

Resonant excitation x-ray fluorescence from C₆₀

J.-H. Guo, P. Glans, P. Skytt, N. Wassdahl, and J. Nordgren
Department of Physics, Uppsala University, Box 530, S-751 21 Uppsala, Sweden

Y. Luo and H. Ågren
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

Y. Ma
*Physics Department, University of Washington, Seattle, Washington 98195
and Molecular Science Research Center, Pacific Northwest Laboratories, Richland, Washington 99352*

T. Warwick and P. Heimann
Lawrence Berkeley Laboratory, Berkeley, California 94720

E. Rotenberg
Department of Physics, University of Oregon, Eugene, Oregon 97403

J. D. Denlinger
*Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211
(Received 25 August 1994; revised manuscript received 5 June 1995)*

X-ray fluorescence of condensed C₆₀ has been recorded in high resolution using monochromatic synchrotron radiation excitation. Strong intensity modulation of constituent spectral features is observed with varying excitation energy up to 10 eV above threshold. The energy dependence is interpreted as due to resonant inelastic x-ray scattering, leading to symmetry selection rules governing the two-photon process in the fully symmetric molecule.

The C₆₀ molecule (fullerene) has the interesting form of a soccerball, with icosahedral (I_h) symmetry in its ground state.¹ In the condensed phase (fullerite), the C₆₀ molecules form van der Waals intermolecular bonds, which are much weaker than the molecular bonds, and IR and Raman spectroscopy studies have indeed shown that the soccerball-shaped structure is retained in the condensed phase.^{2,3} Also, band formation in fullerite is not pronounced and dispersion has been predicted to be small.⁴ Resonant photoemission spectroscopy⁵ and electron-energy-loss spectroscopy⁶ have been used to study the electronic structure of C₆₀. The electronic structure has also been examined theoretically (see, e.g., Refs. 7 and 8). Both the theoretical and the experimental results indicate that the electronic structure of fullerenes is only affected slightly by solidification. The molecular properties of C₆₀ are thus expected to be important for its x-ray emission spectrum, a notion that is confirmed by observations in nonselectively excited emission spectroscopy.⁹⁻¹²

Great progress has been made on the resonant x-ray fluorescence spectroscopy, since the first observation of narrow-bandpass resonant photon emission.¹³ In the present work, we report on resonance x-ray fluorescence measurements of C₆₀. We propose that the resonant x-ray emission of C₆₀ is strongly affected by resonant inelastic x-ray scattering (RIXS), and that the RIXS structure reflects the symmetry of the orbitals engaged in the process by a $1=0, \pm 2$ parity conserving selection rule. Our observations suggest that RIXS is another method of

studying molecular electronic structure in C₆₀ and other molecular systems, and of making assignments of observed spectral features in molecules with an element of symmetry.

The experiments were performed at beamline 7.0 of the Advanced Light Source, Lawrence Berkeley Laboratory. This beamline is comprised of a 5-m, 5-cm-period undulator and a 10 000-resolving-power spherical grating monochromator covering the spectral range from 100 to 1300 eV.¹⁴ The sample was made *in situ* by vacuum evaporation of C₆₀ on a clean stainless steel surface in the experiment chamber. The temperature of the evaporation source was slowly increased to 300 °C for outgassing. The C₆₀ was then evaporated at about 380 °C. The evaporated film with thick enough so that the Fe-substrate $L_{2,3}$ emission lines could not be observed with 3-keV electron-beam excitation. The soft-x-ray fluorescence was recorded in the polarization plane and normal to the incident photon beam, using a high-resolution grazing-incidence grating spectrometer with a two-dimensional detector.¹⁵ The sample was oriented so that the incident photon beam was at an angle of $\sim 70^\circ$ relative to the surface normal, in order to suppress effects due to self-absorption.¹⁶ The bandpass of the exciting photon beam was set to ~ 0.15 and ~ 0.22 eV, respectively, for absorption and emission measurements, and the fluorescence spectrometer resolution was ~ 0.56 eV. The energy scale in the x-ray emission spectra was calibrated using the elastic peak, as well as Cr $L_{2,3}$ emission lines obtained from an electron-beam-excited reference standard and

recorded in the second order of diffraction.

The inset in Fig. 1 displays the x-ray absorption spectrum of solid C_{60} , obtained by measuring the total x-ray fluorescence yield. The spectrum has been normalized to the photocurrent from a clean gold mesh introduced in the synchrotron radiation (SR) beam in order to correct for intensity variations in the excitation beam. The energy scale was calibrated by aligning the first absorption peak at 284.5 eV, a value determined by resonant photoemission measurements of Brühwiler *et al.*⁵ The spectrum is in good agreement with those from other high-

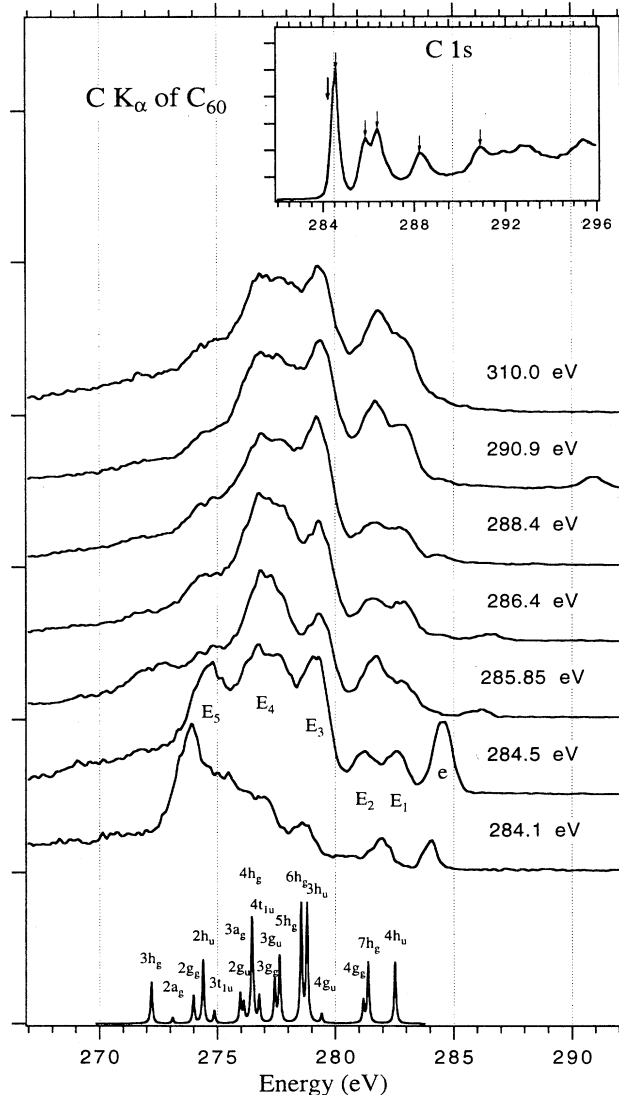


FIG. 1. X-ray fluorescence spectra of fullerite for various excitation energies. The resolution of monochromator and spectrometer are 0.22 and 0.56 eV, respectively. The fluorescence spectra have been obtained by taking the average of three consecutive channels. Results from *ab initio* calculations of x-ray emission from C_{60} are displayed at the bottom (the symmetries of the molecular orbitals are indicated in the figure). The inset shows the x-ray-absorption spectrum of fullerite recorded by measuring the total electron yield. The arrows indicate the excitation energies at which x-ray fluorescence spectra were recorded.

resolution x-ray-absorption spectroscopy measurements,^{6,17,18} indicating that the film was of good quality. We observe four peaks below the ionization threshold at 290.5 eV.¹⁹ The first absorption peak, at 284.5 eV, has been assigned to the lowest unoccupied molecular orbital (LUMO). The LUMO has t_{1u} symmetry in the icosahedral (I_h) point group that the C_{60} molecule assumes in its ground state. The second absorption peak, at 286.0 eV, has been assigned to the second lowest unoccupied orbital with t_{1g} symmetry. The third absorption peak appearing at 286.6 eV represents the third and fourth unoccupied orbitals, with t_{2u} and h_g symmetries, respectively, t_{2u} giving the largest contribution to the peak. The fourth absorption peak at 288.4 eV corresponds to unoccupied orbitals with symmetries a_g , h_u , g_g , g_u , and t_{2g} where a_g dominates the feature. The bars indicate the excitation energies at which the C K emission spectra of C_{60} were recorded.

The fluorescence spectra, excited at various photon energies near threshold, are displayed in Fig. 1. The spectral intensities show a strong dependence on the excitation energy, especially below the ionization threshold. While energies of the different bands seem to change only by small amounts. Quite large energy shifts were obtained in the Cl $K\beta$ resonant x-ray emission spectra from $CFCl_3$ vapor,²⁰ which could be explained in terms of perturbation effects due to the presence of an electron in the first unoccupied MO.²⁰ The small change in energy positions in the spectra of C_{60} can be explained as due to small interaction strengths between the excited and the occupied electrons, something which is likely to be the case for such a large molecule. For assignments of the symmetry character of C_{60} molecular orbitals, the calculated x-ray emission spectrum of the C_{60} molecule in an *ab initio* Hartree-Fock frozen model is shown at the bottom.¹² In all cases, we are probing the bulk properties of the sample, which means that surface contamination effects should be small. We also do not observe any variations of the spectra with time, indicating that sample damage caused by irradiation is negligible. The main effect seems to be an intensity variation of the different features in the spectra, similar to the observation of strong excitation-energy dependence in the x-ray fluorescence spectra of diamond²¹ and of the highly oriented pyrolytic graphite.²² The proposed explanation for the variations in those cases was based on considering the x-ray fluorescence as a scattering process, in which the momentum of the electron-hole pair and the momentum transfer from the photons are related by momentum conservation.²³ We propose that the x-ray emission spectra of fullerite also can be treated in terms of inelastic scattering of the C_{60} molecule. The RIXS process in the molecule is the one-step correspondence to a transition of a core electron into an unoccupied molecular orbital (MO) and the subsequent emission caused by the transition of a valence-electron from an occupied MO to the core hole. The parity of the molecule is conserved in the case of resonant inelastic scattering. As a result, there exists a strong symmetry correlation between unoccupied and occupied MO's, which take part in the RIXS process, ap-

pearing as an $l=0, \pm 2$ selection rule of the x-ray process. A general theoretical description of resonant inelastic scattering of x rays for molecules, including polarization effects, can be found in the references.^{24,25}

The molecular orbitals of the ground-state C_{60} has been assigned in terms of the I_h point group on several occasions in literature, see, e.g., Refs. 4, 12, and 26, however, still not unanimously. The RIXS spectra presented in Fig. 1 contain five pronounced features, labeled with E_1 , E_2 , E_3 , E_4 , and E_5 . Based on *ab initio* calculations of Ref. 12, the first feature E_1 corresponds to the highest occupied molecular orbital with $4h_u$ symmetry, while the second feature E_2 represents a combination of the nearly degenerate $4g_g$ and $7h_g$ orbitals. Features E_3 and E_4 contain more complicated molecular-orbital combinations as shown in Fig. 1. Feature E_5 contains the $2h_u$, $3t_{1u}$, and $2g_g$ orbitals. A strong excitation-energy dependence for all these features can clearly be discerned. At the photon energy of 284.5 eV, the core electron has been resonantly excited to the LUMO level (t_{1u}). According to the parity selection rule for RIXS transitions, i.e., only the valence MO's with the same parity as the unoccupied MO are transition allowed, one can expect that feature E_2 should be absent. However, this is not the case in the spectrum of Fig. 1 which, on the contrary, presents a quite significant intensity for E_2 . This indicates that contributions from symmetry forbidden (Jahn-Teller induced) vibrational levels, the frequencies of which are in the order of 0.1–0.2 eV, have taken part in this scattering process. To examine the possibility of the interference in the RIXS spectrum for the LUMO level from these vibrational levels, an excitation energy has been selected below the first absorption peak at 284.1 eV. For this energy, the contribution from the nearby vibrational levels should then expectedly be strongly decreased. Indeed, it can be seen from the spectrum that feature E_2 is hardly observable at this excitation energy, whereas the LUMO symmetry allowed E_1 feature still is, thus proving that E_2 does not originate from pure symmetry of the LUMO zero level. At a photon energy of 286.0 eV, where the core electron is excited to the LUMO+1 (t_{1g}) level, the intensity of E_2 gets stronger and E_1 gets weaker (but is

still present, due to tail excitation). An important observation concerning E_5 that can be drawn from Fig. 1 is that this feature is clearly resolved at the photon energy of 284.5 eV, but becomes only a shoulder for other excitation energies. This E_5 feature thus correlates strongly with the excitation to the LUMO level, which is of t_{1u} symmetry. Since E_5 contains important ungerade contributions ($3t_{1u}$ and $2h_u$), we take this as a confirmation of the parity selection rules operating for RIXS spectra.

In the second (286.0 eV) and third (286.6 eV) absorption spectra the elastic peak is much weaker, and in the fourth absorption spectrum (288.4 eV), it is barely noticeable. The strength of the elastic peak should be dependent on the degree of localization of the excited electron at the core hole site. The strong intensity found for the elastic peak at the first absorption threshold indicates that the LUMO derived states are more "excitoniclike" than the higher unoccupied states.

In summary, we have reported the x-ray fluorescence spectra of condensed C_{60} , using energy selective excitation. The spectral profiles of the x-ray fluorescence exhibit a strong photon-energy dependence near the carbon K edge. This photon-energy dependence is interpreted in terms of resonant inelastic x-ray scattering. We propose that resonant inelastic x-ray scattering can be used as an experimental method to study the electronic structures of molecules with an element of symmetry.

This work was supported by the Swedish Natural Science Research Council (NFR) and the Göran Gustafssons Foundation for Research in Natural Science and Medicine. These experiments were initiated at Brookhaven National Laboratory and we would like to thank P. D. Johnson, K. J. Randall, and Z. Xu for assistance. The National Synchrotron Light Source was under DOE Contract No. DE-AC02-76CH00016. The work at ALS, Lawrence Berkeley Laboratory was supported by the director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

¹H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985); W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman; *ibid.* **347**, 354 (1990).

²W. Krätschmer, K. Fostiropoulos, and D. R. Huffman, *Chem. Phys. Lett.* **170**, 167 (1990).

³D. S. Bethune, G. Meijer, W. C. Tang, and H. J. Rosen, *Chem. Phys. Lett.* **174**, 219 (1990).

⁴S. Saito and A. Oshiyama, *Phys. Rev. Lett.* **66**, 2637 (1991).

⁵P. A. Brühwiler, A. J. Maxwell, A. Nilsson, R. L. Whetten, and N. Mårtensson, *Chem. Phys. Lett.* **193**, 311 (1992); S. Krummacher, S. Cramm, K. Szot, W. Eberhardt, and W. Krätschmer, *Europhys. Lett.* **16**, 437 (1991); S. L. Molodtsov, A. Gutierrez, M. Domke, and G. Kaindl, *ibid.* **19**, 369 (1992).

⁶E. Sohmen, J. Fink, and W. Krätschmer, *Europhys. Lett.* **17**, 51 (1992); G. Gensterblum, J. J. Pireaux, P. A. Thiry, R. Cau-

dano, J. P. Vigneron, Ph. Lambin, A. A. Lucas, and W. Krätschmer, *Phys. Rev. Lett.* **67**, 2171 (1991).

⁷B. Wästberg and A. Rosén, *Phys. Scr.* **44**, 276 (1991).

⁸S. Satpathy, *Chem. Phys. Lett.* **130** 545 (1986); Q.-M. Zhang, J.-Y. Yi, and J. Bernholc, *Phys. Rev. Lett.* **66**, 2633 (1991); J. L. Martins, N. Troullier, and J. H. Weaver, *Chem. Phys. Lett.* **180**, 457 (1991).

⁹J. Kawai, K. Maeda, M. Takami, Y. Muramatsu, T. Hayashi, M. Motoyama, and Y. Saito, *J. Chem. Phys.* **98**, 3650 (1993).

¹⁰E. Z. Kurmaev and S. N. Shamin, *Physica C* **195**, 352 (1992).

¹¹G. Wiech, H. Langer, and A. Simunek, *Solid State Commun.* **83**, 731 (1992).

¹²J.-H. Guo, Y. Luo, O. Vahtras, P. Skytt, N. Wassdahl, H. Ågren, and J. Nordgren, *Chem. Phys. Lett.* **227** 98 (1994).

¹³P. Eisenberger, P. M. Platzman, and H. Winick, *Phys. Rev. Lett.* **36**, 623 (1976).

- ¹⁴T. Warwick, P. Heimann, D. Mossessian, and H. Padmore (unpublished).
- ¹⁵J. Nordgren and R. Nyholm, Nucl. Instrum. Meth. Ser. A **246**, 242 (1986); J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.-E. Rubensson, and N. Wassdahl, Rev. Sci. Instrum. **60**, 1690 (1989).
- ¹⁶C. Bonnelle, Ann. Phys. (Paris) **1**, 439 (1966).
- ¹⁷L. J. Terminello, D. K. Shuh, F. J. Himpsel, D. A. Lapiano-Smith, J. Stöhr, D. S. Bethune and G. Meijer, Chem. Phys. Lett. **182**, 491 (1991).
- ¹⁸C. T. Chen, L. H. Tjeng, P. Rudolf, G. Meigs, J. E. Rowe, J. Chen, J. P. McCauley, Jr., A. B. Smith III, A. R. McGhie, W. J. Romanow, and E. W. Plummer, Nature **352**, 603 (1991).
- ¹⁹J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, T. R. Ohno, G. H. Kroll, N. Troullier, R. E. Haufler, and R. E. Smalley, Phys. Rev. Lett. **66**, 1741 (1991).
- ²⁰R. C. C. Perera, R. E. LaVilla, P. L. Cowan, T. Jach, and B. Karlin, Phys. Scr. **36**, 132 (1987).
- ²¹Y. Ma, N. Wassdahl, P. Skytt, J.-H. Guo, J. Nordgren, P. D. Johnson, J.-E. Rubensson, T. Böske, W. Eberhardt, and S. D. Kevan, Phys. Rev. Lett. **69**, 2598 (1992).
- ²²P. Skytt, P. Glans, D. Mancini, J.-H. Guo, N. Wassdahl, J. Nordgren, Y. Ma, and P. D. Johnson (unpublished).
- ²³P. D. Johnson and Y. Ma, Phys. Rev. B **49**, 5024 (1994); Y. Ma, *ibid.* **49**, 5799 (1994).
- ²⁴F. Gel'mukhanov and H. Ågren, Phys. Rev. A **50**, 1129 (1994).
- ²⁵T. Åberg and B. Crasemann, in *X-ray Resonant (Anomalous) Scattering*, edited by K. Fischer, G. Materlik, and C. Sparks (Elsevier, Amsterdam, 1993).
- ²⁶R. L. Disch and J. M. Schulman, Chem. Phys. Lett. **125**, 465 (1986).