The study of the $(T_{1u} + T_{1g}) \otimes (\epsilon_g + \tau_{2g} + \tau_{1u})$ vibronic problem and ESR behaviour of C_{60}^{-} in cubic symmetry

1998 J. Phys.: Condens. Matter 10 7163

(http://iopscience.iop.org/0953-8984/10/32/008)

J. Phys.: Condens. Matter **10** (1998) 7163–7170. Printed in the UK PII: S0953-8984(98)91906-3

The study of the $(T_{1u} + T_{1g}) \otimes (\epsilon_g + \tau_{2g} + \tau_{1u})$ vibronic problem and ESR behaviour of C_{60}^- in cubic symmetry

R Rai

Theory Group, National Physical Laboratory, New Delhi 110012, India

Received 20 February 1998, in final form 24 April 1998

Abstract. The T_{1u} and T_{1g} levels of C_{60}^- in cubic symmetry are both susceptible to Jahn–Teller interaction due to the twofold degenerate ϵ_g and threefold degenerate τ_{2g} vibrations. In addition to this the two levels are admixed under threefold degenerate odd vibrations of τ_{1u} type. An analysis of this problem has shown the possibility of coexistence of two types of site, one having a trigonal type of ground state and the other of orthorhombic type. The ground vibronic T_{1u} levels at the two sites are capable of providing identical broad ESR signals. The sharp line in the spectra, known as a narrow spike, originates from the excited vibronic A_{2u} level, available only at sites with a trigonal type of ground state. The ground states of the similar vibronic problem of C_{60}^- in icosahedral symmetry are of trigonal type resulting in a vibronic ground T_{1u} and an excited A_{2u} level (symmetry group I_h). Hence an isolated C_{60}^-, i.e. without alkali ion ligands, is also capable of providing both broad and sharp ESR signals.

1. Introduction

Electron spin resonance spectra of the C_{60}^- ion [1–4] consist of a broad signal with g-value slightly less than two and a superimposed narrow spike as a sharp signal with spin only g-value $g_s = 2.0023$. The assignment of the spike is not clear. A number of possibilities such as the low lying excited $^2A_1$ state of C_{60}^- [2], ion-paired C_{60}^- [4] and C_{60}^{2-} ion are suggested as sources of this signal.

Recently Chen *et al* [1] have suggested that the narrow signal originates from those C_{60}^- ions which are less affected by surrounding alkali ion ligands, while those C_{60}^- which are perturbed by surrounding alkali ions are responsible for the broad signal. Since AC_{60} forms an NaCl structure [5–8] every C_{60}^- ion in AC_{60} is in a cubic surrounding of six alkali (A) ion ligands. Therefore the suggestion of Chen *et al* [1] is explored here by extending the earlier study, of vibronic interaction in icosahedral symmetry for an isolated C_{60}^- ion [9] to the vibronic interaction in cubic symmetry pertaining to a C_{60}^- ion with surrounding ligands. The ground T_{1u} state and the close by T_{1g} state of C_{60}^- are both susceptible to Jahn–Teller (JT) interaction due to the h_g mode of an icosahedral symmetry and also the two states are admixed under an odd parity vibration of the τ_{1u} mode [9]. In cubic symmetry the h_g mode is split into τ_{2g} and ϵ_g modes while the τ_{1u} mode remains unsplit. Thus the present paper is a study of the $(T_{1u} + T_{1g}) \otimes (\tau_{2g} + \epsilon_g + \tau_{1u})$ vibronic problem in cubic symmetry.

2. Vibronic Hamiltonian

The vibronic Hamiltonian corresponding to $(T_{1u} + T_{1g}) \otimes (\tau_{2g} + \epsilon_g + \tau_{1u})$ interaction in cubic symmetry can be written directly from the Hamiltonian for the $(T_{1u} + T_{1g}) \otimes (h_g + \tau_{1u})$

0953-8984/98/327163+08$19.50

interaction in icosahedral symmetry given earlier [9] by introducing the following two changes and a correction [10]. (i) Instead of a single frequency of h_g mode, two frequencies ω_ϵ and ω_τ for ϵ_g and τ_{2g} modes are involved. (ii) The coupling parameters K_u and K_g in diagonal terms are replaced by K_{ϵ_u} and K_{ϵ_g} respectively and in nondiagonal terms by K_{τ_u} and K_{τ_g} respectively. (iii) The vibronic matrix elements corresponding to the τ_{1u} mode can be written as

$$\langle X_u|V_y|Z_g\rangle = \langle Y_u|V_z|X_g\rangle = \langle Z_u|V_x|Y_g\rangle = a\langle Y_u|V_x|Z_g\rangle = a\langle Z_u|V_y|X_g\rangle = a\langle X_u|V_z|Y_g\rangle \tag{1}$$

where V_i is the potential associated with the normal coordinates Q_i of the τ_{1u} mode. $a = -1$ [10], while in [9] a wrong value of $a = 1$ is used. Despite the above changes and the correction the six-dimensional Hamiltonian is still reducible to two three-dimensional ones $\mathcal{H}_1$ and $\mathcal{H}_{-1}$, in the vector space $\{|X_\lambda\rangle, |Y_\lambda\rangle, |Z_\lambda\rangle\}$, where

$$|A_\lambda\rangle = \frac{1}{2}[(1+\lambda G)|A_u\rangle + (1-\lambda G)|A_g\rangle \tag{2}$$

$\lambda = 1$ or -1, and

$$G = \exp[\mathrm{i}\pi(a_x^+ a_x + a_y^+ a_y + a_z^+ a_z)].$$

Here A_u refers to orbitals of the T_{1u} state, A_g to those of the T_{1g} state and a_x^+ (a_x) etc are phonon operators of the τ_{1u} mode.

$$\begin{aligned}\mathcal{H}_\lambda &= [\omega_\epsilon(a_\theta^+ a_\theta + a_\epsilon^+ a_\epsilon + 1) + \omega_\tau(a_\xi^+ a_\xi + a_\eta^+ a_\eta + a_\zeta^+ a_\zeta + \tfrac{3}{2}) \\ &\quad + \omega'(a_x^+ a_x + a_y^+ a_y + a_z^+ a_z + \tfrac{3}{2}) + \tfrac{1}{2}\Delta(1-\lambda G)]I + V_\lambda \qquad (3)\\ V_\lambda &= \begin{pmatrix} \frac{1}{2}(K_{+\epsilon}+\lambda K_{-\epsilon}G)(-Q_\theta+\sqrt{3}Q_\epsilon) & \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\zeta - K'GQ_z \\ \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\zeta + K'GQ_z & \frac{1}{2}(K_{+\epsilon}+\lambda K_{-\epsilon}G)(-Q_\theta+\sqrt{3}Q_\epsilon) \\ \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\eta - K'GQ_y & \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\xi + K'GQ_x \end{aligned}$$

$$\begin{pmatrix} \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\eta + K'GQ_y \\ \frac{\sqrt{3}}{2}(K_{+\tau}+\lambda K_{-\tau}G)Q_\xi - K'GQ_x \\ (K_{+\epsilon}+\lambda K_{-\epsilon}G)Q_\theta \end{pmatrix}$$

$$K_{\pm\alpha} = \tfrac{1}{2}(K_{\alpha u} \pm K_{\alpha g}) \qquad Q_i = \frac{1}{\sqrt{2}}(a_i^+ + a_i).$$

We restrict further discussion to the lower branch $\mathcal{H}_1$ only. Because of the correction in (1) the present Hamiltonian differs from the one used earlier [9] in two respects. (i) It involves G in the product form with Q_x, Q_y and Q_z and (ii), with respect to the involvement of GQ_i ($i = x, y, z$), it is an antisymmetric matrix operator. This antisymmetry necessitates the use of a slightly different unitary transformation matrix than is usually used in an infinite coupling model to separate out the zero-phonon part of the Hamiltonian. The transformation matrix used here is given by

$$S = \begin{pmatrix} TU_y^{-1}U_zU_x & 0 & 0 \\ 0 & TU_z^{-1}U_xU_y & 0 \\ 0 & 0 & TU_x^{-1}U_yU_z \end{pmatrix} \tag{4}$$

where

$$T = \exp\sum_i \frac{f_i}{\sqrt{2}}(a_i^+ - a_i)$$

$$i = \epsilon, \theta, \xi, \eta, \zeta$$

and

$$U_i = \exp\left[\frac{f_i}{\sqrt{2}}(a_i^+ - a_i)\right]$$
$$i = X, Y, Z$$
$$S\mathcal{H}_1 S^{-1} = \mathcal{H}_1^0 + \mathcal{H}_1'. \tag{5}$$

$\mathcal{H}_1'$ involves coupling to the excited phonon states only and hence is not important for the ground state of the system in an infinite coupling model [11]. The form of the zero-phonon Hamiltonian $\mathcal{H}_1^0$ is the same as given earlier [9] except for the facts that (i) now two frequencies ω_ϵ and ω_τ and two coupling parameters, $K_{1\epsilon}$ in the diagonal and $K_{1\tau}$ in the nondiagonal, are involved and (ii) the variational parameter g_ζ is redefined as $g_\zeta = f_\zeta + \frac{2K'}{\sqrt{3}K_{1\tau}} f_z \, \mathrm{e}^{-f_x^2}$ instead of $g_\zeta = f_\zeta + \frac{2K'}{\sqrt{3}K_{1\tau}} f_z$. There are similar changes for g_ξ and g_η also. However the effect on the ground energy of the parameters f_x, f_y and f_z, reflecting the mixing effect of the excited T_{1g} level with T_{1u}, is expected to be much smaller than the effect of other variational parameters. Therefore to analyse $\mathcal{H}_1^0$ by the method of Opik and Pryce [12] the terms higher than quadratic in polynomials of f_x, f_y and f_z, in the expressions with K' as coefficient, are neglected. With this simplification the present results given in table 1 are similar to those found earlier [9]. The ground state energies are given by

$$E_{tetr} = -\frac{K_{1\epsilon}^2}{2\omega_\epsilon} + \tfrac{1}{2}\omega'(f^2 + 3) + \tfrac{1}{2}\Delta(1 - \mathrm{e}^{-f^2}) + \omega_\epsilon + \tfrac{3}{2}\omega_\tau \tag{6}$$

$$E_{trig} = -\frac{K_{1\tau}^2}{2\omega_\tau} - \frac{2|K'|f}{\sqrt{3}} + \tfrac{1}{2}\omega'(f^2 + 3) + \tfrac{1}{2}\Delta(1 - \mathrm{e}^{-f^2}) + \omega_\epsilon + \tfrac{3}{2}\omega_\tau \tag{7}$$

Table 1. The values of variational parameters for various stationary ground states in the infinite coupling model. Here

$$f_\tau = \frac{K_{1\tau}}{\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}} \qquad f_o = \frac{\sqrt{3}K_{1\tau}}{2\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}}.$$

Nature of stationary ground state	Values of parameters
Tetragonal	$f_\xi = f_\eta = f_\zeta = f_x = f_y = f_z = 0$
	(a) $f_\theta = \frac{K_{1\epsilon}}{\omega_\epsilon}$ $f_\epsilon = 0$
	(b) $f_\theta = -\frac{K_{1\epsilon}}{2\omega_\epsilon}$ $f_\epsilon = \frac{\sqrt{3}K_{1\epsilon}}{2\omega_\epsilon}$
	(c) $f_\theta = -\frac{K_{1\epsilon}}{2\omega_\epsilon}$ $f_\epsilon = -\frac{\sqrt{3}K_{1\epsilon}}{2\omega_\epsilon}$
Trigonal	$f_\theta = f_\epsilon = 0$
	(a) $-g_\xi = -g_\eta = g_\zeta = \frac{1}{\sqrt{3}} f_\tau$ $-f_x = -f_y = f_z = \frac{1}{\sqrt{3}} f$
	(b) $-g_\xi = g_\eta = -g_\zeta = \frac{1}{\sqrt{3}} f_\tau$ $-f_x = f_y = -f_z = \frac{1}{\sqrt{3}} f$
	(c) $g_\xi = -g_\eta = -g_\zeta = \frac{1}{\sqrt{3}} f_\tau$ $f_x = -f_y = -f_z = \frac{1}{\sqrt{3}} f$
	(d) $g_\xi = g_\eta = g_\zeta = \frac{1}{\sqrt{3}} f_\tau$ $f_x = f_y = f_z = \frac{1}{\sqrt{3}} f$
Orthorhombic	(a) $f_\theta = -\frac{K_{1\epsilon}}{2\omega_\epsilon}$ $f_\epsilon = 0$ $g_\zeta = \pm f_o$
	$f_z = \pm f$ $g_\xi = g_\eta = f_x = f_y = 0$
	(b) $f_\theta = \frac{K_{1\epsilon}}{4\omega_\epsilon}$ $f_\epsilon = -\frac{\sqrt{3}K_{1\epsilon}}{4\omega_\epsilon}$ $g_\xi = \pm f_o$
	$f_x = \pm f$ $g_\eta = g_\zeta = f_y = f_z = 0$
	(c) $f_\theta = \frac{K_{1\epsilon}}{4\omega_\epsilon}$ $f_\epsilon = \frac{\sqrt{3}K_{1\epsilon}}{4\omega_\epsilon}$ $g_\eta = \pm f_o$
	$f_y = \pm f$ $g_\zeta = g_\xi = f_z = f_x = 0$

$$E_{orth} = -\frac{K_{1\epsilon}^2}{8\omega_\epsilon} - \frac{3K_{1\tau}^2}{8\omega_\tau} - |K'|f + \tfrac{1}{2}\omega'(f^2+3) + \tfrac{1}{2}\Delta(1-\mathrm{e}^{-f^2}) + \omega_\epsilon + \tfrac{3}{2}\omega_\tau. \tag{8}$$

The parameter f is decided by the condition of extremization of the respective energies. It is obvious from (6) that E_{tetr} extremizes with f at $f = 0$, indicating zero mixing between T_{1u} and T_{1g} levels, which is contradictory to the result of infrared reflectivity measurements [13, 14]. This rules out the possibility of a tetragonal type of ground state. In section 3 the possibility of a trigonal or orthorhombic type of ground state in cubic symmetry is discussed in the light of ESR results. The ground state energies for an isolated C_{60}^- are obtained by substituting $\omega_\epsilon = \omega_\tau = \omega$ and $K_{1\epsilon} = K_{1\tau} = K_1$ in (7) and (8). Here ω is frequency and K_1 the effective coupling parameter for the h_g mode in icosahedral symmetry. In this case since the linear term in f is larger in the expression for E_{trig} compared to that in E_{orth}, the ground state is of trigonal type. The forthcoming section 3.1 about the inversion splitting and ESR behaviour of the trigonal type ground state in cubic symmetry is applicable to C_{60}^- in icosahedral symmetry also, but then the level notations T_{1u} and A_{2u} will refer to the I_h point group and not to cubic symmetry.

3. Inverse splitting and ESR behaviour

3.1. Trigonal type ground state

The ground vibronic wavefunction in this case is written in the form

$$\exp(A_\xi + A_\eta + A_\zeta)\frac{1}{f_\tau}(g_\xi|X_1\rangle + g_\eta|Y_1\rangle + g_\zeta|Z_1\rangle)|0\rangle \tag{9}$$

where $|0\rangle = |0_\xi 0_\eta 0_\zeta\rangle$ is the zero phonon state and

$$A_i = \exp\left[-\frac{g_i}{\sqrt{2}}(a_i^+ - a_i)\right].$$

The vibronic wavefunctions (9) are denoted as $|a\rangle$, $|b\rangle$, $|c\rangle$ and $|d\rangle$ depending upon the four possible sets of values of g_ξ, g_η and g_ζ given in table 1. Under inversion splitting this fourfold degenerate vibronic level is split into a singlet A_{2u} with wavefunctions

$$|A_2\rangle = \frac{1}{2\sqrt{1-S_\tau}}[|a\rangle + |b\rangle + |c\rangle + |d\rangle] \tag{10}$$

and a triplet T_{1u}, whose z-component is written as [11]

$$T_{1z} = \frac{1}{2\sqrt{1+\frac{1}{3}S_\tau}}[-|a\rangle + |b\rangle + |c\rangle - |d\rangle] \tag{11}$$

where

$$S_\tau = \exp\left[-\frac{2}{3}\left(\frac{K_{1\tau}}{\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}}\right)^2\right]. \tag{12}$$

The x- and y-components of T_{1u} are written from T_{1z} by cyclic permutation of a, b and c.

The inversion splitting, calculated by the method of Dunn and Bates [11], is given by

$$E_A - E_T = \frac{8S_\tau\omega_\tau}{(3-2S_\tau-S_\tau^2)}\left(\frac{K_{1\tau}}{\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}}\right)^2. \tag{13}$$

Obviously the vibronic T_{1u} level is lowest; this is split under spin–orbit interaction into a spin orbital vibronic quartet Γ_8 and a doublet Γ_6 with energies $\frac{1}{2}\alpha\lambda\kappa_\tau$ and $-\alpha\lambda\kappa_\tau$. Here

$\alpha = 2.5$ [16, 17] is the orbital Landé splitting factor [18] of the T_{1u} level, λ is the spin–orbit coupling coefficient and κ_τ is the Ham reduction factor given by

$$\kappa_\tau = \frac{4S_\tau}{3 + S_\tau}. \tag{14}$$

The excited vibronic singlet A_{2u} can be the source of a narrow spike with spin-only g-value in the ESR signal provided that its separation from the ground state is within the temperature range of the observation of the signal. An adequate value of the separation $E_A - E_T \approx 270$ cm^{-1} is arrived at from (12) and (13) for $S_\tau = 0.05$ and assuming $\omega_\tau \approx 437$ cm^{-1}, approximately equal to the H_g mode frequency in I_h symmetry with maximum JT coupling [19]. This low value of S_τ implies a very low value of $\kappa_\tau = 0.066$, which amounts to an almost complete quenching of the orbital moment and spin–orbit interaction of the vibronic T_{1u} level. This level will provide a broad magnetic field dependent ESR spectrum, since the spin–orbit interaction is comparable to magnetic field interaction, with the main line g-value slightly less than the spin-only g-value. A similar result is obtained by Tosatti *et al* also [16] for C_{60}^- in the gas phase. This situation corresponds to a strong JT case with JT energy $E_{JT} \approx (K_{1\tau}^2/2\omega_\tau) \approx -\frac{3}{4}[\omega_\tau \ln(S_\tau)] \approx 2.25\omega_\tau$.

In the limit of weak JT interaction there is only small quenching of spin–orbit interaction and magnetic moment of the T_{1u} level. The broad ESR signal can be assigned to the spin–orbital vibronic doublet Γ_6 with $g = \frac{2}{3}\left(2\alpha\kappa_\tau - \frac{1}{2}g_s\right)$, by suitable choice of κ_τ. In this case the inversion splitting, $E_A - E_T$, is very large. Therefore the vibronic singlet A_{2u} is far removed from the ground and we conclude that in the weak JT limit there is no plausible source for the narrow signal.

3.2. Orthorhombic type ground state

The ground level in this case is a sixfold degenerate level corresponding to six possibilities of orthorhombic types of solution (table 1). An inversion splitting removes this degeneracy into two vibronic triplets T_{1u} and T_{2u}; their Z-components can be written using projection operator methods [15] as

$$|T_{1z}\rangle = \frac{N_{T_1}}{\sqrt{2}}[\chi_{zx+}(|Z_1\rangle + |X_1\rangle) + \chi_{zx-}(|Z_1\rangle - |X_1\rangle) + \chi_{yz+}(|Y_1\rangle + |Z_1\rangle) - \chi_{yz-}(|Y_1\rangle - |Z_1\rangle)] \tag{15}$$

$$|T_{2z}\rangle = \frac{N_{T_2}}{\sqrt{2}}[\chi_{zx+}(|Z_1\rangle + |X_1\rangle) + \chi_{zx-}(|Z_1\rangle - |X_1\rangle) - \chi_{yz+}(|Y_1\rangle + |Z_1\rangle) + \chi_{yz-}(|Y_1\rangle - |Z_1\rangle)]. \tag{16}$$

x- and y-components of T_{1u} and T_{2u} are obtained from $|T_{1z}\rangle$ and $|T_{2z}\rangle$ by cyclic permutations of X, Y and Z.

$$\chi_{xy\pm} = \exp\left[\frac{K_{1\epsilon}}{2\sqrt{2}\omega_\epsilon}(a_\theta^+ - a_\theta) \mp \frac{f_o}{\sqrt{2}}(a_\zeta^+ - a_\zeta)\right]|0\rangle$$

$$\chi_{yz\pm} = \exp\left[-\frac{K_{1\epsilon}}{4\sqrt{2}\omega_\epsilon}(a_\theta^+ - a_\theta) + \frac{\sqrt{3}K_{1\epsilon}}{4\sqrt{2}\omega_\epsilon}(a_\epsilon^+ - a_\epsilon) \mp \frac{f_o}{2}(a_\xi^+ - a_\xi)\right]|0\rangle \tag{17}$$

$$\chi_{yz\pm} = \exp\left[-\frac{K_{1\epsilon}}{4\sqrt{2}\omega_\epsilon}(a_\theta^+ - a_\theta) - \frac{3K_{1\epsilon}}{4\sqrt{2}}(a_\epsilon^+ - a_\epsilon) \mp \frac{f_o}{\sqrt{2}}(a_\eta^+ - a_\eta)\right]|0\rangle.$$

Here

$$f_o = \frac{\sqrt{3}K_{1\tau}}{2\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}} \tag{18}$$

and $|0\rangle = |0_\theta, 0_\epsilon, 0_\xi, 0_\eta, 0_\zeta\rangle$ is the zero-phonon state,

$$N_{T_1} = \frac{1}{2\sqrt{1+S_o}} \qquad N_{T_2} = \frac{1}{2\sqrt{1-S_o}} \tag{19}$$

$$S_o = \langle \chi_{xy\pm}|\chi_{yz\pm}\rangle = \langle \chi_{xy\pm}|\chi_{yz\mp}\rangle = \exp\left[-\frac{3K_{1\epsilon}^2}{16\omega_\epsilon^2} - \frac{1}{2}\left(\frac{3K_{1\tau}}{2\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}}\right)^2\right]. \tag{20}$$

Another overlap integral S_o' is defined as

$$S_o' = \langle \chi_{xy\pm}|\chi_{xy\mp}\rangle = \exp\left[-\left(\frac{3K_{1\tau}}{2\omega_\tau} + \frac{2|K'|f}{\sqrt{3}K_{1\tau}}\right)^2\right]. \tag{21}$$

The energy separation between the two triplets calculated using the method of Dunn and Bates [15] is given by

$$E_{T_2} - E_{T_1} = \frac{3S_oK_{1\epsilon}^2}{8(1-S_o^2)\omega_\epsilon}. \tag{22}$$

Obviously the vibronic level T_{1u} lies lowest. The expression for the Ham reduction factor in this case is given by

$$\kappa_o = \frac{3S_o + S_o'}{2(1+S_o)}. \tag{23}$$

It is found from (20), (21) and (23) that for a suitable choice of values of S_o and S_o' the values of κ_o and $E_{JT} \approx [(K_{1\epsilon}^2/8\omega_\epsilon) + (3K_{1\tau}^2/8\omega_\tau)]$ are nearly equal to the corresponding values for the trigonal type of ground state. For $S_o = 0.037$ and $S_o' = 0.026$ these values are $\kappa_o = 0.066$ and $E_{JT} = 2.84\omega$, assuming $\omega_\epsilon \approx \omega_\tau = \omega$. This implies that there is a possibility of coexistence of two types of site, one having a trigonal type of ground state and the other of orthorhombic type. The two will provide identical broad ESR signals but the sharp line in the spectra originates only from sites with trigonal type ground state.

4. Discussion

The ground state of the $(T_{1u} \otimes h_g)$ Jahn–Teller problem of C_{60}^- in icosahedral symmetry lies on a continuous spherical equal-energy surface [20, 21]. In previous studies [22–24] the quadratic and bilinear couplings are used to stabilize the pentagonal D_{5d} and trigonal D_{3d} types of energy minimum. In the present paper, however, the stabilization of the trigonal type of ground state in icosahedral symmetry is the result of vibronic mixing with the T_{1g} level. In cubic symmetry, where a C_{60}^- ion is under the influence of surrounding alkali ion ligands, the analysis of $(T_u - T_{1g}) \otimes (\tau_{2g} + \epsilon_g + \tau_{1u})$ vibronic interaction has shown that there is a possibility of coexistence of both trigonal type and orthorhombic type of ground state. Both the trigonal and orthorhombic types of ground state contribute to the broad line in ESR spectra but the sharp line originates only from sites with the trigonal type of ground state. In $KC_{60}(THF)_x$ with $0 < x < 1$ the C_{60}^- ions fall into two categories [1]: (i) the C_{60}^- in icosahedral symmetry since they are less affected by the surrounding K^+ ions, (ii) those which are strongly perturbed by K^+ ions so that their surrounding symmetry is cubic. In $KC_{60}(THF)$ all the K^+ ligands of the C_{60}^- ion are equally solvated by THF and hence the symmetry is again cubic. Thus the sites with the trigonal type of ground state are more numerous in $KC_{60}(THF)_x$ $(0 < x < 1)$ samples than in $KC_{60}(THF)$. This explains the experimental observation of Chen *et al* [1] that the sharp line is more pronounced in $KC_{60}(THF)_x$ $(0 < x < 1)$ samples than in $KC_{60}(THF)$.

Since the symmetry of the immediate surroundings of C_{60}^- in solution is expected to be the same as in solids, the broad and sharp components are expected to be observed in ESR spectra of C_{60}^- in solution also. Stasko *et al* [25] observed these components in photochemically and electrochemically reduced fullerene anions in aqeous solutions. Bennati *et al* [26] have studied the pulsed EPR of the photoexcited state of C_{60}^- in fluid solution. Apart from the signal due to the triplet state, they have also observed a signal near $g \approx 2$ from C_{60}^- generated via electron transfer from EC4T to $^3C_{60}$. This line can be identified with the broad component of the signal observed by Stasko *et al* [25] since both have the same line width. Nonobservation of the narrow component of C_{60}^- in the experiment of Bennati *et al* [26] suggests that in this system the separation of the excited vibronic singlet A_{2u} is beyond the temperature range of observation. Hwang *et al* [27], on the basis of their observation that on exposure to molecular oxygen the broad band signal diminishes and a narrow signal grows, have concluded that the spike commonly observed in C_{60}^- is most probably due to the oxygenation of the C_{60}^- radical. A change from an orbital triplet to a singlet ground level, resulting from a static distortion of C_{60}^- radical due to oxygenation, will definitely replace the broad signal with a narrow one, but the problem in the ESR behaviour of the C_{60}^- radical is that of coexistence of the narrow spike along with the broad signal and hence the conclusion of Hwang *et al* [27] does not hold.

A major approximation involved in the present work is the consideration of only one mode for each vibrational symmetry instead of the actual eight τ_{2g}, eight ϵ_g and four τ_{1u} modes. Also an actual evaluation of T_{1u}–T_{1g} mixing has not been possible. The conclusions arrived at in section 2 about the nature of the ground state are mainly symmetry based. The proposition in section 3 about a strong JT interaction is invoked to bring the vibronic A_{2u} within the temperature range of ESR experiments, and the low value of Ham reduction factor follows directly from this proposition. The actual values of E_{JT} and κ_τ (κ_o) may probably change but the basic results, concerning the nature of the ground level and the low value of the Ham reduction factor etc, should remain valid even in a more realistic multimode treatment.

Acknowledgments

The author is thankful to the referees of the journal for helpful suggestions. Encouragement by the Director of the National Physical Laboratory is also gratefully acknowledged.

References

[1] Chen J, Shao Q-F, Huang Z-E, Cai R-F and Chen S-M 1995 *Chem. Phys. Lett.* **235** 570
[2] Stinchcombe J, Penicaud A, Bhyrappa P, Boyd P D W and Reed C A 1993 *J. Am. Chem. Soc.* **115** 5212
[3] Dubois D, Jones M T and Kadish K M 1992 *J. Am. Chem. Soc.* **114** 6446
[4] Greaney M A and Gorun S M 1991 *J. Phys. Chem.* **95** 7142
[5] Zhou O and Cox D E 1992 *J. Phys. Chem. Solids* **53** 1373
[6] Poirier D M, Ohno T R, Kroll G H, Benning P J, Stepniak F, Weaver J H, Chibante L P F and Smalley R E 1993 *Phys. Rev.* B **47** 9870
[7] Zhu Q, Zhou O, Fischer J E, McGhie A R, Romanow W J, Strongin R M, Chichy M A and Smith A B III 1993 *Phys. Rev.* B **47** 13 948
[8] Winter J and Kuzmany H 1992 *Solid State Commun.* **84** 935
[9] Rai R 1996 *Z. Phys.* B **99** 327
[10] This error was pointed out by one of the referees of this paper. The correction requires the modification of the transformation matrix S and a minor approximation in the definition of g_i ($i = \xi, \eta, \zeta$). The rest of the calculations, results and conclusions of [9] remain unaltered
[11] Bates C A, Dunn J L and Sigmund E 1987 *J. Phys. C: Solid State Phys.* **20** 1965

[12] Opik U and Pryce M H L 1957 *Proc. R. Soc.* A **238** 425
[13] Rice M J and Choi H-Y 1992 *Phys. Rev.* B **45** 10 173
[14] Pichler T, Winkler R and Kuzmany H 1994 *Phys. Rev.* B **49** 15 879
[15] Dunn J L and Bates C A 1989 *J. Phys.: Condens. Matter* **1** 375. Our coupling parameters K_τ and K_ϵ are equal to $\sqrt{\frac{8}{3}}K_T$ and $\sqrt{8}K_E$ respectively of this paper.
[16] Tosatti E, Manini N and Gunnarsson O 1996 *Phys. Rev.* B **54** 17 184
[17] Troullier N and Martins J L 1992 *Phys. Rev.* B **46** 1754
[18] Abragam A and Pryce M H L 1951 *Proc. R. Soc.* A **205** 135
[19] Gunnarson O, Handschuch H, Bechthold P S, Gantefor G and Eberhardt W 1995 *Phys. Rev. Lett.* **74** 1875
[20] Auerback A, Manini N and Tosatti E 1994 *Phys. Rev.* B **49** 12 998
[21] O'Brien M C M 1996 *Phys. Rev.* B **53** 3775
[22] Ceulemans A and Vanquickenborne L G 1989 *Struct. Bonding* **71** 125
[23] Dunn J L and Bates C A 1995 *Phys. Rev.* B **52** 5996
[24] Liu Y M, Dunn J L, Bates C A and Polinger V Z 1997 *J. Phys.: Condens. Matter* **9** 7119
[25] Stasko A, Brezora V, Rapta P, Asmus K-D and Guldi D M 1996 *Chem. Phys.* **262** 233
[26] Bennati M, Group A, Banerle P and Mchring M 1994 *Chem. Phys.* **185** 221
[27] Hwang L Y, Yang C C and Hwang K C 1997 *J. Phys. Chem.* A **101** 7971