Bulk modulus of the C_{60} molecule via the tight binding method

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The bulk modulus for the C_{60} molecule is calculated using total energy minimization via the tight binding method. The calculated bulk modulus is 717 GPa, which is about 1.6 times larger than that of bulk diamond due to the high symmetry of the C_{60} molecule; a possible explanation is given. This result is compared to a simple estimation from elasticity theory. Electronic structures and vibrational frequencies are also compared to theoretical and experimental results.

The recent success of preparing large amounts of C_{60} by Krätschmer et al. [1] (it was originally prepared by Croto et al.) has attracted many researchers in physics and chemistry. C_{60} consists of 20 six-membered rings and 12 five-membered rings (fig. 1). Each atom has three neighbors with two single bonds and one double bond, and thus saturates four valence electrons. Electronic band structures have been calculated [2–4] and recently confirmed by photoemission spectroscopy giving a reasonable agreement [5]. It is now generally believed that the C_{60} molecule is stable. When C_{60} molecules are placed into a solid form, they form a faulted hexagonal close-packed or face-entered cubic Bravais lattice, interacting via van der Waals attractive forces. The compressibility of solid C_{60} was measured up to 1.2 GPa using a diamond anvil cell [6] and was 7×10^{-12} cm^2/dyne, 40 times larger than that of diamond. This leads to a lower value of the bulk modulus of C_{60} compared to that of diamond. This is a definite proof that a solid C_{60} molecule interacts via weak van der Waals forces. With further increase of hydrostatic pressure, one can expect that the hard
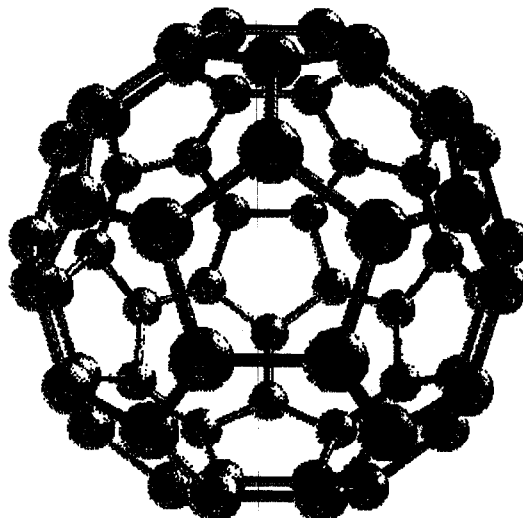

Fig. 1. Sketch of the C_{60} molecule. This structure consists of 20 hexagonal faces and 12 pentagonal faces. Two characteristic bond lengths appear in hexagons while the sides of the pentagons are all single bonds. The TB calculation provides the following values for two bonds: double bond = 1.458 Å, single bond = 1.408 Å.

spheres of C_{60} touch and thus the value of the bulk modulus will approach that of the individual molecules. Using hydrostatic pressure up to 20 GPa, Duclos et al. [7] obtained the bulk modulus of solid

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C_{60}, 18 GPa, which is also characteristic of van der Waals intermolecular bondings.

In order to utilize the hardness of C_{60} molecules for such a thing as artificial molecular bearings, one needs to evaluate its individual bulk modulus. We will use the total energy minimization scheme via the tight binding (TB) method, which uses four valence electrons of the carbon atom. Since C_{60} is a ball-like cluster without its carbon contents inside the ball, one needs to define a surface modulus similar to the bulk modulus. Define the surface modulus B_s,

$$B_s \equiv -A \frac{\partial \phi}{\partial A}, \tag{1}$$

where ϕ is the surface tension and A the surface area. Using the first law of thermodynamics applied to a surface,

$$dQ = dU + \phi \, dA. \tag{2}$$

For $T=0$, $\phi = -\partial U/\partial A$, and the surface modulus can be expressed as

$$B_s = A \frac{\partial^2 U}{\partial A^2} = \frac{1}{16\pi} \frac{\partial^2 U}{\partial r^2}\bigg|_{r_0}. \tag{3}$$

Thus the surface modulus is expressed by the second derivative of the total energy with respect to the radius of C_{60} evaluated in equilibrium. In order to obtain the conventional bulk modulus,

$$B \equiv -V \frac{\partial P}{\partial V}, \tag{4}$$

we divide this equation by eq. (1) in order to get the relationship between B and B_s,

$$\frac{B}{B_s} = \frac{V}{A} \frac{\partial A/\partial r}{\partial V/\partial r} \frac{\partial P}{\partial \phi}. \tag{5}$$

For a spherical interface, the reaction between the surface pressure and the surface tension is [8]

$$P - P_0 = P = 2\phi/r, \tag{6}$$

where P_0 is the pressure inside the ball and assumed to be zero. Thus the bulk modulus is calculated from the surface modulus and is given by

$$B = \frac{4}{3r} B_s = \frac{1}{12\pi r_0} \frac{\partial^2 U}{\partial r^2}\bigg|_{r_0}. \tag{7}$$

Once the total energy is calculated, it is straightfor-

ward to calculate the surface and bulk modulus from eqs. (3) and (7).

We performed total energy minimization through the tight binding (TB) method recently developed for diamond structures [9] assuming sp^3 bond orbitals per atom. These empirical tight binding parameters give vibrational frequencies comparable with experiment for bulk diamond and the calculated bulk modulus is in good agreement with experiment within an error of 1%. The Slater–Koster TB method with first-nearest neighbor interactions is used for the electronic band structure calculation. The ion–ion repulsive interaction is determined by subtracting the band energy from the total energy obtained from the ab initio calculation [10]. The distance dependence of the hopping parameters was assumed to be r^{-2} as proposed by Harrison [11]. Even though this method supplies very accurate results of the bulk properties, the question still remains whether these TB parameters are really transferable even for planar structures such as graphite. Since the transferability of TB parameters increases with lighter atoms, we believe that this calculation is sufficient to provide a reasonable argument for the stability of C_{60} both qualitatively and quantitatively. This will be confirmed later in the phonon spectrum calculated by the TB method combined with the molecular dynamics computer simulation.

The spatial coordinates of icosahedral C_{60} are generated as follows. We first take two vertices of pentagonal pyramids of an icosahedron (20 triangles) and divide the distance of two vertices by approximately three. These points will be the positions of the carbon atoms. By repeating these over all the pentagons, the C_{60} icosahedron (I_h) is generated. The shape of the generated C_{60} is ball-like and this C_{60} will be used for further calculation.

In order to ensure the equilibration of the TB parameters for C_{60}, the configuration is fully relaxed to change the radius of the sphere. The optimal equilibrium radius with total energy minimization of the sphere is 3.57 Å, giving bond lengths of the surface of C_{60} as 1.408 and 1.458 Å for double and single bonds, respectively, where the averages reproduce the graphite bond length (1.42 Å) approximately. These are comparable to the experimental and theoretical values [12].

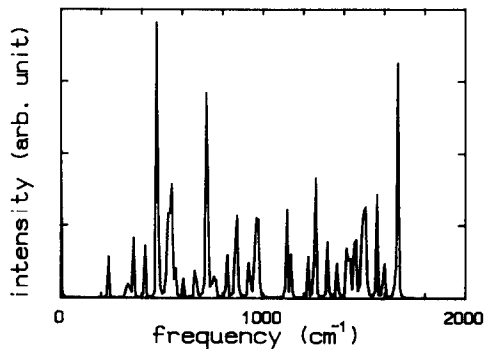Shown in fig. 2 is the molecular energy band cal-

Fig. 2. The molecular energy band for various methods. Shown is only ±10 eV around the HOMO, which is taken to be zero: Our TB calculation with four valence electronic orbitals per atom and with nearest neighbor interactions only. The Hückel method with one valence orbital per atom. The LMTO calculation. The last two are from ref. [3].

culated by the static TB method. The molecular orbitals with sp^2 hybridized bonding orbitals extend between 0 and -24 eV (the highest occupied molecular orbital (HOMO) is taken to be zero). Because of the high symmetry of C_{60}, molecular orbitals show many three-, four-, and five-fold degeneracies. The five-fold h_u symmetry constitutes the HOMO and is separated by a reasonable energy of

2.25 eV from the lowest unoccupied molecular orbital (LUMO) of t_{1u} symmetry, in accordance with Satpathy's LMTO result [3] which shows that the HOMO extends over -23 eV and 2.04 eV of the HOMO–LUMO gap (table 1). This value is a little larger than the experimental value of 1.9 eV. Since the experiment was done on solid phase C_{60}, the van der Waals intermolecular interactions play a role for the overlaps of the energy bands, lowering the HOMO–LUMO gap. One expects that this value should become larger if there are no interactions between the C_{60} molecules and hence the agreement should be better. Interestingly, the ordering of the molecular orbitals is exactly the same in both our calculation and Satpathy's LMTO (from -5 eV to 6.8 eV) and Hückel's calculation with one orbital per atom.

In order to show the validity of our model we have calculated the vibrational frequencies of C_{60}. This was done by combining the TB method with the molecular dynamics computer simulation. One can get the vibrational frequencies of the C_{60} molecule by taking the Fourier transform of the velocity–velocity autocorrelation function [9]. These are illustrated in fig. 3. Frequencies range from 235 to 1658 cm^{-1}. Even though these modes are impossible to identify, we can compare these with experiments as follows. Four t_{1u} frequencies are infrared active and the experimentally measured values are 1429, 1183, 577 and 528 cm^{-1} [12,13]. Among many other theoritical calculations for C_{60} vibrational frequencies, two results are comparable to the experimental results as shown in table 2. The maximum and minimum range of frequencies of these calculations are comparable to our present results. Therefore, our model should be reliable for further calculation. More details for

Table 1
Summary of the electronic band structure of C_{60} for various methods. The first five levels below the HOMO agree well with the ab initio LMTO result. All three results (LMTO, Hückel and our work) show the same ordering of the LUMO energy levels.

Bond length (Å)	Valence band width (eV)	HOMO–LUMO gap (eV)	First five levels below HOMO	Method
1.40 (C–C), 1.474 (C=C)	23	1.9	h_u, g_g, h_g, g_u	experiment [5]
1.42	27	2.18	h_u, g_g, h_g, g_u, h_u [a]	LMTO [3,4]
1.405 (C–C), 1.426 (C=C)			h_u, h_g, g_g, g_u, t_{2u}	Hückel [3,4]
1.408 (C–C), 1.458 (C=C)	24	2.25	h_u, h_g, g_g [b], g_u, t_{2u}	present work

[a] The h_u, h_g, t_{2u} levels are very close to each other.   [b] The h_g and g_g levels are not separable.

Fig. 3. The phonon spectrum of C_{60} calculated by taking the Fourier transform of the velocity–velocity autocorrelation function. The frequencies range from 235 to 1658 cm^{-1}.
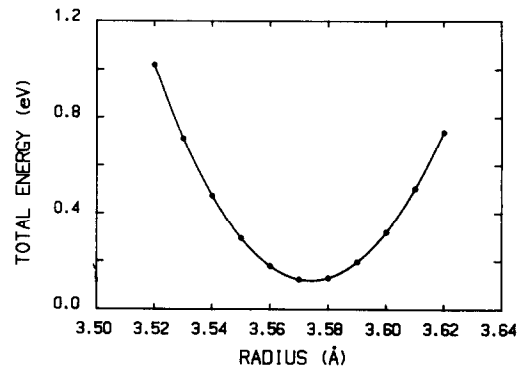

Fig. 4. The total energy in terms of the radius of the C_{60} molecule. The radius is well equilibrated at 3.57 Å.

vibrational frequencies compared to other clusters will be described elsewhere [14].

Since the electronic structure agrees with the ab initio result and the vibrational frequencies are reasonably comparable to the experiment, we go directly to the bulk modulus calculation. Fig. 4 shows the total energy in terms of the radius of the sphere of the C_{60} molecule. It clearly shows the equilibrium position of 3.57 Å, comparable to other results. By taking the second derivative of the total energy with respect to the radius of the sphere, the surface and bulk modulus are calculated and shown in table 3. The bulk modulus of C_{60} is almost 1.62 times larger than that of diamond. This may be estimated as follows.

The total energy of the system for zero temperature with harmonic approximation is

$$U = \tfrac{1}{2} \sum_i k_i x^2 = \tfrac{1}{2} \kappa x^2 , \qquad (8)$$

where the summation is over all the eigenmodes of

C_{60} and κ is the effective force constant. The second derivative of this with respect to the distance, which is κ, is directly related to the bulk modulus. Since $\kappa = m\omega^2$, one can relate the vibrational frequencies of diamond and the C_{60} molecule in order to interpret the 60% increase of the C_{60} bulk modulus. The electronic structure of C_{60} is sp^2 where the local sym-

Table 3
Characteristic vibrational frequencies and the bulk modulus of diamond and the C_{60} molecule.

	Diamond		C_{60}
	TB [9]	experiment [9]	
LTO(Γ) (cm^{-1})	1516	1339	
TA(X) (cm^{-1})	839	815	
TO(X) (cm^{-1})	1202	1273	
LOA(X) (cm^{-1})	1282	1194	
B_s (10^9 erg/cm^2)			1.91
B (GPa)	437	442	717

Table 2
Vibrational frequencies of C_{60}. Shown are Raman and IR active frequencies. Two theoretical calculations show good agreements with experimental IR measurements for IR active t_{1u} modes. All units are in cm^{-1}.

	Ref. [15]	Ref. [16]	Experiment [12,13]	Present work
maximum frequency	1644	1601		1658
minimum frequency	258	218		235
t_{1u}	1437	1434	1429	
	1212	1119	1183	
	607	618	577	
	544	472	528	

metry is that of graphite. However, its special spherical symmetry generates stronger eigenmodes than graphite. Even though IR [12] and Raman [13] experiments for C_{60} vibrational frequencies were done, all the vibrational frequencies cannot be measured due to the limited symmetry requirement. Some of the dipole active modes (t_{1u}) [12] can be compared to the theoretical results as shown in table 2. The highest frequency mode in C_{60} is the five-fold degenerate h_g and is about 1658 cm^{-1}. This highest frequency may be compared to the LTO(Γ) of diamond in order to extract information about the bulk modulus of C_{60}. The frequency ratio of h_g to LTO(Γ) (experiment) $R_\omega = \omega_{C_{60}}/\omega_{diamond}^{expt.} = 1.24$ and thus the force constant k which is proportional to ω^2, gives the ratio, $R_k = k_{C_{60}}/k_{diamond} = R_\omega^2 = 1.54$. Therefore, a 60% increase of the bulk modulus in C_{60} is an acceptable value from these arguments.

Ruoff and Ruoff's [7] estimated value for the bulk modulus of C_{60} from simple elasticity theory is 843 GPa, which is larger than our result. Since they used 3.52 Å for the C_{60} radius and the geometrical factor in their calculation, their value would be reduced to 764 GPa if they used our parameters. Therefore, the agreement should be better.

In summary, the electronic band structure and vibrational frequencies of C_{60} are calculated using total energy minimization via the tight binding method, giving a reasonable agreement with other calculations. The calculated bulk modulus is 717 GPa which is about 1.6 times larger than that of diamond. Since the C_{60} molecule is geometrically highly symmetric, its vibrational eigenfrequencies are larger than those of diamond and hence the bulk modulus which is proportional to the force constant should be larger. Our present calculation is comparable with the previous result from elasticity theory.

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