] H. W. Kroto, J. R. Health, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] For a review, see J. R. Health, S. C. O'Brien, R. F. Curl, H. W. Kroto, and R. E. Smalley, Comments Condens. Matter Phys. **13**, 119 (1987); W. Weltner, Jr., and R. J. Van Zee, Chem. Rev. **89**, 1713 (1989).

[3] W. Krätschmer, K. Fostiropoulos, and D. R. Huffman, Chem. Phys. Lett. **170**, 167 (1990).

[4] G. Meijer and D. S. Bethune, Chem. Phys. Lett. **175**, 1 (1990).

[5] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. J. Huffman, Nature (London) **347**, 354 (1990).

[6] D. M. Cox, S. Behal, K. Creegan, M. Disko, C. S. Hsu, E. Kollin, J. Millar, J. Robbins, W. Robbins, R. Sherwood, P. Tindall, D. Fisher, and G. Meitzner, Mater. Res. Soc. Symp. Proc. (to be published); J. Am. Chem. Soc. **113**, 2940 (1991).

[7] See, also A. D. J. Haymet, J. Am. Chem. Soc. **108**, 319 (1986).

[8] G. Meijer, D. S. Bethune, W. C. Tang, H. J. Rosen, R. D. Johnson, R. J. Wilson, D. D. Chambliss, W. G. Golden, H. Seki, M. S. de Vries, C. A. Brown, J. R. Salem, H. E. Hunziker, and M. R. Wendt, Mater. Res. Soc. Symp. Proc. 206 (to be published).

[9] R. D. Johnson, G. Meijer, and D. S. Bethune, J. Am. Chem. Soc. **112**, 8983 (1990).

[10] D. S. Bethune, G. Meijer, W. C. Tang, and H. J. Rosen, Chem. Phys. Lett. **174**, 219 (1990).

[11] C. I. Frum, R. Engleman, H. G. Hedderich, P. F. Bernath, L. D. Lamb, and D. R. Huffman, Chem. Phys. Lett. **176**, 504 (1991).

[12] H. P. Lüthi and J. Almlöf, Chem. Phys. Lett. **135**, 357 (1987).

[13] R. L. Disch and J. M. Schulman, Chem. Phys. Lett. **125**, 465 (1986).

[14] G. E. Scuseria, Chem. Phys. Lett. **176**, 423 (1991).

[15] A. Rosén and B. Wätsberg, J. Chem. Phys. **90**, 2525 (1989); M. Braga, A. Rosén, and S. Larsson, Z. Phys. D (to be published).

[16] R. C. Haddon, L. E. Brus, and K. Raghavachari, Chem. Phys. Lett. **125**, 459 (1986).

[17] D. J. Klein, T. G. Schmalz, G. E. Hite, and W. A. Seitz, J. Am. Chem. Soc. **108**, 1301 (1986).

[18] M. D. Newton, R. E. Stanton, J. Am. Chem. Soc. **108**, 2469 (1986); R. E. Stanton and M. D. Netwon, J. Phys. Chem. **92**, 2141 (1988).

[19] Z. C. Wu, D. A. Jelski, and T. F. George, Chem. Lett. **137**, 291 (1987).

[20] D. E. Weeks and W. G. Harter, J. Chem. Phys. **90**, 4744 (1989).

[21] E. Brendsal, B. N. Cyvin, J. Brunvoll, and S. J. Cyvin, Spectrosc. Lett. **21**, 313 (1988).

[22] P. Ballone and P. Miliani, Phys. Rev. B **42**, 3201 (1990).

[23] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[24] For a recent review, see W. Andreoni, Z. Phys. D **19**, 31 (1991).

[25] G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. B **42**, 7470 (1990).

[26] R. Car and M. Parrinello, in *Proceedings of NATO ARW: Simple Molecular Systems at Very High Density, Les Houches, France, 1988* (NATO Advanced Study Institutes Ser. (Plenum, New York, 1988), p. 455.

[27] W. Andreoni, D. Scharf, and P. Giannozzi, Chem. Phys. Lett. **173**, 449 (1990).

[28] C. S. Yannoni, P. P. Bernier, D. S. Bethune, G. Meijer, and J. R. Salem, J. Am. Chem. Soc. **113**, 3190 (1991).

[29] E. Brendsdal, Spectrosc. Lett. **21**, 319 (1988).

[30] F. Ancilotto, W. Andreoni, A. Selloni, R. Car, and M. Parrinello, Phys. Rev. Lett. **65**, 3148 (1990).

[31] G. Corongiu and E. Clementi (unpublished).

[32] S. H. Yang, C. L. Pettiette, J. Conceicao, O. Cheshnovsky, and R. E. Smalley, Chem. Phys. Lett. **139**, 233 (1987).

[33] D. L. Lichtenberger, K. W. Nebesny, C. D. Ray, D. R. Huffman, and L. D. Lamb, Chem. Phys. Lett. **176**, 203 (1991).

[34] See, e.g., R. Clauberg, F. H. Frank, J. M. Nicholls, and B. Reihl, Surf. Sci. **189/190**, 44 (1987).