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Authors
Canton, S.E.
Yencha, A.J.
Kukk, E.
et al.

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Experimental evidence of a dynamic Jahn-Teller effect in C_{60}^+

S. E. Canton,[1, 2, *] A. J. Yencha,[3] E. Kukk,[4] J. D. Bozek,[2] M. C. A. Lopes,[5] G. Snell,[1] and N. Berrah[1]

[1]*Department of Physics, Western Michigan University, Kalamazoo MI 49008*
[2]*Lawrence Berkeley National Laboratory, ALS, University of California, Berkeley CA 94720*
[3]*Department of Chemistry, State University of New-York at Albany, Albany, NY 12222*
[4]*Department of Physical Sciences, Oulu University, Linnanmaa, Oulu FIN-90570, Finland*
[5]*Departmento de Fisica, ICE, Universidade Federal de Juiz de Fora, Juiz de Fora-MG, CEP 36036-330, Brazil*
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Detailed analysis of the Highest Occupied Molecular Orbital bandshape in the photoelectron spectrum of gaseous C_{60} reveals a *dynamic* Jahn-Teller effect in the ground state of C_{60}^+. The direct observation of three tunneling states asserts a D_{3d} geometry for the isolated cation, originating from a strong vibronic coupling. These results show that the ionic motion plays an important role in the electron-phonon interaction.

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Since the discovery of C_{60} in 1985 [1], the electronic structure of this non-planar carbon allotrope has been studied intensively. Similar interest aroused for charged fullerenes when it was recognized that many macroscopic properties of the solid compounds, including superconductivity, could be related to the ones of the isolated negative [2, 3] and positive [4] ions due to unusually weak Van der Waals forces [5]. However, the understanding of the ionic electronic structures is complicated by the breakdown of the Born-Oppenheimer approximation [6], which assumes strict separation of electronic and nuclear motion and is solely valid when the energy difference between electronic states is much larger than the quantum of any normal mode. In presence of accidental or intrinsic degeneracy, this condition is clearly not met and such situation gives rise to a special type of vibronic coupling called the Jahn-Teller (JT) effect. Because C_{60} belongs to the extremely symmetric icosahedral group I_h, its molecular orbitals are highly degenerate, and the ionic states are accordingly subject to this non-adiabatic interaction. The JT theorem [7] states that any non-linear system with electronic (non Kramers) degeneracy is distorted by the coupling of the electrons to some specific molecular vibrations called the JT active modes, so as to lift the degeneracy and lower the total energy. Depending on the coupling strength, the ionic zero point motion can be neglected or not and the respective JT effects are then referred to as *static* or *dynamic* [8–11]. One of the most fundamental consequences of this interaction is certainly its influence on the relaxed equilibrium geometry since it determines the spectral properties of the molecular ions. The particular case of C_{60}^+ is of importance for astrophysics as recent observations [12, 13] have identified it as a possible carrier in the long-standing problem of diffuse interstellar bands via its infrared frequencies estimated from laboratory measurements [14–16]. Interpretation of these electronic and IR spectra obtained from C_{60}^+ in glassy or rare gas matrices seems to be compatible with a D_{5d} structure for the trapped ion. On the other hand, such media are known to be quite perturbative and some of the features had to be attributed to another unidentified geometry.

In this letter, we report the first experimental evidence of a *dynamic* JT effect for free C_{60}^+. Analysis of the first ionization band in the valence photoelectron spectrum allows assignment of the JT split component and unambiguous identification of the D_{3d} relaxed geometry of the cationic ground state.

The experiment was performed at the atomic and molecular undulator beamline 10.0.1 at the Advanced Light Source. A resitively heated oven generated an effusive beam of C_{60} that was ionized by synchrotron radiation. The photoelectron spectra were recorded in a crossed beam configuration using a Scienta SES-200 hemispherical analyzer at the magic angle [17]. The spectrometer was operated at 20 eV pass energy and the photon resolution was set to 10 meV. Measurement of the Xenon $5p_{1/2,3/2}$ lines shows an overall instrumental contribution of about 22 meV. The binding energy scale was calibrated using the vertical ionization potential at 7.75 eV corresponding to the maximum of the band.

Ionization of an electron from the Highest Occupied Molecular Orbital (HOMO) produces the first band in the valence photoelectron spectrum. The ionic state undergoes a JT distortion and consequently the band appears as split: the underlying lines correspond to the ionization to the observable vibronic states in the relaxed geometry, their relative weight reflecting their degeneracy. The HOMO photoelectron band displayed in Fig. 1 gives clear evidence of three components, confirmed by the three distinct peaks appearing in the derivative of the photoelectron curve as a function of energy. Early measurements from thin films [18] or gaseous C_{60} [19] could not resolve any structure. The latest high-resolution He II spectrum demonstrated for the first time that the splitting is not due to individual vibrational levels but reported a single shoulder [20]. Relativistic effects can not account for the observed splitting either, because of
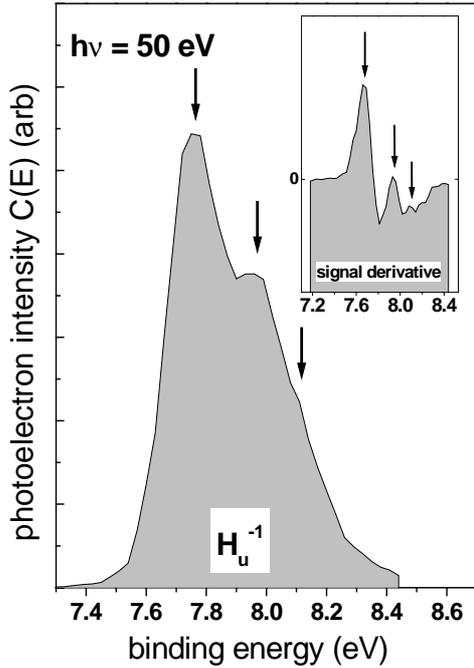
FIG. 1: Photoelectron signal from the HOMO orbital at hν=50 eV. The inset shows its derivative.

the small value of the effective spin-orbit constant for fullerenes (for C_{60}, $\xi_{eff} = 0.057\xi_{C_{2p}}$) [21]. In the presented spectra, the width of the lines is primarily coming from thermal and Doppler broadening, as well as from excitation of the Franck-Condon and the JT active modes. Consequently the ionization profile was fitted by three asymmetric Gaussians since this lineshape has proven efficient in analyzing overlapping bands with unresolved vibrational progressions [22, 23]. In this model, the cation potential well is approximated by two lines tangent to the surface and intersecting at the vertical transition. Due to the curvature, the slope on the high binding energy side is larger than the one on the low side. The electron count C(E) as a function of the binding energy can be written as :

$$C(E) = Ae^{-4ln2[(E-P)/W]^2} \tag{1}$$

A and P being the peak amplitude and position, W the width, with $W = W_l$ if $E < P$ and $W = W_h$ if $E > P$, the two widths reflecting the different slopes of the two tangents. The fitted profiles are displayed in Fig. 2 and the parameters are given in Table I, where I_{rel} gives the relative intensity of the component.

Semi-empirical [24, 25] and ab-initio [26–29] calculations agree to attribute H_u symmetry to the HOMO of C_{60}. The vibrations capable of lifting the five-fold degeneracy can be determined using group theory. Neglecting

any spin-dependence, the irreducible representation symmetry label γ of the normal mode must occur in the symmetric square of the irreducible representation H_u of the electronic state $[H_u \otimes H_u]_s$. Besides 2 a_g modes that can not induce any symmetry lowering, the set of JT active vibrations comprises 8 h_g and 6 g_g modes, which could in principle give rise to multimode coupling. However, as long as the JT interaction is restricted to the *linear* term in the ionic displacements, the multimode problem has exactly the same symmetry characteristic as the so-called single mode approximation, where coupling to only one vibrational mode of each symmetry type is considered [10]. Hinging upon the environment or the electron-phonon coupling strength, either a *static* or *dynamic* JT effect is observed. When the coupling can be considered infinite, or equivalently [9] , when the ionic zero point motion can be neglected, it is necessary to consider the distortions of the degenerate adiabatic potential energy surface under the influence of each JT active modes. This semi-classical treatment results in a set of extrema of lower symmetry, the absolute minimum corresponding to the new equilibrium geometry. The minimum often consists of several energetically equivalent wells and in the static case the coupled system is confined to one of them. The symmetries of the vibronic states are then restricted to the irreducible representations of the point group of the stabilized configuration. As a real symmetry breaking in a finite system can only occur under an external force that tends to effectively fix the direction of the distortion, the static JT effect is most likely to be seen in solids and matrices. If the coupling is finite, quantum corrections due to the ionic motion are important. While the JT effect breaks the Hamiltonian symmetry, fluctuations between the energetically equivalent wells of the distorted geometry (obtained in the static problem) lead to the formation of tunneling states that need to be described in the original symmetry [11]. This dynamic JT effect is usually observed in free complexes. Since the outermost orbital H_u of C_{60} is highly delocalized over the rigid nuclear cage, removal of one of the 240 valence electrons is not expected to cause large changes of bond length. This is confirmed by the relatively narrow width of the band rising from a negligible background. The resulting states of the isolated ion are then best described as originating from a dynamic JT interaction, as it has been shown to be the case for some excited triplet states of neutral C_{60} [30–32].

The corresponding static $H_u \otimes (h_g \oplus g_g)$ *linear* JT problem has been investigated analytically [33, 34]. Minimization of the adiabatic energy surface leads to D_{3d} or D_{5d} possible symmetries. Intermediate Neglect of Differential Overlap (INDO) [35] and density functional [4] calculations predict the D_{5d} distortion to be the energetically favored minimum. This seems to be validated by the measurements performed on C_{60}^+ in matrices [14–16]. When the dynamic JT problem is solved in the tunnel-
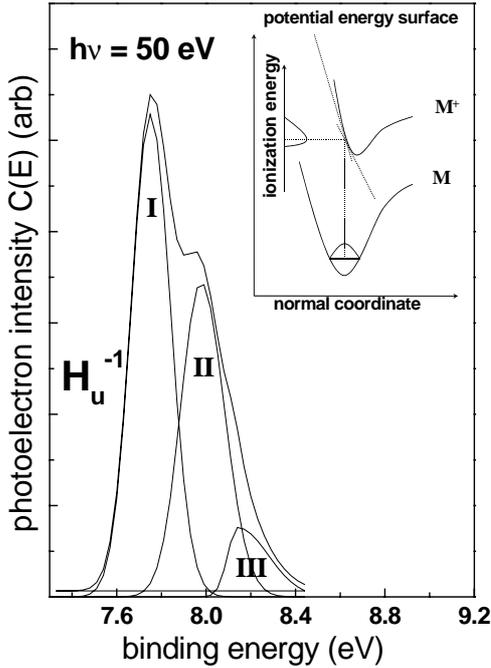
FIG. 2: Fit of the HOMO band by three asymmetric Gaussians. The inset shows a diagram of the model for the lineshape.

TABLE I: Energies, widths (in eV) and relative intensities of the Jahn-Teller split bands from least-squares curve fitting of the photoelectron spectrum in Fig.2 .

band	Sym.	E_b	ΔE_b	W_l	W_h	I_{rel}
I	H_u	7.75	0	0.10	0.10	0.55
II	G_u	7.98	0.23	0.12	0.11	0.36
III	A_u	8.14	0.40	0.16	0.05	0.09

ing regime [39], the same symmetries are found and the I_h symmetrized combinations of the states associated to each geometry are obtained. The relaxed configuration relates to the interaction strength. When the coupling is strong, the absolute minimum is composed of 10 wells of D_{3d} symmetry and 3 tunneling states of H_u, G_u and A_u symmetry can be formed. In the case of intermediate coupling, the absolute minimum consists of 6 wells of D_{5d} symmetry that can support 2 tunneling states of H_u and A_u symmetry.

The present analysis of the HOMO bandshape demonstrates the D_{3d} equilibrium geometry of the isolated cation in its ground state. The fitting procedure, shown in Fig. 2, allows the extraction of three bands I, II and III of areas approximately in the 5:4:1 ratio, corresponding to the tunneling states H_u (I_h ground state), G_u and A_u.

The observation of a three-band structure with appropriate branching ratio rules out the possibility of a D_{5d} geometry predicted by purely static *linear* calculation. An attempt to model the band with only two underlying peaks fails to reproduce the profile and does not give areas in the 5:1 ratio expected for the H_u and A_u states supported by a D_{5d} geometry. The actual splitting of the band implies that the convenient spherical approximation often used to model C_{60} and its ions [36–38] might not be accurate enough if a detailed description of the potential energy surfaces is required. The observation of tunneling states proves that, despite the strength of the coupling, this system cannot be described by a semi-classical model that neglects the ionic motion. It is possible that higher order terms in the JT interaction might have to be taken into account as well.

The moment $M_2 = \int P(E)E^2 dE$, P(E) being the transition probability as a function of energy E, usually gives an approximate measure of the total coupling strength [40]. After instrumental deconvolution, comparison of the moment obtained from the present photoelectron band (~ 0.25 eV) with the one extracted from photoemission spectra of C_{60}^- (~ 0.15 eV) [3] shows that a vacancy in the HOMO couples more strongly than an additional electron in the LUMO. These results are relevant to the characterization of superconductivity. Recent experiments [41, 42] have shown that a monolayer of C_{60} can be positively field doped and exhibits in that state higher resistivity and higher superconducting temperature than if negatively doped. These properties are related to a strong electron-phonon interaction, which can be traced back to the JT effect in the isolated cation. The actual coupling constants at the molecular level enter the expression for the dimensionless electron-phonon coupling constant controlling the phonon contribution to the resistivity in the crystalline phase and the superconductivity [2, 4]. These molecular coupling constants are not known from experiment yet so any modelling of superconductivity for this system has to rely critically on calculation, which has been limited so far to the static case. Although the macroscopic quantities derived from the estimates are of the correct order of magnitude, some discrepancies remain [4], which might originate from the non-inclusion of the ionic dynamics.

In conclusion, this work provides the first experimental evidence for a D_{3d} geometry of free C_{60}^+ by direct observation of the three tunneling states supported by this configuration. The finding of the D_{3d} geometry rather than the D_{5d} expected from the static problem proves that even if the coupling is strong, the effects of the ionic motion cannot be omitted when describing precisely the electronic structure. Unravelling the precise consequences of the Jahn-Teller interaction at the molecular level constitute an important step in understanding how vibronic coupling influences the electronic structure and more generally the numerous properties of the fullerene

based materials.

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* Electronic address: secanton@lbl.gov

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