Vibronic interactions in the visible and near-infrared spectra of C_{60}^{-} anions

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Electron-phonon coupling is an important factor in understanding many properties of the C_{60} fullerides. However, there has been little success in quantifying the strength of the vibronic coupling in C_{60} ions, with considerable disagreement between experimental and theoretical results. We will show that neglect of quadratic coupling in previous models for C_{60}^{-} ions results in a significant overestimate of the linear coupling constants. Including quadratic coupling allows a coherent interpretation to be made of earlier experimental and theoretical results which at first sight are incompatible.

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I. INTRODUCTION

Doped fullerides are of continuing interest to both experimentalists and theoreticians alike, partly because of the ability of some fullerides containing C_{60}^{3-} ions to exhibit superconductivity.[1] The mechanism underlying this ability is still not fully understood, although electron-phonon coupling is thought to be of great relevance. Understanding and quantifying the vibronic coupling in fullerene ions is therefore of paramount importance. Unfortunately, there has been little success in quantifying the vibronic coupling even in the singly charged C_{60}^{-} ion,[2] with experimental results disagreeing with theoretical calculations.[3]

In this paper, we present a theoretical explanation of vibronic coupling in C_{60}^{-} along with experimental results. By incorporating the effects of quadratic coupling, we are able to show how the disparity between theoretical and experimental estimates of the coupling constants may be explained. In particular, we make an analysis of the vibronic detail associated with the $T_{1g} \leftarrow T_{1u}$ transition in C_{60}^{-}, in which both electronic states are subject to a $T_1 \otimes h$ Jahn-Teller (JT) effect. This yields information on the coupling constants in the excited state where values were previously unknown.

There are a number of different spectra from C_{60}^{-} ions in the literature (see, for example Ref. 4, and references therein). Of particular note is a recent gas phase spectrum obtained using C_{60}^{-} ions in a storage ring.[5] The authors of this work interpreted their data using a dynamic JT model based on C_{60}^{-} ions subject to a D_{3d} distortion. It is well known that such JT distortions can only be justified if nonlinear effects are included.[6] This is recognized in Ref. 5, where qualitative discussions of the effects of higher-order couplings are given. However, no numerical estimates are made of these higher-order couplings. Our purpose here is to present an interpretation of the spectra using a dynamic JT model which explicitly includes quadratic coupling in a rigorous and quantitative manner.

II. EXPERIMENT

In order to further explore the electron-phonon coupling in C_{60}^{-} ions, we have recorded our own spectrum at room temperature using electrochemically generated C_{60}^{-} ions in solution. A mixed-polarity solvent is required to simultaneously dissolve C_{60} and the supporting electrolyte (tetrabutylammonium hexafluorophosphate), and to stabilize good yields of the anion. Thus, the solvent used was a 5.4:1 mixture of toluene:acetonitrile which has been used to good effect in previous electrochemical work involving C_{60}.[7] All electrochemistry was performed under an inert N_2 atmosphere using a purpose-built three-electrode spectroelectrochemical cell consisting of a Pt gauze working electrode, Pt wire counter electrode, and Ag/AgCl reference. Cyclic voltammetry was used to establish the required potential for coulometry to ensure virtually complete conversion of C_{60} to C_{60}^{-}.

An Ocean Optics HR2000 spectrometer was subsequently used to record the visible and near infrared spectrum over the range $9000-30\,000$ cm^{-1}. The portion of this spectrum which contains the vibronic transitions of interest is shown in Fig. 1. Ignoring solvent effects, the spectrum is a good match to the previous spectra. It is particularly relevant to note that the peaks in the gas phase spectrum are not much narrower than those in Fig. 1. This suggests that much of the linewidth could be intrinsic to the ions themselves rather than their
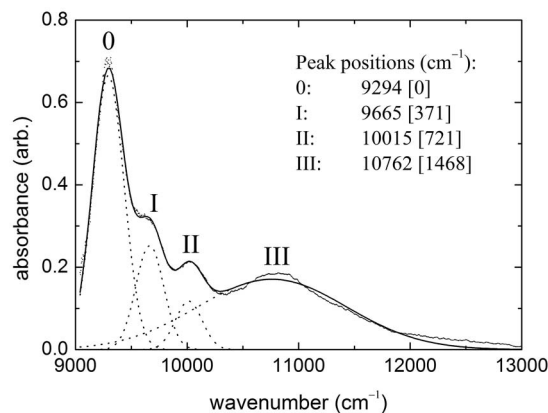

FIG. 1. Electronic spectrum of C_{60}^{-} ions in solution. The data has been fitted to four Gaussians labeled 0-III (dotted lines), giving a very good overall fit (solid line).

environment. However, as pointed out by one of the referees of the present paper, the data in Ref. 5 is produced using a multiphoton absorption technique which may make the peaks much wider than expected for a gas-phase experiment.

For C_{60}^-, the difference in energy between the T_{1u} ground-state molecular orbital (MO) and T_{1g} excited state MO has been calculated to be 1.12 eV using density functional theory.[8] The strongest peak in our near infrared (NIR) spectrum (Fig. 1) at 1.15 eV (9294 cm^{-1}) closely matches this energy difference and so we ascribe these transitions to the $T_{1g} \leftarrow T_{1u}$ electronic transition in C_{60}^-. This assignment does indeed seem to be generally accepted in the literature.[4,5,9] The $^2T_{1u}$ electronic ground state of C_{60}^-, as is well known, is subject to a multimode $T_{1u} \otimes h_g$ JT effect involving vibronic coupling to 8 h_g modes. In a similar vein, the excited state involved in the transitions of interest, $^2T_{1g}$, will be subject to a multimode $T_{1g} \otimes h_g$ JT effect. The spectrum resulting from the vibronic transitions $T_{1g} \leftarrow T_{1u}$ may, therefore, be expected to be reasonably complex. However, the spectrum shown in Fig. 1 reveals four bands, but no detail that can be attributed to separate modes. It is unlikely that this is due to interactions present in solution leading to broadening of the spectral lines because, as noted above, the corresponding gas phase spectrum[5] does not exhibit significantly narrower lines. It is more likely that only one or two modes dominate the spectrum. In order to investigate this possibility, we shall attempt to explain the vibronic transitions using an effective- or single-mode JT model.

III. THEORETICAL DISCUSSION

The single-mode $T_{1u} \otimes h_g$ JT model has been well studied.[6,10,11] If only linear coupling terms are considered then a spherical shell of minimal points in the adiabatic potential energy surface (APES) is obtained. However, nonlinear terms warp the APES producing discrete minima with either D_{5d} or D_{3d} symmetry.[10] Therefore, if the coupling is strong, a static JT effect could produce C_{60}^- ions having either of these symmetries. In reality, warping of the APES is not expected to be great and so migration between equivalent minima should proceed fairly rapidly. This dynamic effect is accounted for by taking linear combinations of the minima to produce vibronic states having the correct symmetry expected of eigenstates of the system Hamiltonian.[10] Thus, the six equivalent D_{5d} potential minima may be combined to produce states having T_{1u} and T_{2u} symmetry, whereas the ten equivalent D_{3d} minima produce T_{1u}, T_{2u}, and G_u states, as shown in Fig. 2, where the relative energies of these states are indicated. Note that the relative energies in the ground state of this figure are labeled Δ_1 and Δ_3 to coincide with notation used in an earlier work.[12]

The excited states in Fig. 2 involve $T_{1g} \otimes h_g$ coupling and the possible vibronic states here are T_{1g}, T_{2g}, G_g, and H_g. If these states also arise from D_{3d} distorted wells then the expected pattern of excited vibronic states is as shown in Fig. 2. Provided the quadratic terms are small, a D_{3d} distortion should produce ions of lower energy compared to those undergoing D_{5d} distortion.[10] Therefore, it is interesting to see that four vibronic transitions are expected to occur if D_{3d}
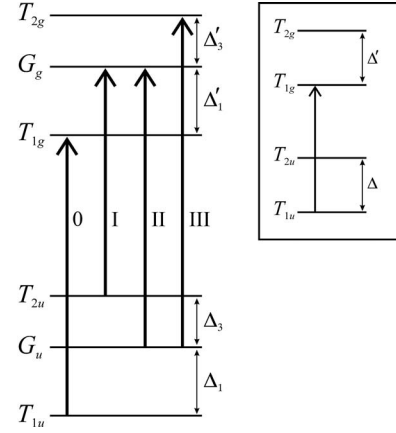

FIG. 2. Allowed vibronic transitions associated with the electronic transition $T_{1g} \leftarrow T_{1u}$ for D_{3d} distorted C_{60}^- ions. The transitions shown correspond to the peaks observed in the NIR spectrum (Fig. 1). The inset shows the comparable picture if transitions were to occur between D_{5d} distorted C_{60}^- ions.

distortion occurs in both the ground and excited states of C_{60}^- (Fig. 2). If D_{5d} distortion were to occur in both states, or if a "mixed" (one state D_{5d} and the other D_{3d}) picture are invoked, then fewer transitions would be expected. Subsequently, we shall attempt to fit the observed NIR spectrum to the D_{3d} distorted picture shown in Fig. 2.

We see that there are more variables to determine than available data. We define an energy ratio $q = \Delta_1 / \Delta_3$ which implies that[10,12]

$$q = \frac{\Delta_1}{\Delta_3} = \frac{(3 - 2S)(X + 2SY)}{(3 + 2S)(X - 2SY)}, \tag{1}$$

where

$$S = \exp\left[-12\left(\frac{V_1}{3\sqrt{10} - 8V_3} \right)^2 \right] \tag{2}$$

is the phonon overlap between adjacent D_{3d} wells, V_1 is the dimensionless linear coupling constant, and[12]

$$X = 10 + \sqrt{2}V_2 - \sqrt{10}V_3,$$

$$Y = 5 + 2\sqrt{2}V_2 - \sqrt{10}V_3 \tag{3}$$

are numerical factors that depend on the dimensionless quadratic coupling constants V_2 and V_3. In terms, of these dimensionless coupling parameters, the energy of the local D_{3d} minima are given by[10]

$$E_{D_{3d}} = -\frac{3V_1^2 \hbar \omega}{15 - 4\sqrt{10}V_3} \tag{4}$$

and the energy of the D_{2h} saddle points in the APES which form the barriers between wells is given by[10]

$$E_{D_{2h}} = -\frac{V_1^2 \hbar \omega}{40}\left(\frac{40 + 5\sqrt{2}V_2 + 9\sqrt{10}V_3}{5 - V_2^2 - 3V_3^2} \right). \tag{5}$$

These expressions give some indication of the effect of the quadratic coupling constants on the warping of the potential

energy surface and, in particular, on the barrier between minima $E_{D_{2h}} - E_{D_{3d}}$. The rate at which tunneling through this barrier occurs clearly depends on the vibronic coupling constants. A method of calculation of this rate for the C_{60}^- ion has been developed,[12] which further highlights the importance of the quadratic coupling constants in determining the dynamics of this system.

If a D_{3d} distortion is to be preferred, the quadratic coupling constants must be nonzero. However, their values are likely to be small (compared to the linear constant) and so, as an initial approximation, we assume that their values are sufficiently small that in Eq. (3), $X \approx 10$ and $Y \approx 5$ so that the ratio q then depends only on the phonon overlap for which $S \approx \exp(-2V_1^2/15)$. This indicates that the value of q is an implicit measure of the strength of the linear vibronic constant, and hence distortion, experienced by the C_{60}^- anion in its ground state.

Fitting the data to the allowed transitions requires that the transitions shown in Fig. 2 correspond to the band labels used in Fig. 1, and that

$$\Delta_3 = E_{II} - E_{I},$$

$$\Delta_3' = E_{III} - E_{II},$$

$$q' = \frac{(1+q)E_{II} - qE_{I}}{E_{III} - E_{II}}, \tag{6}$$

where E_i is the energy of band i relative to the main peak and $q' = \Delta_1'/\Delta_3'$ is the corresponding energy ratio for the excited state. Using the energies shown in Fig. 1, this results in $\Delta_3 = 350$ cm^{-1}, $\Delta_3' = 747$ cm^{-1}, and

$$747q' = 721 + 350q. \tag{7}$$

In order to proceed, we make the initial approximation that the energy ratio for the excited state should be similar to that for the ground state, and so we set $q' = q$. Later, we shall relax this assumption also. This immediately implies that $q' = q \approx 1.816$. From this, the phonon overlap is found to be $S = 0.635$, which corresponds to a linear coupling constant of $V_1 = 1.84$. From Ref. 12, we can derive the expression

$$\hbar\omega = \frac{-(1+S)(3-2S)\Delta_3}{5S \ln S} \tag{8}$$

for the frequency of the vibration involved, giving $\hbar\omega = 687.0$ cm^{-1} and $\hbar\omega' = 1466$ cm^{-1}, where the primed quantity again refers to the excited state. These frequencies could be considered to be effective mode frequencies in this single-mode interpretation and it is quite reassuring that they should fall within range of the known frequencies of the h_g modes of neutral C_{60}.

The picture of the C_{60}^- anion emerging from this analysis can be summarized as consisting of a D_{3d} distorted ground state with the distortion resulting from a normal mode of effective frequency 687.0 cm^{-1} and a D_{3d} distorted excited state distorted by an effective mode with frequency 1466 cm^{-1}. At this level of approximation in our analysis, both modes have an effective dimensionless linear coupling constant of $V_1 = 1.84$. The model further implies that the JT

energies $E_{JT} = \frac{1}{5}V_1^2\hbar\omega$ are 467.3 cm^{-1} (57.94 meV) and 997.4 cm^{-1} (123.7 meV) in the ground and excited states, respectively.

To date, the only experimental work that has attempted to quantify the vibronic coupling in the ground state of C_{60}^- is a photoemission spectroscopy (PES) study of the ions in a supersonic He expansion.[2] To our knowledge, no similar experiment has been attempted on the excited state of interest. One of the guiding principles of PES of JT active molecules[13] is that if the change in the shape of the molecule is small on excitation, then the relative intensity of the line showing excitation of one quantum of the active vibration compared to the intensity of the 0-0 transition should be equal to $E_{JT}/\hbar\omega$. Weak vibronic coupling therefore leads to weak vibronic peaks in the photoemission spectrum. In the PES data,[2] the vibronic side bands are relatively strong and, provided the vibronic detail observed in the PES data can be attributed to the C_{60}^- ion, this indicates a relatively strong JT effect. In the PES spectrum,[2] the first side-band has roughly 2/3 of the intensity of the main peak, which would imply that $E_{JT} \approx \frac{2}{3}\hbar\omega$. In the present model, the JT energy is given by $E_{JT} = \frac{1}{5}V_1^2\hbar\omega$, which is consistent with the PES data if $V_1 = 1.83$. This is in excellent agreement with the value derived above via the NIR data ($V_1 = 1.84$).

In Ref. 2, vibronic coupling parameters are derived for the normal modes $h_g(k)$ using a more rigorous fitting procedure and reported in terms of the superconductivity parameters $\lambda_k/N(0)$, where $N(0)$ is the density of states at the Fermi level and k is a mode label. For all the h_g modes combined it was found that $\Sigma_k\lambda_k/N(0) = 147$ meV. According to Lannoo et al.,[14,15] this will result in a JT energy of $E_{JT} = \frac{3}{5}\Sigma_k\lambda_k/N(0) = 88.2$ meV. This is somewhat larger than our current estimate (57.9 meV) and corresponds to $V_1 = 2.44$. However, it is likely that in fitting their PES data the authors attributed signal intensity to the h_g modes that should be assigned to other modes or other processes[16] and, therefore, overestimates the vibronic coupling.

Numerical calculations seem to result in lower estimates for the vibronic coupling compared to those derived from PES data, for reasons that are currently unknown. For example, recent DFT calculations[3] suggest that the total JT energy derived from the $8h_g$ modes is $E_{JT} = 38.2$ meV. This is about 1.5 times smaller than our estimate and, in terms of our parameters, requires $V_1 = 1.17$.

We now turn to consideration of the effective mode frequencies driving the coupling in the ground and excited states. The different h_g modes are identical symmetrywise but differ in their nuclear motion and so examination of these motions is in order.

It is interesting to see that the effective mode frequency derived for the ground state 687 cm^{-1} lies very close to that of the $h_g(3)$ mode at[17] 711 cm^{-1}. This mode is found to have the greatest degree of radial character of all the h_g modes.[18] Conversely, the effective mode for the excited state 1466 cm^{-1} lies closest to $h_g(7)$, which has the smallest calculated radial character.[18] In earlier work,[19] the authors speculated that the vibronic coupling in the (ground state) C_{60}^- anion might be expected to be strongest in the radial modes of vibration as these modes are expected, on the basis

of simple geometrical arguments, to interact with the electronic T_{1u} orbitals most strongly. In the I_h point group, the T_{1u} irreducible representation transforms as (x, y, z) and so radial translations should successfully couple to such orbitals. On the other hand, tangential modes correspond to rotation of the nuclei with respect to the molecular center. Therefore, it is reasonable that these modes should couple preferentially to orbitals with T_{1g} symmetry which transform as the rotations (R_x, R_y, R_z).

The foregoing analysis has employed several approximations. However, if we use the PES estimate for the effective coupling constant in the ground state, $V_1 = 2.44$, we can relax our initial assumption that $q = q'$ and derive a value for the excited state coupling constant V_1'. In order to fit the data in Fig. 1 this requires $V_1' = 2.04$. If this interpretation of the data is correct, then we have managed to find an (empirical) estimate for the linear coupling parameter for the excited state of the C_{60}^- ion.

We can also explore what happens if we do not assume that $V_2 \approx V_3 \approx 0$. Using the symmetry arguments above, we assume that the coupling is dominated by the modes $h_g(3)$ and $h_g(7)$ to such an extent that $\hbar\omega = 711$ cm^{-1} and $\hbar\omega' = 1427$ cm^{-1}. Let us also suppose that the coupling parameters are the same in both states $V_i' = V_i$. For this to be true, the quotient $\Delta_3/\hbar\omega = 0.492$ for the ground state should be equal to that in the excited state, $(\Delta_3/\hbar\omega)' = 0.523$. This is quite reasonable agreement considering the assumptions made. The limited amount of data available means that our fit is still underdetermined. However, for a given phonon overlap we can find the coupling constants required to fit the data in Fig. 1. This results in the variation shown in Fig. 3. Our fit is based on D_{3d} distorted ions, which restricts us to the zone where[10] $3V_2 < \sqrt{5}V_3$, corresponding to $S > 0.635$.

Figure 3 shows that a fit to the data is possible involving significantly smaller values of the linear coupling constant provided the quadratic constants are sufficiently negative. In fact, $V_1 \sim 1$ towards the right of Fig. 3. Thus, we have an explanation for the discrepancy between theoretical and experimental estimates of the linear constants alluded to earlier. Theoretical calculations that ignore quadratic contributions and single out the linear part might well be expected to give good values for the linear constant (e.g., $V_1 \sim 1.17$ from Ref. 3). However, fitting experimental data, which necessarily in-
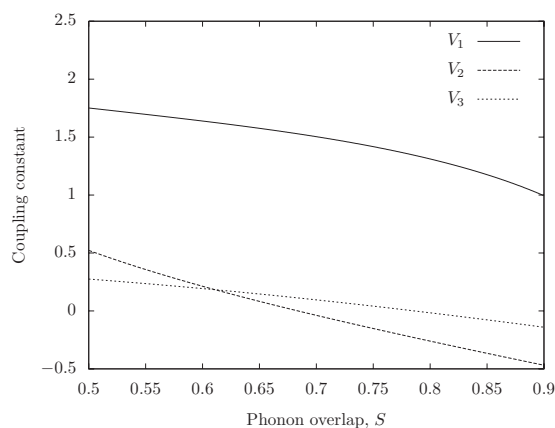

FIG. 3. Effective dimensionless linear (V_1) and quadratic (V_2, V_3) vibronic coupling constants consistent with the data and assignment shown in Figs. 1 and 2 for varying phonon overlap S. Ions with D_{3d} symmetry occur when $S > 0.635$.

cludes effects due to quadratic and higher order terms, using models which ignore such terms could lead to a significant overestimation of V_1.

Finally, there is one other aspect of the NIR data that warrants mention, namely, the breadth of the peaks observed which, as already intimated, appears to be intrinsic to the ion. The states indicated in Fig. 2 are appropriate to a time-averaged picture giving overall I_h symmetry, such as an ensemble of ions in solution. However, individual ions will be pseudorotating dynamically between equivalent potential wells but will not generally be icosahedral. Therefore, the symmetry-adapted states shown in Fig. 2 are not stationary states and will have a finite width which will depend on the coupling constants. Hence, some of the width of the lines should be due to pseudorotation. If this is the case, a detailed study of linewidths could yield valuable information about the quadratic coupling constants.

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