Supporting information

Isomeric broadening of C_{60}^+ electronic excitation in helium droplets: experiments meet theory

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Details of the CASSCF calculation

The C_{60}^+ ion was treated within the C_{2h} symmetry subgroup of its full symmetry group I_h. Only excitation within up to 14 orbitals that are fully occupied in C_{60} were considered as preliminary calculations showed that excitation into unoccupied orbitals lie higher in energy.

The ground state of C_{60}^+ is five-fold degenerate, with state symmetry of 3xA_u and 2xB_u, corresponding to the h_u representation in I_h (five-fold degenerated state, antisymmetric with respect to the inversion operation). The first excited state lies at 1.68 eV and is also five-fold degenerate, with state symmetry of 3xA_g and 2xB_g, corresponding to the h_g representation in I_h.

A second excited state can be found at 2.04 eV, it is four-fold degenerate and composed of 2xA_g and 2xB_g states, corresponding to the g_g representation in I_h (as calculated at the CASSCF(27,14) level of theory, i.e. including 5xh_u, 5xh_g, and 4xg_g orbitals into the active space).

Excitation energies are shifted by about 0.4–0.5 eV from the experimental values[1,2] due to the missing dynamic electron correlation energy. Both $h_u - h_g$ and $h_u - g_g$ excitations are allowed.

(1) Cataldo, F.; Iglesias-Groth, S.; Manchado, A.; *Fullerenes, Nanotubes, and Carbon Nanostructures 20*, **2012**, 565.

(2) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y.; *Chem. Phys. Lett. 180*, **1991**, 446.

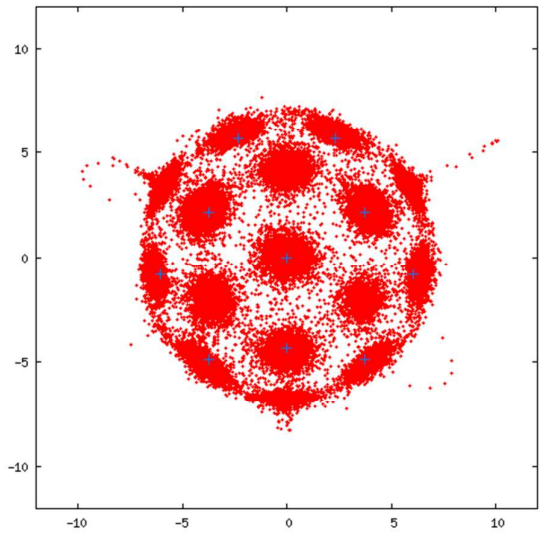

Figure 1S. Positions of He atoms along a $He_{12}C_{60}^{+}$ PIMD trajectory at T = 5 K.

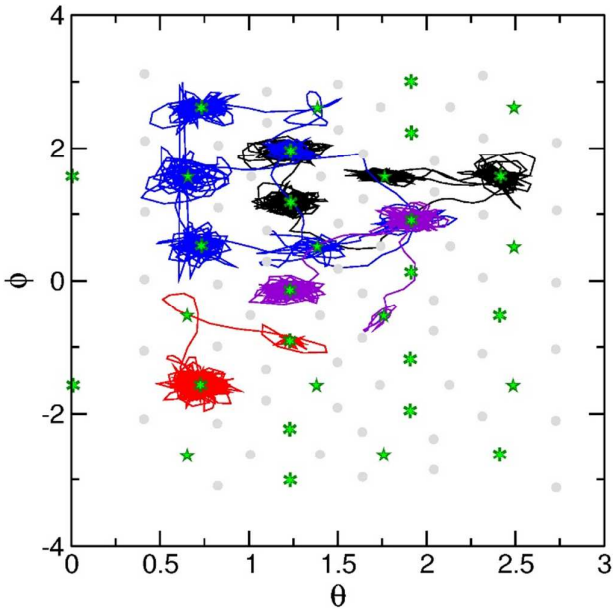

Figure 2S. PIMD trajectories of He atoms in a 2D projection for a calculation of $He_{12}C_{60}^{+}$. The helium avoids carbon positions (gray dots) and prefers hexagonal (6 pointed star) or pentagonal (5 pointed star) binding positions. Helium can change from one binding site to another, an effect which can be due either to kinetic energy values overcoming the small barrier or to quantum tunneling of the He atom between the two sites.

Table 1S. Parameters (in a.u.) of the He-C interaction potential for $He_nC_{60}^+$ PIMD simulations.

A	92.15
b	2.1145
C_6	10.99
C_8	0.105
α (a_0^3)	1.383