

Jahn-Teller effects in the C_{60}^{2+} cation undergoing D_{2h} distortion

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It has recently been shown that the high-spin, doubly hole-doped fullerene cation C_{60}^{2+} is likely to undergo a Jahn-Teller (JT) distortion, which reduces the molecular symmetry from I_h to D_{2h} . A theoretical model for the JT effect describing this situation is presented. The model includes parameters for the energy differences between molecular terms that arise from Coulomb interactions between the holes. Although the magnitudes of these parameters are not known to any degree of certainty for the C_{60}^{2+} cation, they are likely to have an important effect. Results are given for both the static JT effect, where the motion of the system can be considered in terms of vibrations in a potential well, and the dynamic JT effect, where tunneling between equivalent wells must be taken into account.

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I. INTRODUCTION

Although difficult to prepare in the laboratory, hole-doped fullerenes are expected to have exceptional properties that make them even more alluring than their negatively doped counterparts. For example, calculations by Manini *et al.*¹ indicate that the electron-phonon coupling in positively charged fullerene derivatives C_{60}^{n+} is significantly larger than in the corresponding negatively charged ions C_{60}^{n-} . Alternative calculations also allow the deduction that the electron-phonon coupling is stronger in C_{60}^+ than it is in C_{60}^- .² In addition, interpretation of experimental measurements also indicate that the coupling is strong in C_{60}^+ .³ Thus we can expect that there may be hole-doped fullerene derivatives that exhibit critical temperatures for superconductivity that exceed even those found in the electron-doped fullerenes. However, the electron-phonon coupling is in direct competition with the intramolecular Coulomb exchange interaction. Thus both interactions must be considered simultaneously in any theoretical analysis of these ions. The two interactions can lead to opposite conclusions regarding spin. The electron-phonon interaction tends to promote low-spin ground states, while Coulomb interactions lead to high-spin ground states.⁴

The hole(s) of H_u symmetry in C_{60}^{n+} cations can couple to two a_g , six g_g , and eight h_g modes of vibration. However, it has been shown that the a_g and g_g modes do not result in any significant couplings.¹ Also, coupling to one of the h_g modes [namely $h_g(1)$] is believed to be much stronger than the couplings to the other modes.¹ Therefore the electron-phonon coupling may be described, in the first instance, in terms of coupling to a single h_g mode only. If it is found desirable to consider the couplings to all eight h_g modes, then it is possible to formulate the problem in terms of a single effective mode⁵ and so the system can still be treated in terms of a single h_g mode but with different numerical values for the constants than those for the $h_g(1)$ mode alone.

In the singly doped cation C_{60}^+ , the complication presented by Coulomb interactions are absent, and so the model involves Jahn-Teller (JT) interactions only. The system can be represented by a $H_u \otimes h_g$ JT problem, which results in wells in the lowest adiabatic potential energy surface (APES) hav-

ing either D_{5d} or D_{3d} symmetry,⁶⁻⁸ in common with results for the negatively charged fullerene ions. Multiply hole-doped molecules C_{60}^{n+} can be similarly described using, in the notation of Nikolaev *et al.*,⁹ a $(h_u^+)^n \otimes h_g$ JT coupling model. In these cases, Coulomb interactions are important and must be given due consideration alongside the JT effects. It is found that these ions may have distortions that are of D_{2h} or C_{2h} symmetry, in addition to the more usual D_{5d} and D_{3d} ones.^{10,11}

In the present paper, we concentrate on the doubly hole-doped cation C_{60}^{2+} , which we model as a linear $(h_u^+)^2 \otimes h_g$ JT system. In systems with wells in the APES, such as is the case here, the effect of higher-order couplings is only to introduce small changes to the positions and depths of the wells, so can be safely neglected. (This is in contrast to cases where the APES contains a trough of accidentally higher symmetry, in which case higher-order terms will warp the trough and potentially convert rotational motion into vibrations.) Furthermore, numerical values for the linear constants are still not known to any degree of accuracy for the C_{60}^{n+} ions, and values for higher-order constants are not known at all. Hence adding higher-order terms would only introduce additional unknown parameters into an already complicated system.

There are several additional complications that arise in this system. First, the two holes may couple to produce terms having either low ($S=0$) or high ($S=1$) spin. Calculations indicate that the high-spin terms are the lower in energy,⁹ and so we shall henceforth ignore the low-spin terms. The high-spin terms are $\{^3T_{1g}, ^3T_{2g}, ^3G_g\}$, which means that the JT effect must be formulated using a ten-dimensional electronic basis. Second, the three terms used in the basis do not have the same energy because of the Coulomb interaction between the two holes from which the multihole states of the system can be derived. The terms will have different energies, irrespective of any JT interactions. Calculations of the Coulomb term energies for the C_{60}^{2+} ion appearing in the literature are not in agreement with each other.^{4,9,12,13} Thus it is not currently possible to give an unequivocal treatment of the ion. However, we can develop a model in which the term splittings are treated as parameters, and calculate results for various values of those parameters.