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First-principles study of vibrational modes in icosahedral C_{60}

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The vibrational spectrum of the C_{60} molecule is calculated using first-principles density-functional theory. Our approach is based on a combination of the all-electron local-density functional method with group-theoretical analysis. The calculated vibrational frequencies of the icosahedral C_{60} molecule are found to be in excellent agreement with the experimental data available from Raman, infrared, and neutron inelastic-scattering measurements.

The discovery of the icosahedral C_{60} molecule[1] and the subsequent synthesis of C_{60} solid[2] have stimulated a veritable flurry in the study of fullerenes and fullerites. The observation of superconductivity in alkali-metal-doped C_{60} crystals[3] produces further excitement in the interesting properties of this new form of all-carbon material. Phonon-pairing theories based on both low-frequency and high-frequency intramolecular vibrations have been proposed[4,5] to explain the mechanism responsible for superconductivity in such a system. Recent investigations tend to agree that electron-phonon interactions play an important role. In fact, experimental measurements by neutron inelastic-scattering[6] and Raman scattering[7,8] have revealed that the positions and intensities of the peaks corresponding to intramolecular bond-stretching modes of alkali-metal-doped C_{60} change considerably with regard to those of pristine C_{60}, which suggests that these modes are strongly coupled to the electrons. It is clear that detailed information about the vibrational properties would be desirable for an accurate evaluation of deformation potentials and the electron-phonon coupling strength important for understanding the mechanism of superconductivity in these compounds. Because of the molecular nature of the bonding in solid C_{60}, a study of the vibrational modes of the isolated molecule offers a good guide to the phonon spectrum in the solid. Furthermore, the characterization of the vibrational modes for this unique, highly symmetrical structure is an interesting problem in its own right.

A wealth of experimental data has been accumulated for the vibrational frequencies of the C_{60} molecule. The vibrational spectra were measured and identified over a broad range of frequencies by the methods of Raman and infrared spectroscopies,[8,9] as well as neutron inelastic-scattering[10–12] measurements. On the other hand, theoretical calculations of the vibrational frequencies of C_{60} were carried out using various semiempirical and *ab initio* methods: modified neglect of differential overlap (MNDO),[13–15] quantum consistent force field for π electrons (QCFF/PI),[16] tight-binding molecular dynamics (TBMD),[17] real-space quantum molecular dynamics (QMD),[18] and Car-Parrinello molecular dynamics.[19] Of these, *ab initio* results reported so far give deviations of approximately 10% from the experimentally observed values,[18,19] while the reliability of semiempirical results is often a subject of debate. Thus a conclusive assignment of the modes observed from various experiments is still lacking.

Another motivation for this work is to examine the efficiency and accuracy of first-principles methods for the vibrational frequencies of C_{60}. To this end, we pursued a systematic study of the effect of basis sets on the vibrational spectrum. Our results using large basis sets are in excellent accord with the experimental data available from Raman, infrared, and neutron inelastic-scattering measurements,[8–12] which provide a benchmark to identify conclusively the modes observed in various experiments. A detailed analysis of effects of basis set reveals some of the deficiencies of previous theoretical studies. Moreover, the constructed force-constant matrix yields complete information on the vibrational properties at $T = 0$, which, together with the associated eigenfrequencies and eigenvectors, is useful for testing the reliability of empirical methods and for calculating electron-phonon-coupling matrix elements for various phonon modes.

The present calculation was carried out using first-principles density-functional approach for molecules with analytical energy gradients.[20] The Hedin-Lundqvist form was used for the exchange-correlation energy of the electron within the local-density approximation (LDA). The calculation was performed with three different basis sets: minimal (MIN), double numerical (DN), and DN with polarization functions (DNP), i.e., functions with angular momentum one higher than that of the highest occupied orbital in the free atom. It amounts to five, nine, and fourteen atomic orbitals for each carbon atom, for the calculation using MIN, DN, and DNP basis sets, respectively.

The geometry of the icosahedral C_{60} molecule is characterized by two distinct bond lengths: the bond of the

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pentagon edge d_1 (single bond) and the hexagon-hexagon bond d_2 (double bond). For C_{60}, the highest occupied molecular orbital (HOMO) is fivefold degenerate with H_u symmetry, while the lowest unoccupied molecular orbital (LUMO) is threefold degenerate with T_{1u} symmetry. Both HOMO and LUMO are predominantly π molecular orbitals. We carried out geometry optimizations using conjugate-gradient procedures for each basis set. The DNP result is considered to be the most reliable. The corresponding distinct bond lengths are found to be 1.391 and 1.444 Å for double and single bonds, respectively. The HOMO-LUMO gap is found to be 1.67 eV. These results are in good agreement with other first-principles results and the experimentally measured values.

The calculation of the vibrational frequencies of C_{60} is made tractable by the high symmetry of the molecule. In general, the evaluation of the 180×180 dynamical force-constant matrix involves a numerical calculation of finite differences between energy gradients that are computed at displaced geometries corresponding to a distorted C_{60}. This is computationally formidable and demanding with first-principles methods. Owing to the high symmetry of the molecule, only the energy gradients due to the displacements of one atom are needed. The full dynamical matrix can then be constructed by applying the appropriate group symmetry operations of the icosahedral group. Group-theoretical analysis also allows the classification of the vibrational modes in accordance with their symmetry. In the present calculation, the second derivatives required for the force-constant matrix elements were obtained by calculating the forces exerted on all the atoms in the molecule when one of the atoms is displaced in the x, y, and z directions by a distance of 0.03 Å. Both positive and negative displacements were considered to minimize the effects of anharmonicity.

The calculated vibrational frequencies are shown in Table I and compared with the experimental frequencies of the optically active infrared (T_{1u}) and Raman ($A_g + H_g$) modes. The overall agreement with measured spectra is very good, with a maximum deviation of approximately 5% and a mean-square deviation (MSD) of 2.5% with respect to the whole set of 14 modes. Here the MSD is defined as $\sqrt{\sum_{i=1}^{N}[(\omega_i^{\text{theor}} - \omega_i^{\text{expt}})/\omega_i^{\text{expt}}]^2/N}$. This result is to be contrasted with results from other *ab initio* calculations, e.g., QMD (MSD = 10.9%), Car-Parrinello (MSD = 6.9%), and represents an improvement over the semiempirical calculations, e.g., QCFF/PI (MSD = 4.1%), TBMD (MSD = 6.9%), and MNDO (MSD = 13.2%).

The maximum deviation corresponds to a T_{1u} frequency of 548 cm^{-1}, as compared with the experimental value of 577 cm^{-1}.[9] Different experimental measurements reported on this frequency vary from 577 (Ref. 9) and 570 cm^{-1} (Ref. 8) to 563 cm^{-1}.[12] Our result on this mode (548 cm^{-1}) is closer to the neutron inelastic-scattering value of 563 cm^{-1}.

As seen in Table I, the calculation by use of DN and DNP basis sets yields very close vibrational frequencies. By contrast, the MIN calculation yields vibrational frequencies ranging from 246 to 1842 cm^{-1} and a much larger MSD of 19% with respect to the experiment. The general features of the MIN spectrum, namely the systematically underestimation of low-frequency modes and overestimation of high-frequency modes, are also observed in the spectrum obtained by QMD.[18] This is as expected since both calculations used only one atomic orbital for each valence electron. This demonstrates clearly that the MIN type of basis sets is too crude for a quantitative comparison with experimental results.

A previous *ab initio* Car-Parrinello calculation[19] gives vibrational frequencies which are systematically lower than the corresponding experimental values. This may be due to the small energy cutoff used in their plane-wave expansion. Our approach is different in several aspects: we used all-electron calculation with local orbitals instead of pseudopotential and plane-wave expansion. The eigenfrequencies and eigenvectors were calculated from a diagonalization of the dynamical force-constant matrix, while QMD and Car-Parrinello calculations used the symmetry of the eigenvectors to extract the eigenfrequencies from their molecular-dynamics trajectories.

Figures 1 and 2 display the calculated low-frequency and high-frequency density of vibrational states together with the neutron inelastic-scattering spectrum measured by Coulombeau *et al.*[12] In the low-frequency part (see

TABLE I. Comparison between the calculated 46 distinct vibrational frequencies, $\omega_{\text{LDA}}^{(0)}$ and ω_{LDA} (in cm^{-1}), and the experimental Raman and infrared data, ω_{expt} (in cm^{-1}), along with the corresponding irreducible representations $\mathcal{R}$ of the icosahedral group. $\omega_{\text{LDA}}^{(0)}$ and ω_{LDA} are results using DN and DNP basis sets, respectively.

	Even parity				Odd parity		
$\mathcal{R}$	$\omega_{\text{LDA}}^{(0)}$	ω_{LDA}	ω_{expt}	$\mathcal{R}$	$\omega_{\text{LDA}}^{(0)}$	ω_{LDA}	ω_{expt}
A_g	484	483	496	A_u	980	947	
	1547	1529	1470				
				T_{1u}	539	533	528
T_{1g}	566	566			566	548	577
	848	825			1216	1214	1183
	1299	1292			1501	1485	1429
T_{2g}	571	550		T_{2u}	353	344	
	772	771			724	717	
	820	795			997	987	
	1371	1360			1234	1227	
					1566	1558	
G_g	492	484					
	579	564		G_u	353	356	
	765	763			765	752	
	1127	1117			782	784	
	1335	1326			984	977	
	1535	1528			1346	1339	
					1472	1467	
H_g	272	263	273				
	439	432	437	H_u	406	396	
	720	713	710		544	534	
	782	778	774		680	663	
	1121	1111	1099		750	742	
	1285	1282	1250		1234	1230	
	1478	1469	1428		1368	1360	
	1606	1598	1575		1596	1588	

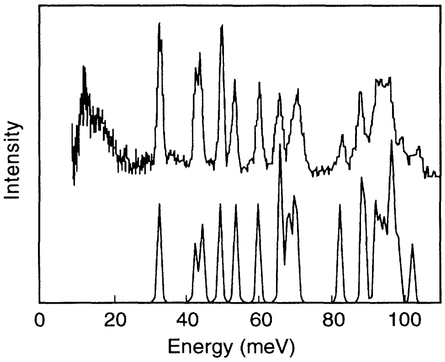

FIG. 1. Comparison between the experimental neutron inelastic-scattering spectrum (Ref. 12) (top) and the calculated total density of vibrational states of the icosahedral C_{60} molecule (bottom) for low-frequency modes. First-principles results are broadened by a Gaussian function with a standard deviation of 0.5 meV.

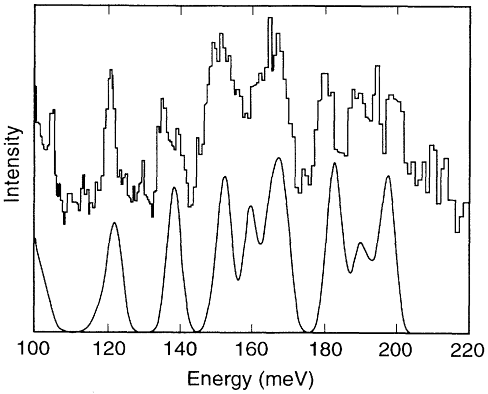

FIG. 2. Comparison between the experimental neutron inelastic-scattering spectrum (Ref. 12) (top) and the calculated total density of vibrational states of the icosahedral C_{60} molecule (bottom) for high-frequency modes. First-principles results are broadened by a Gaussian function with a standard deviation of 1.9 meV.

Fig. 1), the five peaks observed by Cappelletti *et al.*[10] are all present in the experimental spectrum but are split into twelve distinct peaks with better resolution. Our calculated spectrum exhibits an impressive one-to-one agreement with the experimental spectrum for the position of the peaks. In the high-frequency part (see Fig. 2), eight bands in our spectrum correspond to several well-separated bands in the experimental spectrum, with a very good agreement for the peak positions. The results demonstrate the desirable efficiency and accuracy of the first-principles approach for obtaining important quantitative information on the vibrational properties of the system. It is therefore evident that a conclusive assignment of the vibrational modes can be achieved. After this work was completed, we became aware of the measurement of a richly structured C_{60} vibrational spectrum reported by Nissen, Wilson, and Thewalt.[21] Our study provides a timely classification of the symmetry for their observed vibrational modes.

The detailed information on geometrical and vibrational properties obtained in this work will be useful for the construction of empirical carbon interatomic potentials which can be applied to systems involving a larger number of atoms. In this regard, we note that several empirical calculations based on bond-charge model[22] and force-constant model[23] give a very good fit to the optically active vibrational modes. However, a detailed comparison of our complete spectra with those of empirical calculations reveals that there exist substantial deviations for the frequencies of other modes, indicating that those empirical models are not very accurate for the description of modes not included in the fitting database. To provide useful insights into the range of interatomic interactions in this system, we diagonalized the dynamical force-constant matrix with truncation of the matrix elements beyond a range R. The resulting spectra have MSD 9.0%, 7.0%, and 1.2% for $R = 2.52, 3.56$, and 4.36 Å, respectively, from the results at $R = \infty$. This indicates that interactions between the carbon atoms in the C_{60} molecule are quite long ranged, and the inclusion of up to fourth-neighbor interactions seems necessary for empirical models.

Another interesting topic is to study the softening of the vibrational modes when the C_{60} molecule becomes negatively charged. Unfortunately, for the most interesting case, $C_{60}{}^{3-}$, the LDA calculations show that some of the occupied electronic orbitals become unbound due to the inaccuracy of LDA in describing electronic correlation effects in inhomogeneous systems. Furthermore, the present LDA calculation of negatively charged C_{60} shows that the optimized geometry undergoes Jahn-Teller distortion which lowers the icosahedral symmetry of the system. Although the above-mentioned factors hamper the resolution of the interesting topic within this LDA scheme, it is instructive that the application of this type of group-theoretical analysis will be fruitful for other first-principles calculations.

In summary, we have reported a first-principles calculation of vibrational properties of the icosahedral C_{60} molecule. A group-theoretical analysis is applied to greatly simplify the calculation. The computed vibrational frequencies agree in detail with experimental data available from Raman, infrared, and neutron inelastic-scattering measurements. Our study reveals the importance of using large basis sets in this type of dynamical calculation, and settles the issue of assignment of vibrational modes for this remarkable molecule.

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