REVISITING THE GROUND STATE SYMMETRY OF C_{60}^{+} VIA VUV PHOTOIONIZATION AND DFTB CALCULATIONS

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Recently we reviewed and studied the photoionization dynamics of C_{60} that are of great interest to the astrochemical community as four of the diffuse interstellar bands have been assigned to electronic transitions in the C_{60}^{+} cation. However, there is still ambiguity about the absolute ground state symmetry of the C_{60}^{+} cation and our previous analysis appeared to indicate D_{3d} symmetry in stark contrast to theoretical predictions of D_{5d} symmetry. We have revisited our experimental measurements to compare with theoretical works of the frequencies of the hg Jahn-Teller active modes which couple to the $2H_u$ ground state of the C_{60}^{+} cation. By reanalyzing our measured threshold photoelectron spectrum (TPES) of the ground state of C_{60}, we find a striking resemblance to the theoretical spectrum and we provide tentative assignments for many of the h_g modes. In light of both the high temperature of our experiment and that the ab initio works could not account for anharmonicities, we also performed Molecule Dynamics (MD) simulations with the Density Functional based Tight Binding (DFTB) potential to assess the effects of temperature on the vibrational bands of C_{60} and C_{60}^{+} and derive anharmonicity factors to aid the interpretation of our measured TPES and the comparisons to the ab initio spectrum. We showcase the complementarity of utilizing MD calculations to predict the anharmonicities at high temperatures expected in our experiment. This allows us to provide robust evidence for a D_{5d} symmetric ground state of the C_{60}^{+} cation, rather than a D_{3d} symmetric minimum which has been proposed in other experiments. This allows us to assign the first adiabatic ionization transition and thus determine the ionization energy of C_{60} with greater accuracy than has been achieved at 7.595 $\pm$ 0.003 eV; and postulate on the energetics of additional DIBs that could be assigned to C_{60}^{+} in the future.