

Experimental evidence of a dynamic Jahn-Teller effect in $D_{3d} C_{60}^+$

S.E. Canton^{1,2}, A.J. Yencha⁴, M.C.A. Lopes⁵,
E. Kukk³, J.D. Bozek¹, G. Snell² and N. Berrah²

¹ Lawrence Berkeley National Laboratory, Advanced Light Source,
University of California, Berkeley CA 94720.

² Department of Physics, Western Michigan University, Kalamazoo MI 49008.

³ Department of Physical Sciences, Oulu University, Linnanmaa, Oulu FIN-90570, Finland.

⁴ Department of Chemistry, State University of New-York at Albany, Albany NY 122222

⁵ Departamento de Fisica, ICE, Universidade Federal de Juiz de Fora, Juiz de Fora-MG,
CEP 36036-330 Brazil.

INTRODUCTION

Since its discovery in 1985, C_{60} has been the subject of intense studies. Most of its astonishing properties can be explained by its particular electronic structure. However, very little is known about C_{60}^+ , which is of great interest for astrophysics and solid state physics. Characteristics as fundamental as the shape of the cation are still under debate. Because of its high symmetry, C_{60}^+ experiences a Jahn-Teller distortion and the Born-Oppenheimer approximation commonly used to obtain adiabatic potential energy surfaces is not applicable in this case. A recent analytical model [2] predicts different equilibrium geometry depending on the electron-phonon coupling strength. The number of vibronic states is shown to be directly correlated to the geometry. We have recently measured the valence photoelectron spectrum of C_{60} . The three-peak structure of the Highest Occupied Molecular Orbital (HOMO) is clearly resolved and strongly supports a D_{3d} geometry for C_{60}^+ in its ground state.

EXPERIMENT

The experiment was performed on beamline 10.0.1 at the ALS. A resistively heated oven generated an effusive beam of C_{60} . The photoelectron spectra were recorded in a crossed beam configuration using a Scienta SES-200 hemispherical analyzer at the magic angle. The spectrometer was operated at 20 eV pass energy and the photon resolution was set to 10 meV.

RESULTS

Semi classical and ab-initio calculations agree to attribute H_u symmetry to the highest occupied molecular orbital (HOMO) of C_{60} . The JT active modes are then of h and g symmetry. As this outermost orbital is highly delocalized over the rigid frame of 60 carbon atoms, any distortion is supposed to be small and the resulting ionized states are going to be best described as originating from a dynamic JT effect. The corresponding static $H \otimes (h \oplus g)$ JT problem was investigated analytically [1]. Minimization of the adiabatic energy surface for this problem results in wells of either D_{5d} or D_{3d} symmetry depending on the coupling strength. The dynamic JT problem can then be solved in the tunneling regime [2] to find the I_h symmetrized combinations of the states associated with the wells. The findings are the following: if the coupling is very strong, the absolute minimum has a D_{3d} symmetry and there are 3 tunneling states of A (not degenerate), G (4 times degenerate) and H (5 times degenerate) symmetry. In the case of weaker coupling, the absolute minimum is of D_{5d} symmetry and there are 2 tunneling states of A and H symmetry.

The present analysis of the bandshape in photoelectron spectra recorded at the magic angle strongly supports the first experimental evidence of a D_{3h} equilibrium geometry. The fitting procedure with asymmetric gaussians (Fig 1), allows the extraction of 3 bands I, II and III of area in the 1:4:5 ratio, corresponding to the tunneling states. An attempt to model the envelope with only 2 underlying peaks fails to reproduce the overall shape and doesn't give the areas in the 1:5 ratio. This rules out the possibility of a D_{5h} geometry predicted by an INDO calculation [3] and raises the question of the validity of the perturbative approach often used to derive some of the properties of this material, as the D_{3h} geometry is the signature of a strong electron-phonon interaction [2].

REFERENCES

- [1] A. Ceulemans, P.W. Fowler, J. Chem. Phys. **93**, 1221 (1990).
- [2] C. P. Moate et al, J. Phys. Condens. Matter **9**, 6049 (1997).
- [3] R.D. Bendale et al, Chem. Phys. Lett., **194**, 467 (1992).

ACKNOWLEDGEMENTS

M.C.A. Lopes gratefully acknowledges financial support from CNPq (Brazil)
This work was funded by the Department of Energy, Office of Science, Basic Energy Sciences, Chemical Science Division, under the contract No. DE-AC03-76SF00098.

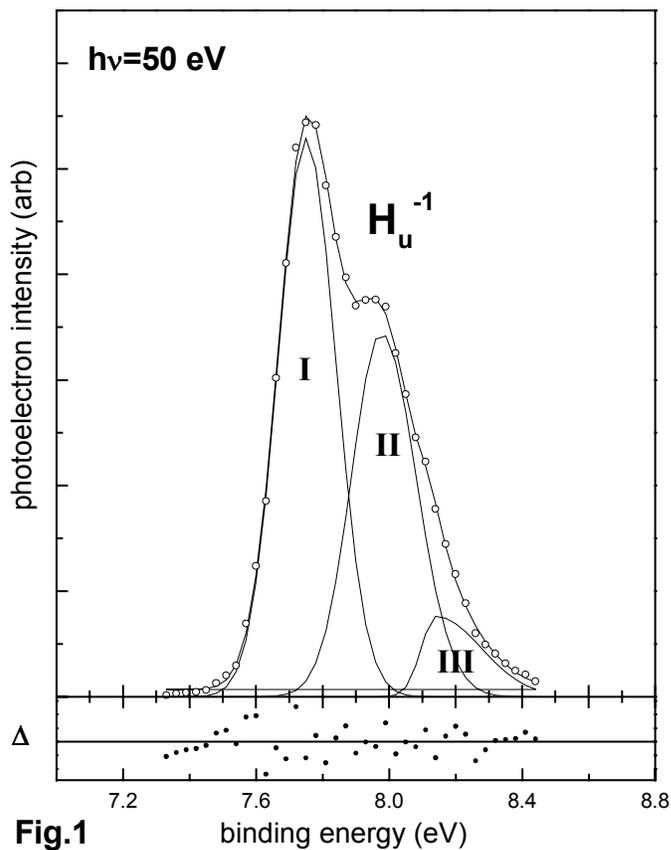


Fig.1: Fit of the HOMO band by three asymmetric gaussians. Δ indicates the difference between the data points and the fit.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Principal investigator: Nora Berrah, Western Michigan University. Email: berrah@wmich.edu.
Telephone: 616-387-4955.