Rotation–vibration scalar coupling ζ coefficients and spectroscopic band shapes of buckminsterfullerene

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The Maxwell–Boltzmann distribution is used to calculate J_{max} for the proposed icosahedrally symmetric structure of C_{60} called buckminsterfullerene. The results are used with calculated rotation–vibration scalar coupling ζ coefficients to make predictions for the dipole active rovibrational band shapes. Stereoscopic figures of the corresponding normal modes are shown in the body fixed rotating frame. Rotational constants and spectral features of CH_4, CF_4, and SF_6 are included for comparison.

1. Introduction

As interest in both the terrestrial and interstellar carbon chemistry of the recently proposed "fullerenes" continues to increase it is becoming more imperative than ever to clearly identify the truncated icosahedral structure of the seminal fullerene, C_{60} [1–3]. The most direct determination of the structure of C_{60}, or buckyball, may be obtained from its spectrum. Presently there are several theoretical predictions for the optical spectrum of buckyball [4–6]. In addition, vibrational spectra of buckyball have been calculated [7–9], and predictions have been made for the fine and superfine rotational spectral structure of buckyball [10,11]. Recently, the infrared and ultraviolet absorption spectra of carbon clusters collected on a substrate have been measured and support the proposed truncated icosahedral structure of C_{60} [12].

Using the T_{1u} dipole active vibrational normal modes of buckyball calculated in refs. [7,8], rovibrational scalar coupling ζ coefficients are determined and used with the Maxwell–Boltzmann distribution to predict the dipole active T_{1u} rovibrational

band shapes. The T_{1u} ζ coefficients sum to the correct value of -1 [13]. First-order approximations of the classical rovibrational normal modes in the rotating body fixed frame are shown in 3D stereoscopic figures that permit a qualitative visual estimation of the ζ coefficients. Several well known rotational constants and observed spectral features of CH_4, CF_4, and SF_6, are compared with calculated values of a possible spectra of buckyball.

2. Spectral features

Using the normalized Maxwell–Boltzmann distribution for spherical top molecules,

$$P(J) = N(2J+1)^2 \exp[(-T_0/T)J(J+1)], \qquad (1)$$

the relative population $P(J)$, of molecules with rotational quantum number J, may be determined for a given temperature T. The normalization N is chosen so that

$$\int_0^\infty P(J)\,\mathrm{d}J = 1 \,,$$

and is given by

$$N=\sqrt{1/\pi}\,(T_0/T)^{3/2}\exp(-T_0/4T)\,.$$

The constant T_0 is a function of molecular species and is roughly the temperature needed to populate the $J=1$ rotational level. This "quantum temperature" is defined as $T_0 = hcB/K$ where h is Planck's constant, c is the speed of light, and K is Boltzmann's constant. The constant B is defined as

$$B = \frac{h}{8\pi^2 cI} = \frac{2.7993 \times 10^{-39}}{I}\ \mathrm{g\,cm}\,,$$

where I is the equilibrium value of the moment of inertia of a spherical top molecule.

By taking the derivative of eq. (1) with respect to J and setting the result to zero, the maximally populated value of J for a given temperature T, is calculated to be

$$J_{max} = -\tfrac{1}{2} + \sqrt{T/T_0}\,.$$

Plots of the normalized $P(J)$ given in eq. (1) are shown in fig. 1 for CF_4, SF_6, and buckyball. A temperature of 30 K is used as rough estimate of the conditions found in the Egg Nebula (CRL 2688) [14], a likely source of extraterrestrial C_{60} [1]. Immediately apparent is the very broad distribution of ex-
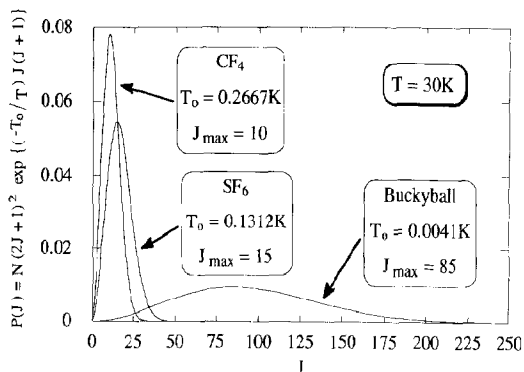

Fig. 1. Relative population of rotational energy levels for CF_4, SF_6, and buckyball as determined by the Maxwell–Boltzmann distribution at 30 K. The area under each curve is normalized to unity.

cited rotational energy levels of buckyball and a value of J_{max} that is over five times as large as J_{max} of SF_6. At 30 K appreciable populations of buckyball exist for $J=175$ and even $J=200$. At room temperature appreciable populations of buckyball exist for $J=500$ and even $J=600$. These high values of J will be very important when considering the rotational fine and superfine spectral structure of buckyball. A table of B values, calculated J_{max} values, and observed J_{max} values are given for CH_4, CF_4, SF_6, and buckyball in the upper half of table 1.

Scalar coupling between the vibration and rotation of spherical molecules is given by the third term in the rovibrational Hamiltonian,

$$H_{rovib} = H_{vib} + H_{rot} + H_{v,r} = H_{vib} + B\hat{J} - 2B\zeta\hat{J}\cdot\hat{l}\,. \quad (2)$$

Expectation values of eq. (2) are,

$$\langle H_{rovib}\rangle = \nu_{vib} + BJ(J+1) - 2B\zeta\langle\hat{J}\cdot\hat{l}\rangle$$

$$= \nu_{vib} + BJ(J+1)$$

$$- B\zeta[J(J+1) - R(R+1) + l(l+1)]\,, \quad (3)$$

where J is the total angular momentum, R is the rotational angular momentum, l is the vibrational angular momentum, and $2\hat{J}\cdot\hat{l} = J^2 - (J-l)^2 + l^2 = J^2 - R^2 + l^2$. The dipole active modes of buckyball have T_{1u} type icosahedral symmetry and contribute $l=1$ quanta of vibrational angular momentum in eq. (3). Possible couplings between R and $l=1$ are $J=R+1$, $J=R$, and $J=R-1$. This coupling results in a modification of the spherical top rotational energy level spacing,

$$\langle H_{rovib}\rangle = \nu_{vib} + BJ(J+1) - 2B\zeta - 2B\zeta J$$

$$\text{for } R = J-1\,;$$

$$\langle H_{rovib}\rangle = \nu_{vib} + BJ(J+1) - 2B\zeta$$

$$\text{for } R = J\,;$$

$$\langle H_{rovib}\rangle = \nu_{vib} + BJ(J+1) - 2B\zeta + 2B\zeta(J+1)$$

$$\text{for } R = J+1\,, \quad (4)$$

where the Jth energy level is split into three levels by an amount proportional to $B\zeta$. For negative ζ, the lowest of the three levels occurs when the vibrational and rotational angular momentum are anti-aligned $(R=J+1)$ and the highest occurs when the vibrational and rotational angular momentum are aligned

Table 1
Rovibrational constants and spectral features of CH_4, CF_4, SF_6, and buckyball. Buckyball modes (1)–(4) correspond to modes (a)–(d) in fig. 2

Molecule	CH_4	CF_4	SF_6		buckyball			
	$B=5.3226$ cm^{-1}	$B=0.1854$ cm^{-1}	$B=0.09118$ cm^{-1}		$B=0.00278$ cm^{-1}			
	$\nu_3=3020$ cm^{-1}	$\nu_4=631$ cm^{-1}	$\nu_3=948$ cm^{-1}	$\nu_4=617$ cm^{-1}	$\nu_1^{T_{1u}}=1868$ cm^{-1}	$\nu_2^{T_{1u}}=1462$ cm^{-1}	$\nu_3^{T_{1u}}=618$ cm^{-1}	$\nu_4^{T_{1u}}=478$ cm^{-1}
J_{max} (293 K)								
calculated	6	33	47		266			
observed P branch	7–8	≈ 30	N/A	≈ 45	N/A	N/A	N/A	N/A
observed R branch	7–8	≈ 35	N/A	≈ 40	N/A	N/A	N/A	N/A
J_{max} (30 K)								
calculated	1	10	15		85			
ζ	0.05	-0.3614	0.6937	-0.2156	-0.0761	-0.3193	-0.4976	-0.1070
$\Delta=2B(1-\zeta)$ (cm^{-1})	10.113	0.505	0.0559	0.222	0.0062	0.0076	0.0086	0.0064
ΔJ_{max} (293 K) (cm^{-1})								
calculated	61	17	2.6	10.4	1.7	2.0	2.3	1.7
observed P branch	≈ 70	≈ 16	N/A	≈ 10	N/A	N/A	N/A	N/A
observed R branch	≈ 70	≈ 18	N/A	≈ 10	N/A	N/A	N/A	N/A
ΔJ_{max} (30 K) (cm^{-1})								
calculated	10	5.05	0.84	3.33	0.527	0.646	0.731	0.544
P, R branch peak to peak (293 K) (cm^{-1})								
calculated	122	34	5.25	21	3.4	4.0	4.6	3.4
observed	140	≈ 34	N/A	≈ 20	N/A	N/A	N/A	N/A
peak to peak (30 K) (cm^{-1})								
calculated	20	10.1	1.68	6.66	1.054	1.292	1.462	1.088

$(R = J - 1)$. Only transitions that conserve R are allowed resulting in P, Q, and R branches that are split by more (or less) than $2B$ of a rigid spherical top when ζ is negative (or positive). Calculated ζ coefficients of buckyball are given in table 1 and are all negative because buckyball is hollow and lacks a central atom. Buckyball ζ coefficients may be compared with observed ζ coefficients of CH_4, CF_4, and SF_6 which are also listed in table 1.

3. ζ calculation

The ζ coefficients of any molecule may be calculated using a number of different methods. Each of these equivalent methods may be derived from the general definition of the zeta operator,

$$\zeta^\alpha = \sum_{i=1}^n |\beta i\rangle\langle\gamma i| - |\gamma i\rangle\langle\beta i|, \quad \alpha \neq \beta \neq \gamma,$$

where α, β, and γ are the spatial coordinates x, y, and z of a body fixed coordinate system, and i labels the $1, 2, ..., n$ nuclei. The bra-kets $|\beta i\rangle$ correspond to the displacement of the ith nuclei in the β direction. By representing ζ^α in a basis spanned by the normal coordinates $|l\rangle$, the general definition of the ζ coefficient is obtained,

$$\zeta_{l,k}^\alpha = \zeta_l = \sum_{i=1}^n \langle l|\beta i\rangle\langle\gamma i|k\rangle - \langle l|\gamma i\rangle\langle\beta i|k\rangle$$

$$= \sum_{i=1}^n Q_{\beta i,l}^* Q_{\gamma i,k} - Q_{\gamma i,l}^* Q_{\beta i,k}, \quad (5)$$

where the $Q_{\beta i,l}$ are coefficients of the lth normal mode expressed as displacements of the ith nuclei in the βth direction of the body fixed coordinate system. Using standing waves as defined in ref. [8], the $Q_{\beta i,l}$ are pure real and eq. (5) is identical to the usual definitions of the ζ coefficients [13,15].

In the absence of rotation, the T_{1u} dipole active modes of buckyball consist of four sets of threefold degenerate genuine vibrations and a threefold degenerate set of zero frequency translations. The threefold degenerate standing waves of a given eigenfrequency form a set of three partners each of which has an induced dipole moment orthogonal to the other two. These induced dipole moments are used to define a right-hand body fixed coordinate

system. Rotation about the z axis of this coordinate system causes a Coriolis mixing of the x and y partners,

$$z \to z, \quad x \to x + iy, \quad y \to x - iy \quad (6)$$

forming complex moving normal modes defined in ref. [8]. The coupling between the rotational and resulting vibrational momentum then splits the threefold vibrational degeneracy. The ζ^z coefficient calculated from the $l = x$ and $k = y$ partners in eq. (5) is equal to the ζ^x coefficient calculated from the $l = y$ and $k = z$ partners, and the ζ^y coefficient calculated from the $l = z$ and $k = y$ partners. Thus the superscript α of ζ in eq. (5) may be suppressed. For standing waves, the sign of the ζ coefficient is defined by the order of partners $l = \alpha$ and $k = \beta$ used in eq. (5) where

$$\alpha, \beta \to \epsilon_{\alpha\beta\gamma}\zeta^\gamma,$$

$$\epsilon_{\alpha\beta\gamma} = \quad 1 \quad \text{for cyclic permutations of } \alpha, \beta, \gamma;$$

$$= \quad 0 \quad \text{for any two indices equal;}$$

$$= -1 \quad \text{for any two indices switched.}$$

Once the sign has been defined, the only label needed for the ζ coefficients is one that distinguishes between the four sets of threefold degenerate partners which is precisely the label used for the corresponding eigenvalues. Following ref. [8] these labels are the icosahedral irreducible representation label T_{1u} and column label $c = 1, 2, 3, 4$. A list of buckyball dipole active ζ coefficients using spring constants given in ref. [8], is given in table 2.

Using subgroup chain defined icosahedral irreducible representations (irreps), T_{1u} vibrational

Table 2

ζ coefficients of the four T_{1u} dipole active modes of buckyball. ($p = h = 7.6$, $\pi = \eta = 0.7$.) Mode labels (1)–(4) correspond to modes (a)–(d) in fig. 2. Spring constants are the same as those in refs. [7,8]

$$\zeta_1^{T_{1u}} = -0.07613$$
$$\zeta_2^{T_{1u}} = -0.31933$$
$$\zeta_3^{T_{1u}} = -0.49757$$
$$\zeta_4^{T_{1u}} = -0.10698$$
$$\sum_{i=1}^4 \zeta_i^{T_{1u}} = -1$$
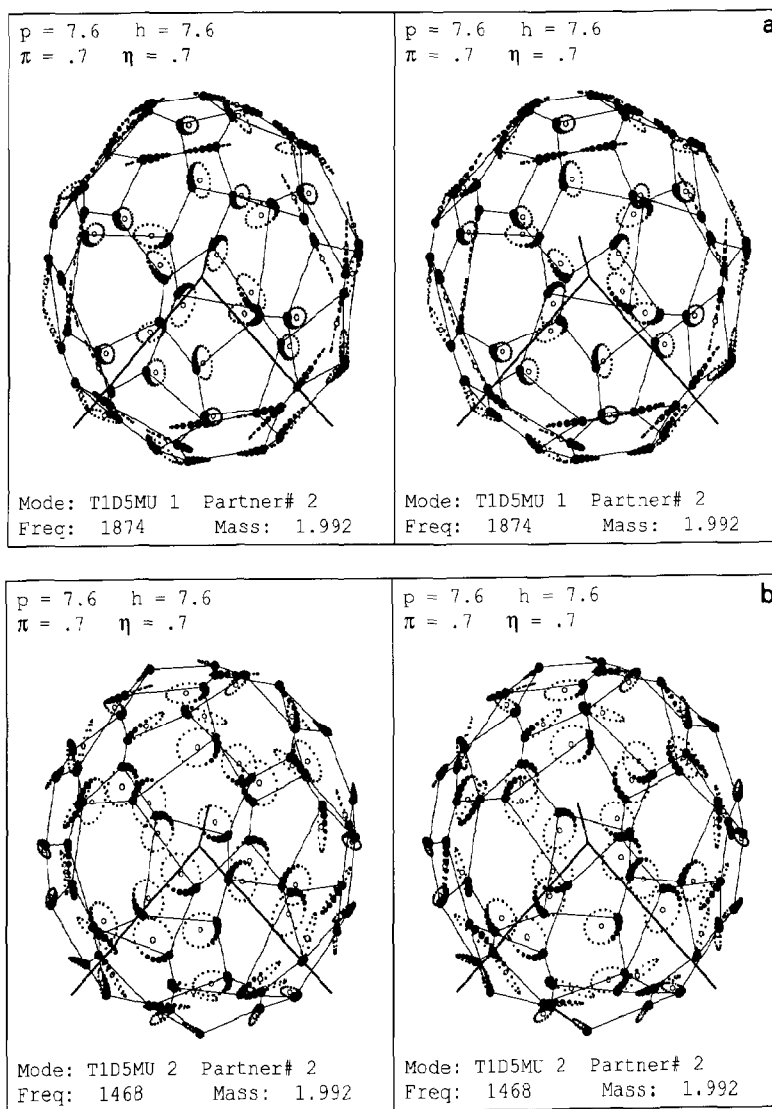$$\zeta_5^{T_{1u}} = 1 \text{ (translation)}$$

Fig. 2. The I, D_5, C_5 defined normal modes of buckyball. The I, D_5, C_2 defined coordinate system is shown with the z axis pointing out of the page and is collinear with the axis of rotation. The direction the nuclei are moving is indicated by the variable dot size along the nuclear trajectories. The slight difference between frequencies at the bottom of the figures and those reported in refs. [7,8] is due to the use of 1.992×10^{-23} g instead of 2×10^{-23} g for the mass of the carbon nuclei. Modes (a)–(d) correspond to rovibrational band shapes shown in fig. 3.

normal mode x, y, and z partners are automatically defined along with the corresponding body fixed coordinate system. Standing waves defined by the I,D_5,C_2 subgroup chain are shown in ref. [8]. The transformation in eq. (6) from standing to moving waves is precisely the transformation from the I,D_5,C_2 subgroup chain defined T_{1u} icosahedral irreps to the equivalent set of T_{1u} I,D_5,C_5 irreps. The com-

plex normal modes defined by the I,D_5,C_5 T_{1u} irreps may be used *individually* to calculate *diagonal* elements of the ζ operator, where the $Q_{Bi,j}$ correspond to the position and scaled momentum of the ith nuclei. These complex normal modes are the first-order approximation of the rovibrational eigenfunctions of a rotating molecule of buckyball, and are shown in the body fixed coordinate system defined by the
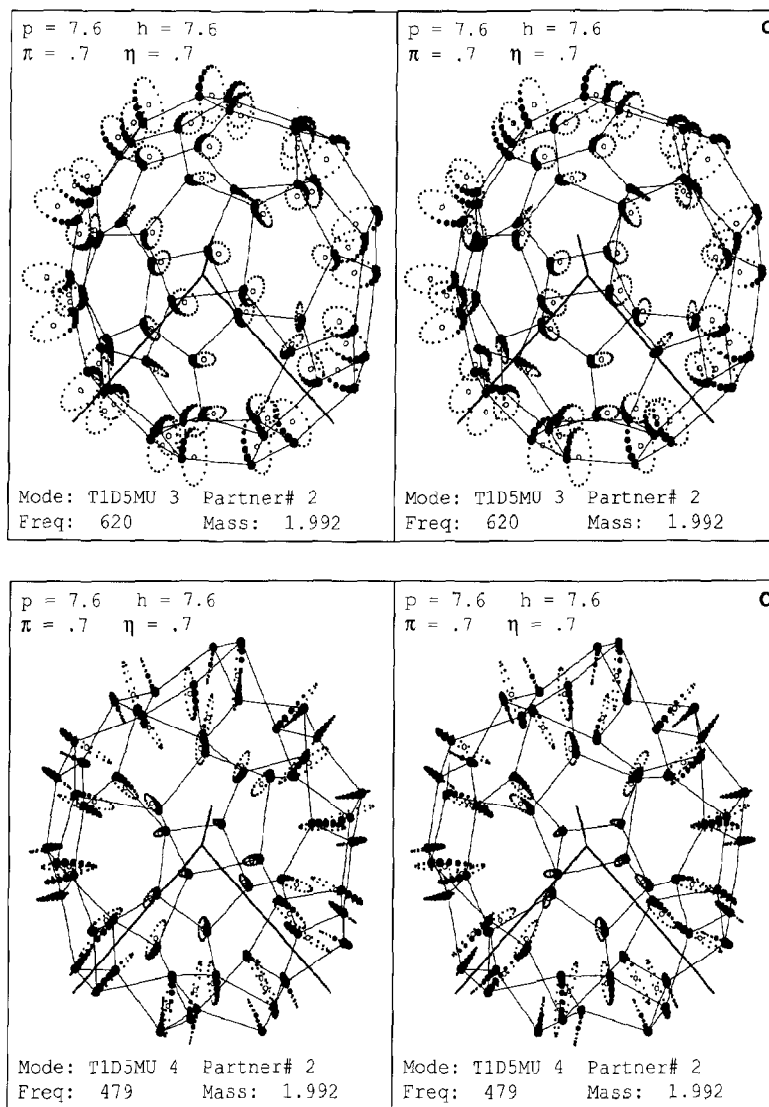
Fig. 2. Continued.

I,D_5,C_2 subgroup chain in the 3D stereoscopic figures 2a–2d. The rotational angular momentum vector is collinear with the z axis which is also an axis of fivefold rotational symmetry. With the observation that the nuclei travel along elliptical paths that encompass an area proportional to the vibrational angular momentum of each nuclei, and that this angular momentum is perpendicular to the plane containing the ellipse with a direction determined by the motion of the nuclei, it is possible to make a qualitative visual estimation of the ζ coefficients of different modes. For example, in fig. 1a the nuclei near the z axis are moving in a counterclockwise direction with large open orbits while those a little farther away are moving in a clockwise direction with slightly smaller orbits. The vibrational angular momentum of the nuclei moving in the clockwise direction almost cancel the vibrational angular momentum of the nuclei moving in the counterclockwise direction resulting in the smallest T_{1u} ζ coefficient. In fig. 1c it is clear that there are an overwhelming number of nuclei moving in large open counterclockwise tra-

jectories resulting in the largest T_{1u} ζ coefficient. Modes defined by the I,D_3,C_3 subgroup chain have been used to calculate an identical set of ζ coefficients for rotations of buckyball around an axis of threefold symmetry.

4. Rovibrational band shapes

Predictions of the rovibrational band shapes of the T_{1u} dipole active modes of buckyball are given in fig. 3 and are based on the assumption that a large number of buckyball molecules are in the A_{1g} symmetric ground vibrational state at a temperature of 30 K. Initial studies using a vibrational partition function in the harmonic limit [16], with frequencies and degeneracies from refs. [7,8] indicate that at 30 K over 99% of the buckyball molecules will be in the ground vibrational state. At 150 K about 1/3 will be in the ground state, and at room temperature ($T=293$ K) only 1/5000 will be in the ground state. Also assumed are equal transition probabilities from the rotational levels of the A_{1g} ground vibrational state to the rotational levels of the T_{1u} excited vibrational states. The energy spacing between adjacent values of J is calculated from the difference between the $J=1$, $R=1$ and $J=0$, $R=1$ levels in eq. (4),
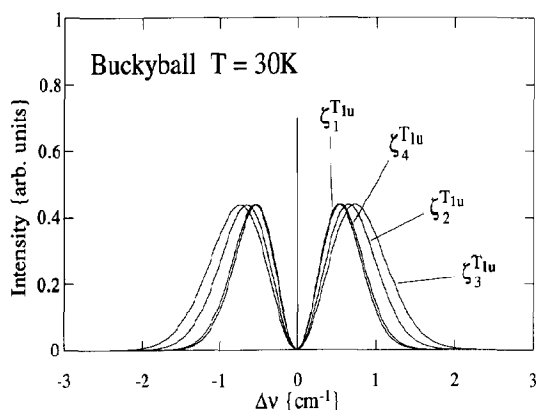
$$\Delta = 2B(1-\zeta) .$$

Fig. 3. Rovibrational band shapes of the four T_{1u} dipole active modes of buckyball at 30 K plotted as a function of the frequency shift $\Delta\nu$ from the centers of each band. Values of the band centers are given in table 1. The maximum intensities of each band are unknown and arbitrarily set equal to each other.

The relative amplitude of the bands as a function of J is given by the vibrational ground state population $P(J)$. The Q branches in fig. 3 are artificial and included only for reference. Values of Δ and ΔJ_{max} for buckyball are given in table 1. Peak to peak differences between the P and R branches of buckyball provide a measure of the rovibrational band width and are also included in table 1. For the purpose of comparison, calculated and observed values of Δ, ΔJ_{max}, and P–R branch differences are given for CH_4, CF_4, and SF_6 in table 1 as well. The peak to peak differences between the P and R branches of buckyball given in table 1 and shown in fig. 3 indicate that the rovibrational lines of buckyball will be relatively narrow and comparable with the ν_3 bandwidth of SF_6.

The predictions of the P and R branch splittings of buckyball include coupling between degenerate T_{1u} dipole active modes only. By "Jahn's rule" [17] any two modes will couple if the cross product of their symmetry species includes the rotational symmetry species. The strength of the coupling depends on the difference in vibrational frequency. For the icosahedral group, the rotational species is labeled T_{1g} and the following additional couplings between T_{1u} modes and other modes of buckyball will be allowed,

$$T_{1u} \otimes A_u = T_{1g} ,$$

$$T_{1u} \otimes T_{1u} = A_g \oplus T_{1g} \oplus H_g ,$$

$$T_{1u} \otimes H_u = T_{1g} \oplus T_{3g} \oplus G_g \oplus H_g .$$

5. Conclusion

The Maxwell–Boltzmann distribution is used with calculated ζ coefficients to determine the T_{1u} dipole active rovibrational band shapes expected in a spectrum of buckyball. The large value of $J_{max}=85$ at $T=30$ K is moderated by the small value of $B=0.0028$ cm^{-1} resulting in relatively narrow rovibrational bands that are about 1 to 1.5 cm^{-1} across. Stereoscopic figures of the corresponding moving dipole active T_{1u} modes are shown which permit the visualization of the ζ coefficients. A computer program for the MacIntosh that generates 3D animated movies of the normal modes of buckyball is available.

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