Comment on "Experimental Evidence of a Dynamic Jahn-Teller Effect in $C_{60}{}^{+}$"

A recent Letter [1] reports photoemission (PE) data for the free C_{60} molecule, showing an interesting three-peak structure, presented as evidence of dynamic Jahn-Teller (DJT) effect in the $C_{60}{}^{+}$ ion. Those data constitute, along with earlier spectra by the Uppsala group [2], the best available experimental evidence about the spectrum of a hole in fullerene. DJT must indeed affect the fivefold-degenerate h_u hole molecular orbital [3], but we contend that the energy separation of these three peaks is far too large for the proposed tunneling interpretation to be correct.

In detail, the observed structure is claimed to indicate a D_{3d} distortion in the lowest-energy JT well, accompanied by tunneling between the local minima. The main argument offered is that the ten D_{3d} valleys yield three tunnel-split states $H_u(5) + G_u(4) + A_u(1)$, to be identified with the three observed structures. Alternatively, six D_{5d} valleys would split into two $H_u(5) + A_u(1)$, while valleys of lower symmetry (D_{2h}, C_{2h}) would split more than threefold. Given this interpretation, however, the tunnel splitting magnitudes between D_{3d} valleys would amount to 230 meV ($H_u - G_u$) and 390 meV ($H_u - A_u$). Both splittings are alarmingly larger than any of the vibrational frequencies of fullerene (32–195 meV).

Our contention is precisely that these supposed splittings are far too large for the tunneling interpretation to be valid. Tunnel splittings make sense only in the large-barrier limit, when they are smaller than the *smallest* vibrational quantum $\hbar\omega$, here of 32 meV [Fig. 1(a)], and the model of cited Ref. [36] applies. In the opposite limit [Fig. 1(b)], barriers between valleys are lower than the kinetic energy, and tunneling-split levels are replaced by extended anharmonic excitations, delocalized over all valleys. To estimate the two lowest excitations to be expected for $C_{60}{}^{+}$, we carried out a realistic calculation of the lowest H_u, G_u, and A_u vibronic states of an h_u electronic level JT coupled to eight fivefold H_g and to six fourfold G_g vibrational modes [3]. Using the *ab initio* JT coupling parameters and frequencies of Ref. [3] in a symmetry-restricted Lanczos diagonalization, we obtain 18 and 30 meV ($\lesssim \hbar\omega$) for the excitation energies from the H_u ground state to the lowest A_u and G_u vibronic states, respectively. These values are an order of magnitude smaller than the PE structures [1].

Is this discrepancy due to uncertainty in the precise values of the coupling parameters? We think not. If the actual couplings were smaller or, as is more likely, larger than those assumed, or if they made D_{3d} wells lower than D_{5d} wells, then the lowest A_u, G_u, and H_u states would always lie within a range of $\sim\hbar\omega \simeq 30$ meV. The spectral structures above 200 meV might reflect high frequency vibrons, or else they might be due to an electronic splitting, in analogy to the interpretation of the PE spectrum of $Fe(CO)_5$ in cited Ref. [23]. The observed splittings would be in the same range ($\approx$ 180 meV) as the computed electronic JT splitting of Fig. 3 of Ref. [3]. A full calculation of the spectrum that will include both low-energy (tunneling) and high-energy "electronic" splittings could, in principle, be done based on Fermi's golden rule [4] but is at present still unavailable.

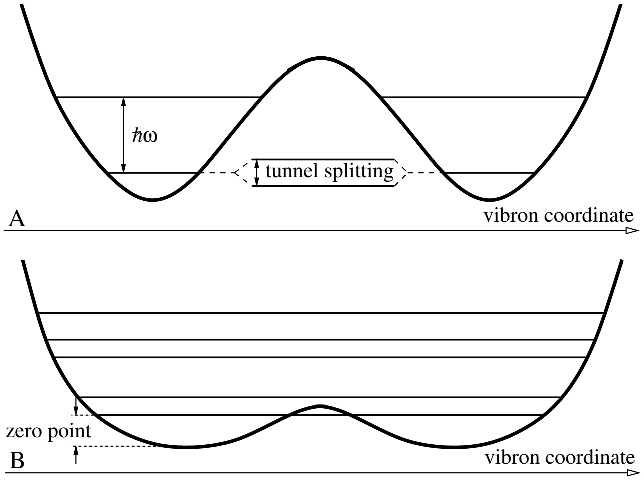

FIG. 1. A pictorial of (a) tunneling and (b) extended anharmonic excitations.

In summary, it would seem that the three-peak structure, though certainly related to DJT, does not particularly provide evidence for tunneling among D_{3d} valleys as claimed. A full explanation of this spectrum must await further work.

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