Low lying excitations of the Dynamical Jahn-Teller 
ions $C_{60}^-$ and $C_{60}^{2-}$

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Abstract

We compute the vibronic spectrum of gas phase fullerene negative ions $C_{60}^-$ and $C_{60}^{2-}$. We treat accurately the linear dynamical Jahn-Teller of these ions in their ground state. In particular, coupling of the $t_{1u}$ orbital to the eight $H_g$ vibrational modes is handled by exact diagonalizations including up to six vibrons. The resulting spectrum is characterized by large splittings, which should be readily observable spectroscopically. The lowest excitation symmetry is argued to be related to the Berry phase present in this problem.
I. INTRODUCTION

Due to the partial filling of the degenerate $t_{1u}$ orbital, the fullerene anions $C_{60}^-$ are Jahn-Teller (JT) distorted [1–4]. We have recently argued that dynamical JT phenomena must be of relevance in the ground state, at least for the gas-phase isolated negative ions. Realistic values for the coupling between the $t_{1u}$ electronic orbital (which is derived from a molecular $L=5$ state, but can be treated effectively as an $L=1$ state) and the $H_g$ vibrations (quadrupolar, $L=2$) have been estimated in literature [1–8].

The electron-vibron coupled problem in $C_{60}$ ions is affected by a Berry phase [5,6,9], which is intriguing and interesting per se. We have shown [5,6] that the presence of a Berry phase implies a number of signatures:

1. a $T_{1u}$ ($L=1$) ground state for $C_{60}^-$ with odd $n$, and with even $n$ and high spin ($S=1$), against an $A_g$ ($L=0$) ground state for even $n$ and $S=0$;

2. impossibility of s-wave electron attachment to $C_{60}$ [10,11] due to non-existence of $A_g$ states in the excitation spectrum of $C_{60}^-;

3. large and characteristic splittings in the excitation spectrum of vibronic states derived from the JT active $H_g$ modes. For $^2C_{60}^-$ (and $^3C_{60}^-$, whose JT energy shift and excitation spectrum is identical, due to electron-hole symmetry) the lowest excitation is a $T_{2u} + G_u$ nearly degenerate multiplet ($L=3$ in spherical symmetry). This is a remnant of the ortho-hydrogen-like series $L=1,3,5,...$ predicted by the Berry phase in the semiclassical limit [4]. For $^1C_{60}^-$, conversely, the lowest excitation above the $L=0$ ground state should be $H_g$ ($L=2$ in spherical symmetry), which in turn is the remnant of the para-hydrogen-like series $L=0,2,4,...$, predicted semiclassically.

Of the above, points 1 and 2 are well-established, but very little [12,13] is known about the negative ion vibronic excitations of point 3. The scope of this paper is to make quantitative predictions on the low-lying excitation spectrum of $^2C_{60}^-$, $^3C_{60}^-$ and $^1C_{60}^-$, which could enable a future precise assessment of the coupling constant values, and of the Berry phase effect on the dynamics of these interesting molecular ions. Both the $C_{60}^-$ [12] and $C_{60}^{2-}$ [4] ions have been shown to exist in gas phase and vibronic spectroscopy should be feasible in the near future. For $C_{60}^{2-}$ one would also obtain in this way a clear indication of whether the ground state is $S=1$ or $S=0$, since the spectra are very different in the two cases.
II. CALCULATIONS

In $C_{60}^-$, $n$ electron in the $t_{1u}$ state are JT-coupled to the $H_g$ molecular vibrations. Due to extreme stiffness and harmonicity of the $C_{60}$ cage, linear coupling provides an accurate description of this JT problem for $n = 1$ and $n = 2$ ($S = 1$), and a less accurate but still qualitatively correct description for $n = 2$ ($S = 0$) [6]. The Hamiltonian describing the coupling to the eight (fivefold degenerate) $H_g$ modes is [15,2,6]

$$H = \sum_{k=1}^{8} H_k^0 + H_k^{e-v}$$

$$H_k^0 = \frac{\hbar \omega_k}{2} \sum_{\mu} \left( p_{k,\mu}^2 + Q_{k,\mu}^2 \right) I$$

$$H_k^{e-v} = g_k \frac{\sqrt{3}}{2} \hbar \omega_k \sum_{\sigma}$$

$$(c_{x\sigma}^\dagger, c_{y\sigma}^\dagger, c_{z\sigma}^\dagger) \begin{pmatrix} \frac{1}{\sqrt{3}} Q_0 + Q_2 & -Q_2 & -Q_1 \\ -Q_2 & \frac{1}{\sqrt{3}} Q_0 - Q_2 & -Q_1 \\ -Q_1 & -Q_1 & -\frac{2}{3} Q_0 \end{pmatrix} \begin{pmatrix} c_{x\sigma} \\ c_{y\sigma} \\ c_{z\sigma} \end{pmatrix} + \ldots \quad (1)$$

where $Q_{k,\mu}$ is the normal co-ordinate of mode $k$, of spherical component $\mu$, $p_{k,\mu}$ is its canonical conjugate momentum operator, and $c_{\alpha\sigma}^\dagger$ are fermion operators creating an electron in orbital $\alpha$ with spin $\sigma$. This Hamiltonian is derived on the basis on the icosahedral symmetry of the buckyball. The icosahedral group $I_h$ is a subgroup of the full rotation group in three dimensions $O(3)$: when reducing the symmetry from $O(3)$ to $I_h$, the representations $D^{(0+)}$, $D^{(1-)}$ and $D^{(2+)}$ go into $a_g$, $t_{1u}$ and $h_g$ respectively, unsplit. The Clebsch-Gordan coefficients for these representations of the two groups are thus the same [16]. As Hamiltonian [6] is restricted to $t_{1u}$ and $H_g$ states, it has actually full spherical symmetry: the Hamiltonian for a $L = 1$ “superatomic” electronic state interacting with the normal vibrations of a concentric elastic sphere looks exactly the same. Linear JT coupling hides a higher-than-icosahedral symmetry, and yields states with degeneracies characteristic of the spherical group. Higher order terms (indicated with dots in Eq. [6] we neglect them in the present treatment) would split these degeneracies into the appropriate $I_h$ representations. For this reason, we use a hybrid notation, and label states with icosahedral or spherical representations, according to convenience.

The unperturbed frequencies $\omega_k$ of the eight $H_g$ modes of neutral C$_{60}$ are experimentally well-known (see Table I). $A_g$ modes do not split the $t_{1u}$ level, and are not included in this calculation. Shifts of these $H_g$ frequencies from the neutral molecule are not expected to be large, and will be neglected here. If needed, corrections can be
made using, e.g., the shifted frequencies calculated in solid state $A_nC_{60}$ by Andreoni and collaborators \[17\]. The dimensionless JT coupling parameters $g_k$ are more uncertain. Here we shall adopt the recent values empirically extracted by Gunnarsson \[8\] by fitting photoemission spectra of $C_{60}$ in gas phase.

In an earlier work \[5,6\], we diagonalized Hamiltonian (1) both approximately, using perturbation theory (where all modes can be superposed linearly), and numerically, including however a single vibrational mode. Subsequently Gunnarsson calculated the ground state energy accurately, including all modes \[8\].

Here, aiming at gas phase spectroscopy, we shall diagonalize (1) accurately, including all modes, and we shall obtain in addition the lowest excitation spectrum as well, for $n=1$ and 2 electrons.

The vibron operators $Q_{k,\mu}$, $P_{k,\mu}$ in Hamiltonian (1) are conveniently rewritten in terms of standard boson operators $b_{k,\mu}$. A generic vibronic state is expanded as

$$
\Psi = \sum \epsilon_{k_1\mu_1,\ldots,k_N\mu_N,\alpha_1\sigma_1,\ldots,\alpha_n\sigma_n} b_{k_1\mu_1}^\dagger \cdots b_{k_N\mu_N}^\dagger c_{\alpha_1\sigma_1}^\dagger \cdots c_{\alpha_n\sigma_n}^\dagger |0> \tag{2}
$$

where $|0>$ is the state with no vibrons and no electrons. The sum in Eq. 2 extends to states with any number of vibrons, but a linear e-v coupling implies decay as $\exp(-N)$ of components with $N$-vibron states, for large enough $N$. For this reason, a truncated basis set including all states up to $N$ vibrons gives a variational estimate of the lowest eigenvalues, with hopefully good convergence with increasing $N$.

It is straightforward to compute the Hamiltonian matrix elements on the truncated basis. This matrix is sparse, involving nonzero terms only between states whose numbers of vibrons differ by exactly one. As mentioned above, the approximate Hamiltonian (1) has full rotational symmetry. We work on a basis in which the $z$-component $M$ of total angular momentum is diagonal, selecting therefore a well defined value of this component, usually $M = 0$. (At this stage we do not try to exploit the full rotational symmetry of (1), and to work on a diagonal basis for the total angular momentum $L$.) In the set of coupling parameters which we use (see Table I), mode $H_{g6}$ has vanishing coupling; therefore we need only to include in the diagonalization the remaining 7 modes. In Table II and III, we list the size $d$ of the truncated Hilbert space at different values of $N$, for $M = 0$. The structure of the problem is suitable for a Lanczos algorithm. Our computational resources allow us to solve such a problem for $d < 5 \times 10^6$, thus including up to $N = 6$ vibrons. Tables II and III also show the ground state JT energy gain so obtained. These values are very close, as they should, to those found by Gunnarsson \[8\]. The numbers show a clear trend towards convergence, which is better for $n = 1$. For $n = 2$ ($S = 0$), the JT distortion is stronger, and convergence much more problematic. The convergence behavior for a few low-lying levels is illustrated in Fig. 1 as a function of $1/N^2$: panel
(a) refers to \( n = 1 \) (and equivalently to the \( n = 2, S = 1 \)), while panel (b) is for \( n = 2, S = 0 \). We have indicated a polynomial interpolation (continuous curves) simply as a guide to the eye. We have restricted this calculation to the lowest 5-6 eigenvalues, covering excitation energies only up to 400-500 cm\(^{-1}\). This is the region where the results are more reliable, within the limits imposed by the residual uncertainties in the coupling constants \( g_k \). At higher excitation energies, multi-mode combinations make the spectrum increasingly dense, and unreliable. Moreover, the Lanczos algorithm, as implemented, is unsuitable for computing accurately a large number of excited levels.

III. RESULTS AND DISCUSSION

The predicted excitation spectrum of gas phase \( ^2C_{60}^- \) and \( ^3C_{60}^2^- \) within the linear coupling spherical approximation is shown in Fig. 2 (a), and is reported in Table II. The four lowest excitations are essentially derived from the \( H_g1 \) mode at 270 cm\(^{-1}\), which is split in a qualitatively similar manner as predicted by perturbation theory [6]. The numerical value of the splitting which we find here is rather large, and should be readily observable in future Raman or EELS spectroscopy, if feasible, in gas phase. The lowest excitation is confirmed to be the \( T_{2u} + G_u (L = 3) \) doublet near 200 cm\(^{-1}\). As discussed above this doublet will in reality be split by higher order, nonspherical terms, absent in the Hamiltonian (4). However, we expect that the nonspherical splitting should be rather small relative to that to the next \( H_u \) state (\( \approx 70 \) cm\(^{-1}\)). Experimental confirmation of the overall “\( L = 3 \)” nature of the lowest excitation doublet would provide an interesting check for the Berry phase in \( C_{60}^- \).

Below 300 cm\(^{-1}\) the remaining excitations (\( H_u, T_{1u} \)) retain a prevalent \( \nu_1 \) character.

Above the \( \nu_1 \)-derived multiplet, the next \( L = 3 \) excitation, near 357 cm\(^{-1}\), has largely \( \nu_2 \) character, but there is also admixture with 2\( \nu_1 \) components. We note that there are no low-lying \( L = 0 \) states. It is interesting that among all \( N \)-vibron states, only those which involve different \( H_g \) modes can give rise to an overall \( L = 0 \) state. The lowest \( L = 0 \) state is expected to originate from the coupling with states belonging to \( \nu_1 + \nu_2 \), while none is originated from a pure overtone, such as 2\( \nu_1 \). The reason for this is the following. Since the bare electronic state is \( L = 1 \), we need another \( L = 1 \) (of vibrational nature) to get an overall \( L = 0 \). In the combinations of two different \( L = 2 \) vibrons, \( L = 4, 3, 2, 1, 0 \) states are generated, and these contain an \( L = 1 \) (\( T_{1g} \)) state. For two (or more) identical vibrons, however, only \( L = 4, 2, 0 \) are generated, the odd states vanishing due to permutation symmetry. Hence, there is no \( L = 1 \) in the overtones, and no overall \( L = 0 \). We expect, accordingly, the lowest \( L = 0 \) state at \( \approx 700 \) cm\(^{-1}\), close to the \( C_{60}^- \nu_1 + \nu_2 \) origin. In the icosahedral group,
however this kind of state will have $A_u$ symmetry. Conversely, $A_g$ states can only be generated by involving “$u$” vibrons. But these are linearly uncoupled to the electronic state, and thus very hard to excite. Thus it is confirmed that an approaching s-wave electron cannot efficiently attach to the C$_{60}$ molecule and end up (at least for the $t_{1u}$ orbital) in a global $A_g$ ($L = 0$) state [11].

The predicted low-lying excitation spectrum of a hypothetical gas phase $^1$C$_{60}^{2-}$ is given in Fig. 2 (b), and in Table III. Convergence is in this case much more problematic than for $n = 1$, or $n = 2$, $S = 1$. There is a new feature, consisting in a crossing of levels (of different symmetry), upon increasing $N$ (Fig. 1 (b)). For these reasons, error-bars on the extrapolated values are larger, probably exceeding 10 cm$^{-1}$.

In contrast to the $n = 1$ case discussed above, for $n = 2$, $S = 0$ not all the lowest excitations can be classified as derived mainly from the lowest vibrational mode $H_{g1}$. The 6 two-electron $S = 0$ states with no vibrons are split by e-v coupling into $^1|L = 0 > \oplus ^1|L = 2 >$ vibronic states. The singlet ground state is $^1|L = 0 >$, and the $^1|L = 2 >$ state is left as a low-lying excitation. In the weak coupling limit its energy goes to zero as $\sum g_k^2 \hbar \omega_k$ (see Fig.5 in Ref. [5]). For finite coupling, contributions to this excitation wave function come simultaneously from all $H_g$ modes, and are not dominated by lowest mode $H_{g1}$, unlike, e.g., the lowest $L = 3$ excitation of $^3$C$_{60}^{2-}$. If $H_{g1}$ were the only mode coupled to the $t_{1u}$ orbital, then the predicted excitation energy for this lowest $L = 2$ state, would be 69.9 cm$^{-1}$. The energy we find when all the modes are included (Table III) is significantly smaller, approximately 40cm$^{-1}$, confirming the participation of all modes.

The next higher excitations are an $L = 4$ state (unsplit doublet $G_g + H_g$), followed by an $L = 6$, $L = 2$ and $L = 3$, all essentially of $H_{g1}$ origin. This sequence constitutes a clear remnant of the para-hydrogen-like series $L = 0, 2, 4, 6,...$ predicted semiclassically when the Berry phase cancels, as in this case. The first level originating from $H_{g2}$ is, as expected, a state of symmetry $L = 4$ around 330 cm$^{-1}$ above the ground state, identically beginning another series $L = 4, 6, 8,...$. It should be noted here that icosahedral splittings (not included) are probably larger in this case relative to $n = 1$.

The pure JT energetics (see Table II and III) indicates the spin singlet configuration as the preferred ground state of C$_{60}^{2-}$. However our calculation does not include Coulomb e-e repulsion, which is not negligible in this state. There is in fact some experimental evidence [13] that C$_{60}^{2-}$ ions in a matrix may prefer an $S = 1$ configuration, as expected from Hund’s rule. The reduction of screening in vacuum could imply an even stronger Coulomb repulsion, further favoring an $S = 1$ ground state. It should be noted however that large $U$ Hubbard models, as well as PPP calculations appear to favor a singlet ground state for $n = 2$, even without JT effect [14,15]. On the other hand, the dynamical JT effect of the ion when in a matrix is likely to be quenched (by
crystal fields or by polarization of the surrounding medium) to a static JT distortion, which gains considerably less energy than the dynamic JT effect considered here [8]. This leaves open a residual chance of a $^1C_{2^-}^{60}$ ground state in gas phase.

We stress here finally, that our spectra have been computed neglecting spin-orbit effects. Since the intra-carbon spin-orbit coupling is $\zeta(2p_c) \approx 28 \text{ cm}^{-1}$ [21], it can be expected to yield additional splittings, both in the ground state and the low lying excitations, of comparable magnitude. Splittings of 30 and 75 cm$^{-1}$ reported in the near IR spectrum of $C_{60}^-$ in solid Ar have in fact been attributed to spin-orbit [22]. Interpretation of the actual spectra of $C_{60}^-$ and $C_{2^-}^{60}$ will have to include consideration of spin-orbit effects, to be calculated in the future.

IV. CONCLUSIONS

We have calculated the lowest excitation spectrum, derived by JT coupling of the $H_g$ modes for $C_{60}^-$ and $C_{2^-}^{60}$ in gas phase. The calculation involves neglecting nonspherical and nonlinear effects, as well as spin-orbit coupling, but is otherwise fully quantitative. Common characters of these spectra are sizable splittings, in the order of several tens of cm$^{-1}$, and a substantial lowering of the transition energy to the lowest mode, in comparison with the lowest $H_g$ mode of neutral $C_{60}$. The symmetry of this lowest excitation, in particular, should be revealing in connection with the Berry phase which affects this Jahn-Teller problem [9,5]. Gas phase vibron spectroscopy of these negative ions will be very important in the future, to check these predictions.

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| $H_{gk}$ | $h\omega_k$ [cm$^{-1}$] | $g_k$ |
|---------|---------------------|-----|
| 1       | 270.0               | .868|
| 2       | 430.5               | .924|
| 3       | 708.5               | .405|
| 4       | 772.5               | .448|
| 5       | 1099.0              | .325|
| 6       | 1248.0              | .000|
| 7       | 1426.0              | .368|
| 8       | 1575.0              | .368|

TABLE I. The vibrational frequencies and couplings for the JT-active $H_g$ modes of fullerene.
| $N$ | $d$ | $L = 1$ | $L = 3$ | $L = 2$ | $L = 1$ | $L = 3$ | $L = 5$ | $L = 3$ |
|-----|-----|---------|---------|---------|---------|---------|---------|---------|
| 3   | 3662| -1094.6| -810.2  | -742.2  | -721.3  | -657.1  | -350.8  | -314.8  |
| 4   | 31459| -1117.8 | -855.6  | -814.3  | -793.6  | -729.5  | -588.3  | -548.2  |
| 5   | 225716| -1124.2 | -910.1  | -837.8  | -818.5  | -753.1  | -665.7  | -625.0  |
| 6   | 1405972| -1125.7 | -917.0  | -844.3  | -826.2  | -759.7  | -691.1  | -650.5  |
| 7   | 7775140| -       | -       | -       | -       | -       | -       | -       |
| $\infty$ | - | -1126.3 | -926.7  | -853.5  | -838.9  | -768.8  | -728.6  | -689.3  |

**TABLE II.** Low lying levels obtained by exact diagonalization of Hamiltonian (1) for $C_{60}^-$ or for $C_{60}^{2-}$ ($S = 1$) for increasing vibron number $N$. Symmetries of these vibronic states are indicated at the top. The extrapolated $N \rightarrow \infty$ energies (see figure 1) are at bottom. The energy zero is the undistorted molecule, and energies are in cm$^{-1}$.

| $N$ | $d$ | $L = 0$ | $L = 2$ | $L = 4$ | $L = 6$ | $L = 2$ | $L = 3$ | $L = 4$ |
|-----|-----|---------|---------|---------|---------|---------|---------|---------|
| 3   | 10650| -2898.3 | -2643.7 | -2075.7 | -947.3  | -2278.4 | -1880.9 | -1840.8 |
| 4   | 91689| -3085.2 | -2907.7 | -2547.7 | -1934.1 | -2591.9 | -2343.4 | -2310.8 |
| 5   | 660936| -3201.0 | -3068.2 | -2808.2 | -2409.9 | -2778.9 | -2606.9 | -2574.8 |
| 6   | 4130556| -3274.0 | -3167.8 | -2964.6 | -2670.1 | -2896.3 | -2768.6 | -2735.2 |
| 7   | 22907016| -       | -       | -       | -       | -       | -       | -       |
| $\infty$ | - | -3459.5 | -3419.9 | -3348.2 | -3275.9 | -3190.9 | -3168.9 | -3130.6 |

**TABLE III.** Low lying levels obtained by exact diagonalization of Hamiltonian (1) for $C_{60}^{2-}$ ($S = 0$) for increasing vibron number $N$. Symmetries are indicated at the top. The extrapolated energy (see figure 1) is at bottom. As discussed in the text, the uncertainty on these extrapolated energies is rather large. The energy zero is the undistorted molecule, and energies are in cm$^{-1}$.
FIGURES

FIG. 1. The $C_{60}^{ni}$ ground state and low excitation energies, (a) for $n = 1$ and $n = 2$ $S = 1$, and (b) for $n = 2$ $S = 0$, as a function $1/N^2$ ($N$ is the number of vibrons included in the calculation). Continuous lines are fits for $N > 3$.

FIG. 2. Extrapolation for $N \to \infty$ of the $C_{60}^{ni}$ excitation spectra, (a) for $n = 1$ and $n = 2$ $S = 1$, and (b) for $n = 2$ $S = 0$. The symmetry species of the levels are indicated. All non-Jahn-Teller excitations are omitted.
(a) $n=1$

$T_{1u} + G_{u}$

$T_{1u} + T_{2u} + H_{u}$

$T_{1u} + G_{u}$

$H_{u}$

$T_{1u} + G_{u}$

(b) $n=2$, $S=0$

$G_{g} + H_{g}$

$T_{2g} + G_{g}$

$H_{g}$

$A_{g} + T_{1g} + G_{g} + H_{g}$

$G_{g} + H_{g}$

$A_{g} + H_{g}$