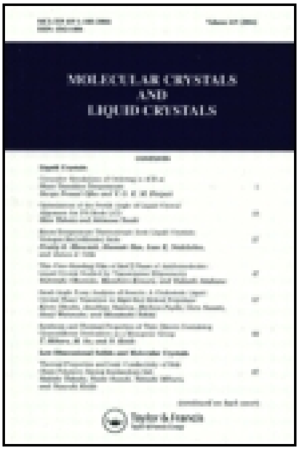

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Analysis of the Raman Spectra of A3C60 and A_6C_{60}

Fabrizia Negri [a], Giorgio Orlandi [a] & Francesco Zerbetto [a]

[a] Dipartimento di Chimica, “G. Ciamician”, Università di Bologna, Via F. Selmi 2, 40126, Bologna, Italy

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ANALYSIS OF THE RAMAN SPECTRA OF A_3C_{60} AND A_6C_{60}

FABRIZIA NEGRI, GIORGIO ORLANDI and FRANCESCO ZERBETTO
Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F.
Selmi 2, 40126, Bologna, Italy

Abstract The vibrational frequencies and the vibronic activity of normal modes of $C_{60}{}^{6-}$ and $C_{60}{}^{3-}$ are calculated with the QCFF/PI quantum chemical method. The results are discussed in the light of recent infrared and Raman data of A_6C_{60} and A_3C_{60} (with A an alkali atom).

INTRODUCTION

The spectroscopy of doped fullerenes is presently attracting considerable interest because of the relatively high temperature at which the doped films of A_3C_{60}, with A an alkali atom, become superconductive. The spectroscopic activity has been aimed at determining both the intra- and inter-molecular vibrational frequencies of A_3C_{60} [1,2] and A_6C_{60} [1]. Since the Raman active intramolecular frequencies of A_6C_{60} are affected to less than 10 cm^{-1} upon dopant substitution (K, Cs, Rb) [1], it is of interest to calculate structure, vibrational frequencies and vibronic activity of $C_{60}{}^{6-}$ and $C_{60}{}^{3-}$ anions and to discuss on this basis the infrared and Raman spectra of doped fullerenes.

MOLECULAR ORBITAL METHOD

The optimization of structural parameters and of vibrational frequencies and normal coordinates were performed with an upgraded version of the QCFF/PI (Quantum Chemical Force Field / π electrons) program[3]. This model employs an empirical potential fo the σ-electron framework and uses a quantum chemical scheme for the π electrons which are treated by a Self Consistent Field procedure followed by Configuration Interaction. Both the one electon (t or hopping) integrals and the two-electron (U or Coulomb) integrals are functions of the interatomic distances. The two-electron integrals are calculated for any pair of atoms, while the one-electron ones are limited to one center and near neighbours interaction. All the determinants arising from the one- to six-electron excitations in the space spanned by the triply degenerate LUMO and the triply degenerate LUMO+1 of C_{60} are included in the calculation.

VIBRATIONAL FREQUENCIES OF C_{60}^{6-}

MO-SCF-CI calculations indicate that the ground state of C_{60}^{6-} is a totally symmetric singlet, ^1A_g, [4]. The optimized structure of the isolated ion mantains I_h symmetry. The long bonds are slightly shortened by the six extra charges and result of 1.464 A(-0.007 A), while short bonds increase to 1.453 A (+0.042 A). In Table I we show calculated and experimental frequencies of infrared and Raman active modes of C_{60}^{6-}. The composition of the normal modes in terms of linear combinations of the modes of the neutral compound reveals little or no rotation of normal modes of vibration upon going from C_{60} to C_{60}^{6-}.

The t_{1u} frequencies are calculated with a precision similar to that of neutral C_{60}. For this set of frequencies, the standard deviations are 23 cm^{-1} for C_{60} and 30 cm^{-1} for C_{60}^{6-}. The below 1300 cm^{-1} frequency region of the h_g and a_g modes of the hexa-anion is nicely reproduced with the largest discrepancy of ca. 30 cm^{-1} for the lowest energy h_g mode. The standard deviation for these nine modes is 16 cm^{-1}. The agreement between experiment and theory is less satisfactory for the highest a_g and the two highest h_g frequencies. If one accepts the assignment of ref. 1, the differences between calculation and experiment is $1h_g$=70 cm^{-1}, $2h_g$=-17 cm^{-1}, $1a_g$=-105 cm^{-1}. The error for the frequency of the totally symmetric mode appears to be too large for the method used in this work. Thus, we propose to reverse the assignment of the $2h_g$ and $1a_g$ frequencies. In this way, the pattern of frequency lowering upon going from C_{60} to A_6C_{60} is more satisfatory.

TABLE I. QCFF/PI calculated and experimental infrared and Raman active frequencies (cm^{-1}) of C_{60}^{6-} and of C_{60}^{3-}.

	Calc[a]	Exp[b]		Calc[a]	Exp[b]
	C_{60}^{6-}			C_{60}^{3-}	
t_{1u}[c]	1313	1340		1345	
	1205	1185		1207	
	591	564		603	
	516	546		531	
a_g[d]	1327	1432	1385[e]	1442	1453
	507	500		513	497
h_g[d]	1557	1483		1510	1547?
	1368	1385	1432[e]	1393	1408?
	1215	1238		1229	
	1124	1092		1139	
	773	760		789	782[f]
	649	657		672	701[f]
	414	421		428	397[f]
	244	271		250	271

a) this work, b) Raman spectra of ref. 1 and infrared spectra of ref. 8, c) infrared active, d) Raman active, e) alternative assignment, f) from inelastic neutron scattering, ref. 2.

Now, we discuss the origin of frequency lowering observed upon going from the neutral to the doped system. To a first approximation, the frequency lowering in the anions of C_{60} can be ascribed to the extra electrons which fill antibonding orbitals and diminish the strength of the carbon carbon bond. However, the values of the vibrational frequencies are not only due to the intrinsic strength of the bond, but may also be affected through another mechanism of vibronic origin. A review of this phenomenon in polyenic compounds can be found in ref. [5]. The ground state frequencies are decreased through this mechanism while the excited state frequencies are increased. C_{60}^{6-} has very low lying electronically excited states [4] and we may therefore expect that vibronic coupling will have a sizeable effect, larger than in the neutral molecule, on its ground state vibrational frequencies. In ref. 6, we have shown how to calculate quantum chemically diabatic (not including vibronic effects) and adiabatic (including vibronic effects) force fields. We calculated[7] the diabatic and adiabatic frequencies of C_{60} and C_{60}^{6-}. The results are the following:

i) in the diabatic picture, the addition of six electrons to the antibonding orbitals alters significantly only frequencies above 1300 cm^{-1}.

ii) in both species, vibronic coupling diminishes only frequencies higher than 1300 cm^{-1}. As expected, the frequency lowering is larger in the hexaanion. The modes affected the most are $1t_{1u}$, $1a_g$ and $2h_g$; a sizeable activity is also found for $1h_g$ and $3h_g$ in C_{60}^{6-}.

Thus the frequency lowering upon doping is caused by the joint effect of the increased bond distances and a vibronic coupling mechanism.

THE STRUCTURE AND VIBRATIONAL FREQUENCIES OF C_{60}^{3-}

The trianion of C_{60} is of relevance for the electron transport and the superconductivity which is greatest in the alkali intercalated solid phase. It is puzzling that most of the h_g frequencies do not show up in the Raman spectrum of C_{60}^{3-}, while they are present in the spectrum of the neutral molecule and of the hexaanion. Several explanations may be considered for this effect: lowering of symmetry, change in the scattering matrix and electron-phonon (i.e. vibronic) coupling.

Due to the presence of 3 electrons in a triply degenerate set of T_{1u} orbital, one can expect a doublet or a quartet ground state. The ground state is the quartet ^4A_u [4]. The optimized structure in this state is I_h. The calculated long and short bonds are 1.466 and 1.430 A, respectively. These bond lengths are intermediate between those of the neutral molecule and those of the hexaanion. The calculated frequencies of infrared and Raman active modes of C_{60}^{3-} in the ^4A_u state are shown in Table 1 together with the few available experimental frequencies. These frequencies are intermediate between the frequencies of the hexaanion and of the neutral molecule. Like in A_3C_{60}, vibronic coupling decreases only frequencies above 1300 cm^{-1}.

The lowest doublet state is calculated of T_{1u} symmetry and, while being about half eV above the ground state in the isolated anion, could become the ground state in the film. The $^2T_{1u}$ doublet can undergo Jahn-Teller effect at variance with the lowest quartet state, ^4A_u, which cannot be distorted along a Jahn-Teller active coordinate. The Jahn-Teller distortion is calculated to stabilize the molecule by 440 cm^{-1}: the $1h_g$ and the $8h_g$ contribute with a coupling of 244 and 104 cm^{-1}, respectively. A full geometry optimization shows that there are also pseudo Jahn-Teller active coordinates. The pseudo Jahn-Teller effect is the distortion of the molecular symmetry in a given electronic state through the interaction with a higher state. If the coupling with the higher states is large enough, the lower will form a double minimum potential. This coupling is given by the Herzberg-Teller parameter divided the energy difference between the two interacting states. As shown previously[4], C_{60}^{3-} has a number of low lying excited states. Because of the favorable energy denominator, even small electron-phonon of Herzberg-Teller interactions can cause distortion. Also the pseudo Jahn-Teller effect of C_{60}^{3-} is dynamical according to the calculations.

Because of distortion, the optimized structure results of C_1 symmetry. This bears also on the vibrational frequencies and the normal modes of vibration. The degeneracy between h_g modes is lifted and the Raman activity of h_g parentage is dispersed among a large number of modes, giving rise to broad and weak bands in the doublet ground state of C_{60}^{3-}.

A study of Raman spectra of A_3C_{60} taken with exciting beams of different wavelengths is called for to resolve present ambiguities.

CONCLUSIONS

The vibrational frequencies of C_{60}^{6-} are in good agreement with the observed spectra of A_6C_{60} films. The calculated spectra of C_{60}^{3-} are intermediate between the spectra of C_{60} and of C_{60}^{6-} and are close to the available experimental frequencies. Only tangential (high-frequency) modes have been found vibronically active. The lowest frequency h_g mode has been found active in the Jahn-Teller distortion of $^2T_{1g}$.

The absence and the broadness of many h_g bands in spectra of A_3C_{60} films may have several explanations. A reliable interpretation of Raman spectra require the measure of excitation profiles and the calculation of the scattering matrix.

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