Structure and dynamics of C_{60} and C_{70} from tight-binding molecular dynamics

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Structural and vibrational properties of C_{60} and C_{70} fullerenes are studied by molecular dynamics using a recently developed tight-binding potential model. It is shown that this tight-binding molecular-dynamics scheme has accuracy comparable to *ab initio* techniques and is very efficient for studying the finite temperature properties of fullerenes.

I. INTRODUCTION

The breakthrough in synthesis[1] of C_{60} and other fullerenes created a very active research area in physics and chemistry. With the success in producing macroscopic quantities of C_{60} and C_{70}, experimentalists have been able to use nuclear magnetic resonance (NMR) to clarify the structure of these two molecules as having I_h and D_{5h} point-group symmetries, respectively,[2,3] confirming the predictions made several years ago by Kroto *et al.*[4,5] At the same time, other experimental techniques such as infrared absorption and Raman and neutron scattering[6–8] have also been widely applied to investigate the dynamical properties of these prototype fullerenes.

On the theoretical side, the structural and dynamical properties of the fullerenes have been calculated extensively by various techniques. Most of the calculations are performed at zero temperature except for molecular-dynamics (MD) simulations using the Car-Parrinello method performed by Zhang, Yi, and Bernholc[9] and by Feuston *et al.*[10] Nevertheless, due to the heavy computational cost, Car-Parrinello simulations have been limited to very short simulation time and many dynamical properties which require longer simulation time have not been well characterized.

Recently, we have undertaken molecular-dynamics simulation studies of the structures and dynamics of the fullerenes using a tight-binding potential model developed in our group. We find that the tight-binding molecular-dynamics (TBMD) scheme, though simple, is very efficient and accurate for use in the study of various properties of the fullerenes. In this paper, we report on the calculations of the structural and vibrational properties of C_{60} and C_{70} at both zero and finite temperatures. Comparisons with other theoretical calculations and experimental data are also discussed.

II. TIGHT-BINDING MOLECULAR-DYNAMICS SCHEME

Newton's equations of motion for atoms involved in tight-binding molecular dynamics are derived from a Hamiltonian with the form

$$H(\{\mathbf{r}_i\})=\sum_i \frac{\mathbf{P}_i^2}{2m}+\sum_n^{\text{occupied}} \langle \psi_n | H_{\text{TB}}(\{\mathbf{r}_i\}) | \psi_n \rangle + E_{\text{rep}}(\{\mathbf{r}_i\}) , \quad (1)$$

where $\{\mathbf{r}_i\}$ denotes the positions of the atoms ($i=1,2,\ldots,N$) and $\mathbf{P}_i$ stands for the momentum of atom i. The first term in (1) is the kinetic energy of the ions, the second term is the electronic band-structure energy calculated by a parametrized tight-binding Hamiltonian $H_{\text{TB}}(\{\mathbf{r}_i\})$, and the third term is a short-ranged repulsive energy. Electronic degrees of freedom are explicitly involved in the force calculation but are not explicitly involved in the dynamics. The latter feature allows a larger time step to be used in the simulation. The time step used in this study (0.7×10^{-15} s) is about a factor of 10 larger than that used in Car-Parrinello simulations.[10]

The tight-binding Hamiltonian $H_{\text{TB}}(\{\mathbf{r}_i\})$ for carbon is constructed using an orthogonal sp^3 basis,

$$H_{\text{TB}}(\{\mathbf{r}_i\})=\sum_i \sum_{\alpha=s,p} \varepsilon_\alpha a_{i\alpha}^\dagger a_{i\alpha}+\sum_{i,j} \sum_{\alpha,\beta=s,p} v_{\alpha,\beta}(r_{ij}) a_{i\alpha}^\dagger a_{j\beta} , \quad (2)$$

where $a_{i,\alpha}$ represents the α orbital on the ith atom, ε_s and ε_p are the on-site energies of the carbon $2s$ and $2p$ orbitals, and $v_{ss\sigma}(r_{ij})$, $v_{sp\sigma}(r_{ij})$, $v_{pp\sigma}(r_{ij})$, and $v_{pp\pi}(r_{ij})$ are overlap parameters between two orbitals whose centers are separated by distance r_{ij}. The repulsive energy is expressed in the form $E_{\text{rep}}=\sum_i f[\sum_j \phi(r_{ij})]$, where $\phi(r_{ij})$ is a pairwise potential between atoms i and j, and f is a fourth-order polynomial function.

The parameters and scaling functions used in the present calculations are taken from our previous work.[11] Such a tight-binding potential model not only reproduces well the binding energies and bond lengths of crystalline carbon phases with different coordination numbers, but also describes well the properties of several complex carbon systems far away from the ground state such as liquid and amorphous carbon. The reliability of the model for applications to carbon clusters is demonstrated by comparing the ground-state geometries obtained by the present tight-binding model with the results of accurate

quantum-mechanical calculations for small clusters. In the range $5 \leq n \leq 11$, we found that odd-numbered clusters prefer a ring structure.[11] This result agrees well with the accurate *ab initio* calculations of Raghavachari and Binkley.[12] Since the potential parameters are determined by fitting to the bulk properties, we expect that the potential will become even more reliable as the cluster size gets bigger.

III. GROUND-STATE PROPERTIES

The tight-binding potential model discussed in Sec. II is first used to calculate the ground-state properties of C_{60} and C_{70}. The geometries of the fullerenes are optimized by simulated annealing using the tight-binding molecular-dynamics scheme. The initial configurations used for the structural optimization are distorted C_{60} spheroid-shaped and C_{70} ellipsoid-shaped cages with the atoms in the correct topological framework but with distorted bond angles and bond lengths. We heat the molecules up to 500 K and gradually cool them down to 0 K without any constraint. This optimization process leads to ideal fullerene structures for C_{60} and C_{70} as shown in Fig. 1. The C_{60} molecule is a truncated icosahedron (I_h point-group symmetry) in which all atoms have the same environment. The carbon-carbon bond lengths are 1.396 Å for the "double bonds" (the shared hexagon edges) and 1.458 Å for the "single bonds" (the pentagon edges), respectively. These values are in very good agreement with experimental data[13–15] and *ab initio* calculation results[9,10,16] (see Table I). The symmetry of the C_{70} molecule is D_{5h}. This molecule contains five types of nonequivalent atoms (as labeled $a-e$ in Fig. 1) with the ratio $a:b:c:d:e = 10:10:20:10:10$. There are eight distinct carbon-carbon bond lengths among the five nonequivalent atoms. As one can see from Table II, the bond lengths of C_{70} obtained from our tight-binding calculation are also in good agreement with other theoretical calculations[16,17] and the available experimental data.[18]

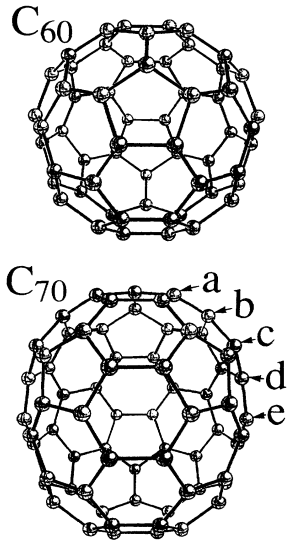

FIG. 1. Perspective views of C_{60} and C_{70}. The letters *a*, *b*, *c*, *d*, and *e* label the five nonequivalent atoms of C_{70}.

TABLE I. Bond lengths of C_{60}. Present results are compared to local-density approximation (LDA), modified neglect of differential overlap (MNDO), and Hartree-Fock calculation results, and to experimental NMR and neutron-scattering data. All results are given in Å.

	Double bond	Single bond
Present	1.396	1.458
LDA	1.40,[a] 1.39[b]	1.45[a,b]
MNDO	1.40[c]	1.474[c]
HF/3-21G	1.365[c]	1.453[c]
NMR	1.40±0.015[d]	1.45±0.015[d]
Neutron	1.39,[e] 1.391[f]	1.46,[e] 1.455[f]

[a]Reference 9.
[b]Reference 10.
[c]Reference 16.
[d]Reference 13.
[e]Reference 14.
[f]Reference 15.

The vibrational properties of C_{60} and C_{70} at $T=0$ K are studied by solving the eigenvalues and eigenfunctions of a 180×180 (for C_{60}) or a 210×210 (for C_{70}) force constant matrix derived from the Hamiltonian of Eq. (1). The results of the vibrational frequencies are classified according to the symmetry of the I_h and D_{5h} point groups and listed in Tables III and IV, respectively. We found that the 46 distinct vibrational modes of C_{60} are equally divided into even and odd parities. The modes with T_{1u} symmetry are infrared active and those with A_g and H_g symmetries are observable by Raman spectroscopy. As one can see from Table III, the present theoretical results are in good agreement with the available infrared and Raman data,[6,7] particularly considering that the properties of C_{60} have not been used in the fitting database to determine the tight-binding potential parameters. For C_{70}, the 204 normal modes as listed in Table IV have the following symmetry structure:

$$\Gamma_{D_{5h}} = 12A_1' + 9A_2' + 9A_1'' + 10A_2'' + 21E_1' + 22E_2' + 19E_1'' + 20E_2'' \ . \quad (3)$$

There are only onefold- and twofold-degenerate vibrational modes. According to the symmetry selection rule, the Raman active modes are those with A_1', E_2', and E_1'' symmetries and the infrared-active modes are those with A_2'' and E_1' symmetries. The Raman and infrared spectra of C_{70} have been reported by Bethune *et al.*[7] However, since so many modes are Raman and infrared active, it is still very difficult to compare the present results with the experimental data without knowing the scattering matrix elements.

IV. FINITE TEMPERATURE PROPERTIES

Using the tight-binding molecular-dynamics scheme, we have investigated the behavior of C_{60} and C_{70} mole-

TABLE II. Bond lengths of C_{70}. Present results are compared to LDA, MNDO, and Hartree-Fock calculation results, and to experimental data. All results are given in Å.

	Present	LDA[a]	MNDO[b]	HF/3-21G[b]	Expt.[c]
C_a-C_a	1.457	1.448	1.473	1.452	1.464±0.009
C_a-C_b	1.397	1.393	1.402	1.370	1.37±0.01
C_a-C_c	1.454	1.444	1.469	1.447	1.47±0.01
C_c-C_c	1.389	1.386	1.389	1.356	1.37±0.01
C_c-C_d	1.456	1.442	1.478	1.458	1.46±0.01
C_d-C_d	1.443	1.434	1.442	1.414	$1.47^{+0.01}_{-0.03}$
C_d-C_e	1.418	1.415	1.430	1.403	1.39±0.01
C_e-C_e	1.452	1.467	1.484	1.475	$1.41^{+0.03}_{-0.01}$

[a]Reference 17.
[b]Reference 16.
[c]Reference 18.

cules at finite temperatures. In our simulations, the structural properties are monitored by calculating the radial distribution function $j(r)$ and the angular distribution functions $g_3(\theta)$. $j(r)$ is defined such that $j(r)dr$ gives the average number of atoms whose distance from a given atom is between r and $r+dr$. The $g_3(\theta)$ counts only those angles spanned by bonds with bond lengths less than 1.80 Å. The dynamical properties of the fullerenes at finite temperatures are studied by calculating the vibration spectra of the fullerenes through Fourier transformation of the velocity-velocity correlation functions using the trajectories generated by the molecular-dynamics simulation. The overall vibrational density of states is given by

$$I(\omega)=\sum_{n=1}^{N}\int_0^\infty dt\, e^{i\omega t}\langle \mathbf{v}_n(t)\cdot\mathbf{v}_n(0)\rangle\ , \tag{4}$$

where N is the total number of atoms in the molecule.

TABLE III. Vibration frequencies of the C_{60} molecule. The numbers inside the parentheses next to the I_h group representation labels indicate the degeneracies of the corresponding group representations. Experimental Raman and infrared data from Ref. 7 are also listed (values inside the parentheses next to the calculated frequencies) for the purpose of comparison.

I_h label (even parity)	Frequency (cm^{-1})	I_h label (odd parity)	Frequency (cm^{-1})
$A_g(1)$	1610(1470)	$A_u(1)$	968
	509(496)		
$T_{1g}(3)$	1293	$T_{1u}(3)$	1573(1428)
	823		1201(1183)
	551		602(577)
			485(527)
$T_{3g}(3)$	1369	$T_{3u}(3)$	1619
	880		1197
	800		1027
	520		694
			327
$G_g(4)$	1585	$G_u(4)$	1524
	1321		1338
	1100		955
	807		875
	549		752
	454		318
$H_g(5)$	1653(1575)	$H_u(5)$	1642
	1538(1428)		1357
	1273(1250)		1230
	1135(1099)		768
	786(774)		633
	690(710)		516
	392(437)		360
	237(273)		

TABLE IV. Vibration frequencies of C_{70} in units of cm^{-1}.

A_1'	A_2'	A_1''	A_2''	E_1'	E_2'	E_1''	E_2''
232	460	301	307	297	201	224	288
366	524	509	420	329	279	369	343
469	632	581	590	385	410	445	371
533	752	774	686	479	474	486	498
688	904	816	946	547	501	525	528
716	957	904	1159	558	638	654	612
1115	1243	1248	1233	620	679	728	699
1246	1349	1361	1438	661	745	755	736
1248	1497	1630	1591	780	764	800	792
1551			1659	830	787	822	872
1601				892	832	1059	939
1659				906	884	1180	1107
				1124	973	1242	1167
				1203	1082	1315	1268
				1269	1208	1334	1330
				1328	1282	1467	1352
				1352	1370	1548	1508
				1481	1378	1596	1543
				1533	1460	1654	1599
				1572	1575		1641
				1648	1596		
					1644		

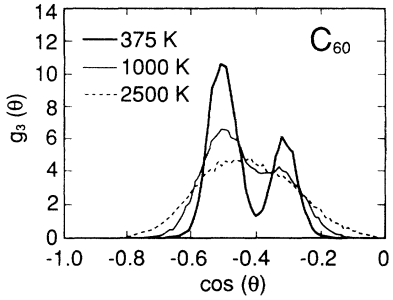

FIG. 3. Angular distribution functions of C_{60}.

For C_{60}, we also calculate the vibrational spectra for the even- and odd-parity modes separately,

$$I_{\text{even}}(\omega) = \sum_{I=1}^{N/2} \int_0^\infty dt\, e^{i\omega t} \langle [\mathbf{v}_I(t) - \mathbf{v}_{-I}(t)] \cdot [\mathbf{v}_I(0) - \mathbf{v}_{-I}(0)] \rangle \,, \tag{5}$$

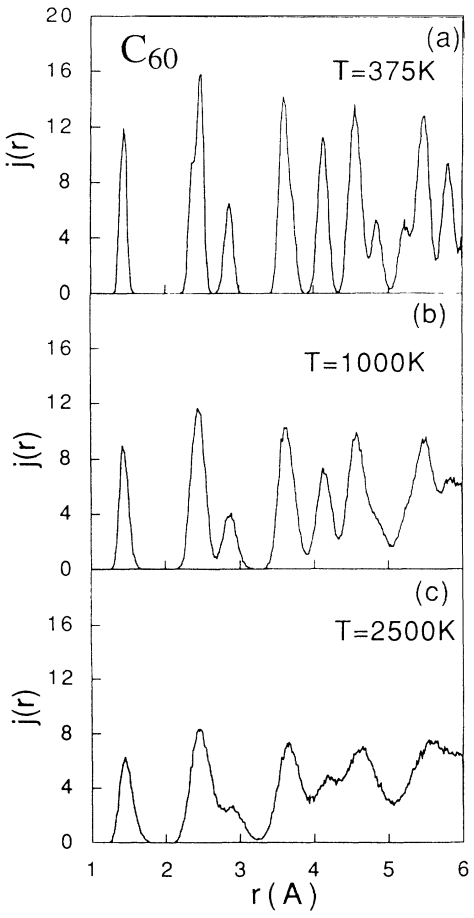

FIG. 2. Radial distribution functions of C_{60}.

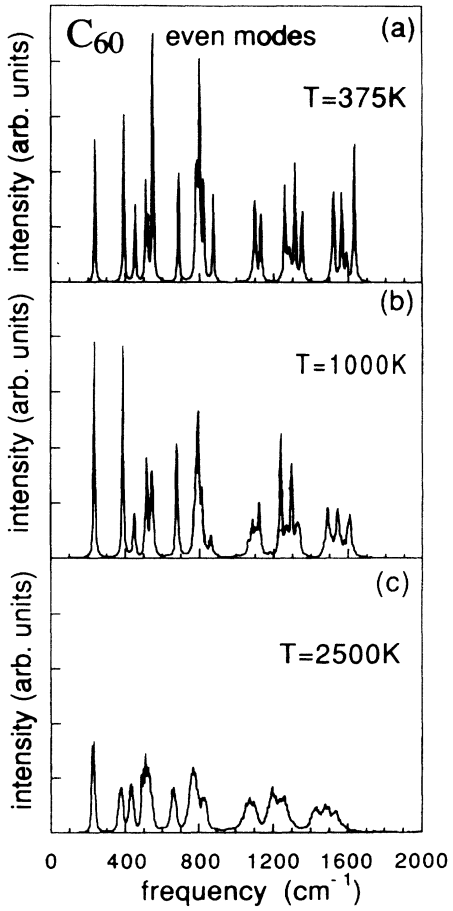

FIG. 4. Temperature dependence of the vibrational spectra of the even-parity modes of C_{60}. The spectra have been normalized and broadened by a Gaussian function with a width of 4 cm^{-1}.

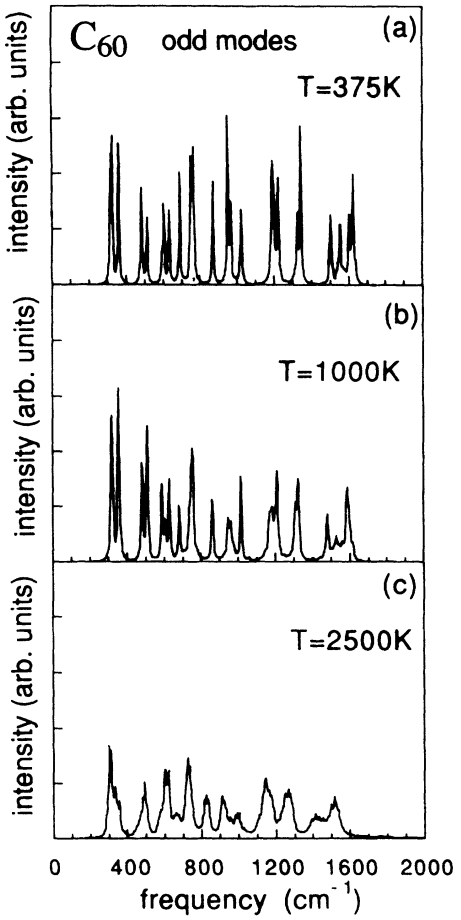

FIG. 5. Temperature dependence of the vibrational spectra of the odd-parity modes of C_{60}. The spectra have been normalized and broadened by a Gaussian function with a width of 4 cm^{-1}.

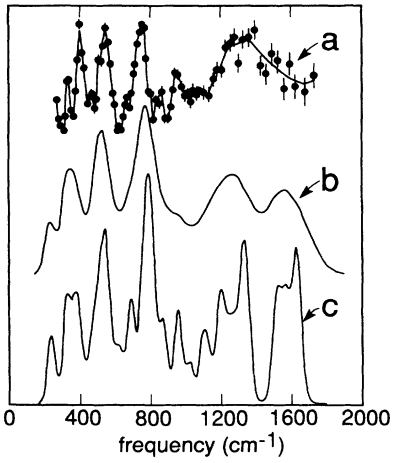

FIG. 6. Vibrational density of states of C_{60}. Upper: Neutron-scattering results (Ref. 8); middle: TBMD results at 375 K broadened by a Gaussian function with experimental instrument resolution quoted from Ref. 8 (low-resolution scan); lower: TBMD result at 375 K broadened by a Gaussian function with width of 30 cm^{-1}.

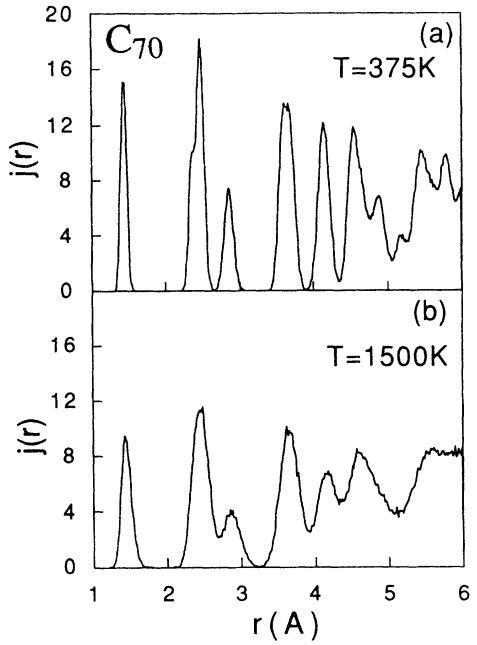

FIG. 7. Radial distribution functions of C_{70}.

$$I_{\text{odd}}(\omega) = \sum_{I=1}^{N/2} \int_0^\infty dt\, e^{i\omega t} \langle [\mathbf{v}_I(t) + \mathbf{v}_{-I}(t)] \cdot [\mathbf{v}_I(0) + \mathbf{v}_{-I}(0)] \rangle \,, \tag{6}$$

where the subscripts I and $-I$ denote a pair of atoms which are equivalent under inversion in the ideal C_{60} molecule. At each temperature, 4000 to 6000 MD steps with the temperature control method of Andersen,[19] followed by 2000 MD steps without temperature control are used to thermalize the system. Then the trajectory over an additional 8096 MD steps (corresponding to 6.3 ps) without temperature control is used to perform the statistical average and to calculate the velocity-velocity correlation functions.

The results of radial distribution functions and angular distribution functions of C_{60} are shown, respectively, in Figs. 2 and 3 for several temperatures ranging from 375 to 2500 K. At 375 K, the peaks in the radial distribution functions are sharp and well defined. The positions of the

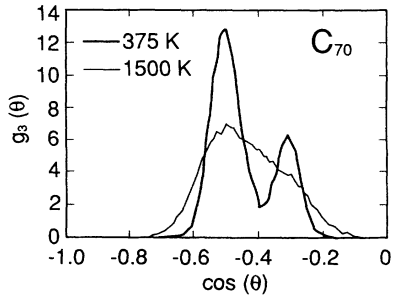

FIG. 8. Angular distribution functions of C_{70}.

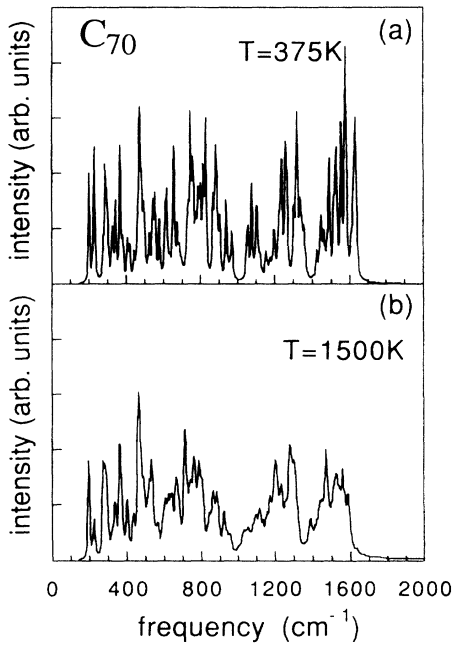

FIG. 9. Temperature dependence of the vibrational spectra of C_{70}. The spectra have been normalized and broadened by a Gaussian function with a width of 4 cm^{-1}.

peaks compare well with the results of *ab initio* molecular-dynamics simulation[10] and neutron diffraction.[14] As the temperature is increased, the peaks become broad but are still distinguishable even at 2500 K. This result is consistent with the strong carbon-carbon bond in the fullerenes. In the angular distribution of Fig. 3, two peaks around 180° and 120° are clearly seen at 375 K. However, these two peaks broaden rapidly with temperature and merge together already at 1000 K. Only a single broad peak is observed at 2500 K.

The vibrational spectra of C_{60} as a function of temperature are shown in Fig. 4 for even-parity modes and in Fig. 5 for odd-parity modes, respectively. At 375 K, the peaks in the spectra are in one-to-one correspondence with the vibration frequencies at 0 K as listed in Table III although some frequencies are slightly shifted due to temperature effects. These peaks broaden and shift towards lower frequencies as the temperature is increased. The frequency shifts of the higher-energy modes are found to be much larger than those of the lower-energy modes.

The vibration spectrum of C_{60} has also been measured recently by neutron-scattering experimentation.[8] Unlike Raman or infrared, neutron scattering provides the overall vibrational density of states rather than certain selected individual modes. As shown in Fig. 6, we found

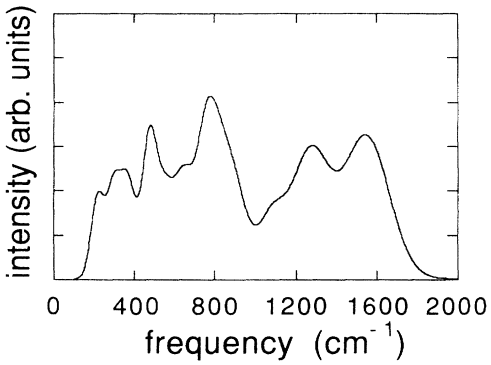

FIG. 10. Vibrational density of states of C_{70} at 375 K. The spectra have been broadened by a Gaussian function with experimental instrument resolution quoted from Ref. 8 (low-resolution scan).

that the overall vibrational density of states obtained by our TBMD scheme at 375 K is in good agreement with the neutron-diffraction data.

In Figs. 7–10, the structural and dynamical properties of C_{70} at finite temperatures are presented. The temperature dependence of these properties is very similar to that of C_{60}. Although the numbers and symmetries of individual vibrational modes of C_{60} and C_{70} are very different (see Table III and IV), their overall vibrational density of states is very similar and will be difficult to distinguish by neutron-diffraction experiments.

V. SUMMARY

In summary, we have demonstrated that tight-binding molecular dynamics is sufficiently accurate and efficient to allow us to perform realistic simulations of fullerenes. The structural and vibrational properties of C_{60} and C_{70} calculated from the present scheme compare well with experimental data and *ab initio* calculations. We anticipate that the scheme will be very useful in the study of more complex processes such as nucleation and reaction as well as fragmentation.

ACKNOWLEDGMENTS

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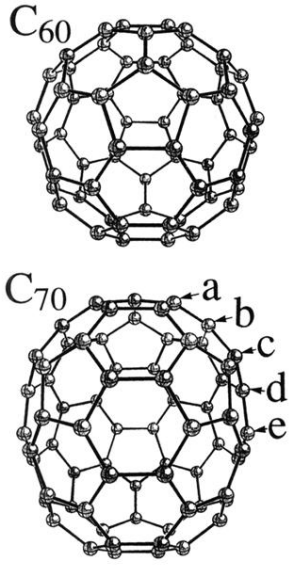

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