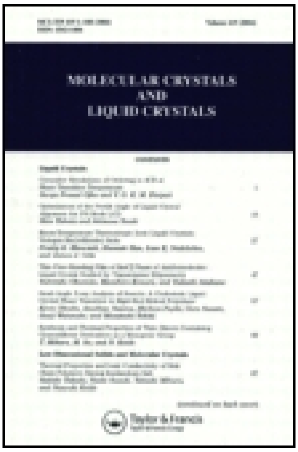

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A Vibrational Potential Function for Molecular Dynamics Simulation of Buckminsterfullerene

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A VIBRATIONAL POTENTIAL FUNCTION FOR MOLECULAR DYNAMICS SIMULATION OF BUCKMINSTERFULLERENE

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Abstract A vibrational potential function is proposed for Buckminsterfullerene (C_{60}) in terms of stretching, bending and torsional coordinates. Good agreement of calculated with experimental frequencies is found. On the basis of this potential function a molecular dynamics study of C_{60} is performed with simulation of the Raman spectrum.

INTRODUCTION

The vibrational properties of C_{60} have been the object of considerable interest since the first report on this molecule [1]. Following synthesis and isolation [2] ir and Raman spectra of C_{60} have been measured and discussed on the basis of icosahedral (I_h) symmetry [3-7]. On the same time, normal mode calculations were performed on C_{60} to predict vibrational frequencies [8-11]. The calculated frequencies by semiempirical QCFF/PI method [10] were in particular good agreement with experimental data.

The vibrational analysis of C_{60} may be approached also by force field calculations, i.e. in terms of force constants suitably chosen [8] or transferred from higher aromatics [11]. Since no experimental frequencies were known, no refinement of calculated values was attempted [8, 11]. Due to the appealing simplicity of the model and to the high symmetry of the molecule, the force field method is worth reconsideration. Hopefully, with a small number of potential parameters and a convenient choice of force constants, experimental data may be reproduced satisfactorily. On the other hand, spectroscopic properties may be investigated also by the method of molecular dynamics (MD) once the potential between interacting particles is known [12]. Coupling of harmonic and MD calculations has proved valuable in the analysis of vibrational motion of model alkanes [13]. The two different techniques may therefore be used to give the same answer as to the vibrational frequencies of C_{60}. Moreover, MD calculations may be related to spectroscopic properties such as the inelastic incoherent neutron spectrum [14, 15] and the Raman spectrum [6].

Here we report a vibrational analysis of C_{60} in terms of a modified Urey-Bradley potential, including stretching, bending and torsional coordinates. With dense sampling of force constant values we have been able to calculate frequencies in good agreement with experimental data. On the basis of this potential and by a proper correlation of atomic positions at different times, the power spectrum of the position dyadic product may be obtained. This is related to the Raman spectrum. The simulated Raman spectrum may be factored into its irreducible contributions of A_g and H_g symmetry and symmetry assignments may be discussed.

VIBRATIONAL FREQUENCIES

In the harmonic approximation the potential function of C_{60} molecule may be expanded around the equilibrium configuration in terms of internal contributions, including stretching, bending, torsional and non-bonded interactions, as follows

$$2V = \sum_{i,j}^{bonded} f_{ij}^{r}(\Delta r_{ij})^2 + \sum_{i} f_{i}^{\alpha}(\Delta\alpha_i)^2 + \sum_{i,j}^{non-bonded} f_{ij}^{q}(\Delta q_{ij})^2 + \sum_{i} f_{i}^{\tau}(\Delta\tau_i)^2 \qquad (1)$$

In eq.(1) Δr_{ij} is the stretching between bonded ("1-2") atoms, Δq_{ij} the distance coordinate between non-bonded ("1-3") atoms, $\Delta\alpha_i$ the bending involving three atoms ("1-2-3") and $\Delta\tau_i$ the torsional coordinate due to four consecutive atoms ("1-2-3-4"), with i running in the last two cases over all possible bendings and torsions, respectively. In the highly symmetrical C_{60} structure there are only two "1-2" bond stretchings, two "1-3" non-bonded stretchings, two "1-2-3" bendings and three "1-2-3-4" torsions, as better shown in the inset of Table II. Our potential depends on $2f^r$, $2f^\alpha$, $3f^\tau$ and $2f^q$ values. The force constant matrix may be easily computed in cartesian coordinates starting from eq.(1) and expressing the internal coordinates as a function of atomic displacements. For the sake of clarity, Δr_{12} and $\Delta\alpha_{123}$ result

$$\Delta r_{12} = |\mathbf{r}_{12} - \mathbf{r}_{12}^o| = [(x_{12} - x_{12}^o)^2 + (y_{12} - y_{12}^o)^2 + (z_{12} - z_{12}^o)^2]^{1/2} \tag{2a}$$

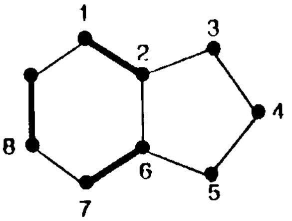
$$\Delta\alpha_{123} = \alpha_{123} - \alpha_{123}^o = arccos\left[\frac{\mathbf{r}_{12} \bullet \mathbf{r}_{23}}{|\mathbf{r}_{12}||\mathbf{r}_{32}|}\right] - \alpha_{123}^o \tag{2b}$$

where the zero superscript refers to the equilibrium configuration. Δq_{13} has a definition similar to eq.(2a). The torsional coordinate $\Delta\tau_i$ has been approximated by a stretching-type coordinate between end atoms ("1-4"). On the whole, our potential model resembles the Urey-Bradley force field [16]. The cartesian matrix of the force constants may be obtained analytically from eq.(1) and eq.(2a-2b) thus enabling to calculate the vibrational frequencies.

The normal coordinates of fullerene are classified as $2A_g + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + 1A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u$. All infrared ($T_{1u}$) and Raman ($A_g + H_g$) active modes have been observed experimentally [3-7]. Force constants have been varied randomly with dense sampling scanning large intervals of values. A minimization procedure was performed for best fit of calculated to experimental frequencies. Calculation was efficiently carried out considering only sets of force constants giving a mean square deviation from experimental data below a given threshold. The best fit force constants and calculated frequencies are shown in Table I and II, respectively. The agreement with experimental frequencies is very good and the root-mean-square deviation is $\simeq$ 34 cm^{-1}, which compares well with that corresponding to QCFF/PI calculation [10].

Table I. Best fit parameters of the vibrational potential function: f^r, f^q, f^α, f^τ are stretching, bending and torsional force constants (mdyne/Å) as defined in the right inset reproducing the typical hexagon-pentagon arrangement of C_{60}.

$f^r_{12} = 2.823$	$f^q_{13} = 0.228$
$f^r_{23} = 2.458$	$f^q_{24} = 1.743$
$f^\alpha_{123} = 0.681$	$f^\tau_{1267} = 0.35$
$f^\alpha_{234} = 0.585$	$f^\tau_{1234} = 0.07$
	$f^\tau_{7623} = 0.20$



There is a good internal consistency in our force field. In fact, the stretching constants scale appropriately with the distance, as expected, while the bending constant involving one double bond is higher than that relative to two single bonds. Comparison with a previous force field of equivalent complexity [11] is also satisfactory, being the constants similar in the two cases. In our calculation the stretching constants for bonded atoms result smaller than in ref.11. This seems reasonable considering that their force field was transferred without modification from polycyclic aromatics and that our minimization procedure is very efficient for best fit results.

Table II. Calculated and experimental [4, 6] (in parenthesis) frequencies of C_{60}. The values are expressed in cm^{-1}.

A_u 1313	G_u 851	A_g 527(496)	G_g 1039
T_{1u} 521(527)	G_u 1005	A_g 1435(1470)	G_g 1458
T_{1u} 608(577)	G_u 1367	T_{1g} 552	G_g 1566
T_{1u} 1166(1183)	G_u 1529	T_{1g} 994	H_g 284(273)
T_{1u} 1415(1428)	H_u 419	T_{1g} 1408	H_g 422(437)
T_{2u} 363	H_u 469	T_{2g} 674	H_g 622(710)
T_{2u} 631	H_u 661	T_{2g} 735	H_g 761(774)
T_{2u} 1044	H_u 831	T_{2g} 1130	H_g 1144(1099)
T_{2u} 1235	H_u 1253	T_{2g} 1448	H_g 1244(1250)
T_{2u} 1543	H_u 1473	G_g 435	H_g 1438(1428)
G_u 367	H_u 1620	G_g 620	H_g 1619(1575)
G_u 727		G_g 723	

THE MOLECULAR DYNAMICS SIMULATION

In classical molecular dynamics (MD) the time evolution of a system is known if the interaction potential among its constituent particles is given. By solving the newtonian equation of motion information about structural and spectroscopic properties is obtained through correlation of the particle motion at different times. Vibrational properties may be calculated from the Fourier transform of the velocity autocorrelation function [13]. In the harmonic approximation this method is entirely equivalent to solving the dynamical matrix of the traditional GF Wilson method, as it has been recently shown [13]. As a simple application of the method we have simulated the Raman spectrum of C_{60} at $T=1$ K. The Raman intensity $I(\omega)$ may be calculated as the Fourier transform of the polarizability autocorrelation function as follows

$$I(\omega) \propto \int \sum_n < \alpha_n(t)\alpha_n(0) > e^{i\omega t} dt \tag{3}$$

where $\alpha_n(t)$ and $\alpha_n(0)$ are atomic polarizability tensors at time t and 0, respectively, which are assumed to be proportional to $\mathbf{r}_n\mathbf{r}_n$, the dyadic product of the vector position of the n-th atom with itself. This is quite reasonable considering that α has cartesian elements of the type xx, xy, yy, ...

The simulation is divided into three parts. First the system is thermalized at the desired temperature with a stochastic procedure already reported [13]. Second, the system evolves freely in time for $\simeq$ 20 psec and finally the dynamical trajectories are saved for spectral analysis over a period of $\simeq$ 53 psec.

The polarizability tensor of C_{60} decomposes in A_g and H_g symmetry species whose elements are $(x^2+y^2+z^2)$ and $(2z^2-x^2-y^2, x^2-y^2, xy, yz, xz)$, respectively. We have calculated the autocorrelation function according to eq.3 for all elements of the polarizability tensor and taken the appropriate combination to obtain the symmetry-adapted functions of A_g and H_g symmetry. The results are shown in Fig.1. The frequencies of C_{60} calculated according to the GF method or in the molecular dynamics simulation are essentially identical. The overall Raman spectrum is nicely decomposed into two portions of A_g and H_g symmetry. In the first, two bands are calculated at 527 and 1435 cm^{-1} and therefore

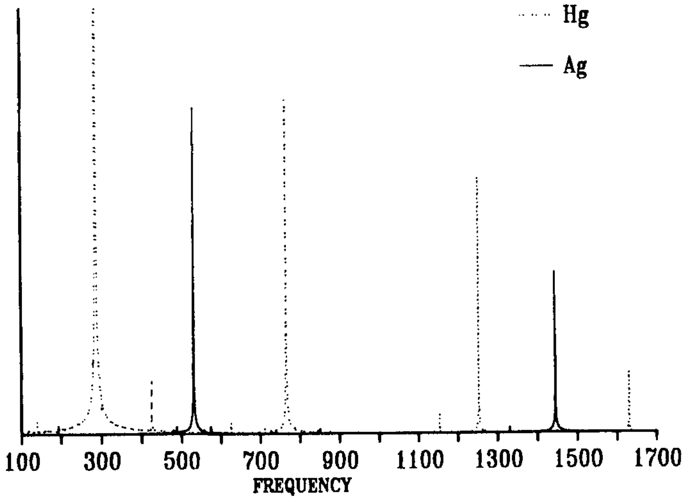


Figure 1. : Calculated polarized A_g(—) and H_g(---) Raman spectra from MD data at 1 K.

assigned to A_g symmetry, as expected. In the second, seven peaks are clearly observed whose frequencies coincide with those of H_g modes of Table II. The last H_g peak is weak and hidden under the strong 1435 cm^{-1} A_g line. The MD simulation may be used with confidence for vibrational assignment since no peak occurring in one polarization is present in the other and viceversa.

The intensity of each Raman spectrum is distributed mostly on the low- frequency peaks. This is in fair agreement with experimental intensities of H_g modes while the comparison with A_g intensities is less satisfying. This may be due to the simplicity of the model as well as to poor thermalization mainly as a consequence of the purely harmonic form of the potential. Obtainment of an effective energy redistribution would require an extremely long computational time which for the present purposes was felt unnecessary.

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