Fine structure of K_3C_{60} photoionization cross-section oscillations*

LI Hong-Nian(李宏年)[1;1)] YING Li-Jian(应理建)[1] NI Jing-Fu(倪敬付)[1] LI Gang(李刚)[1]
WANG Peng(王鹏)[1] KURASH Ibrahim(奎热西·易卜拉欣)[2] QIAN Hai-Jie(钱海杰)[2]

1 (Department of Physics, Zhejiang University, Hangzhou 310027, China)
2 (Laboratory of Synchrotron Radiation, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China)

Abstract The synchrotron radiation angle-resolved photoemission data of K_3C_{60} single crystal film are analyzed, aiming at the photoionization cross-sections of the LUMO, HOMO and HOMO-1 bands in low photon energy region (14.5—27.5 eV). Many fine structures of the HOMO/HOMO-1 intensity ratios are observed, which support the general validity of a quantum chemistry model. However, the experimental data and the theoretical results have some disagreement in the energy positions and magnitudes of the fine structures, and the disagreement is more outstanding than the case of pure C_{60}. So the photoemission data of K_3C_{60} afford valuable experimental reference to further theoretical developments. The LUMO cross-section data, which cannot be discussed with the quantum chemistry description due to strong solid state effects, are also reported for further studies.

Key words photoionization cross-section, fine structure, K_3C_{60}

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1 Introduction

One fascinating phenomenon of C_{60} is the photoionization cross-section oscillations[1, 2]. Most recently, we[3] have observed fine structures of the oscillations for the highest-occupied-molecular-orbital (HOMO) and HOMO-1 derived bands in low photon energy region (13.0—34.0 eV). The cross-sections in the low energy region can vary significantly within several electron-volts (photon energy)[3], in comparison with the usual oscillations[1, 2] having the periods greater than 20 eV. The observation of the fine structures verified the general validity of a quantum chemistry model[4—6] in low photon energy region, and indicated that other theoretical models[7—10] were only applicable in high photon energy region (e.g., greater than 40 eV). The necessity of further developments of theoretical models was also suggested[3]. In this paper, we extend our work to the case of K_3C_{60}.

The lowest-unoccupied-molecular-orbital (LUMO) derived band of C_{60} is half filled by the charge transfer of K 4s electrons in K_3C_{60}. The band filling does not change the symmetries and angular momenta of the HOMO and HOMO-1 orbitals, and we can expect the fine structures also exist for K_3C_{60}. On the other hand, the filling of the LUMO band surely alters the collective excitation (plasmon and screening effects) of C_{60} molecule because of the increased number of valence electrons, and thus the HOMO and HOMO-1 cross-sections should have some differences from that of pure C_{60}. The differences are valuable to a thorough understanding of the photoionization cross-sections.

Solid state effects are minor (even negligible) for the photoionization cross-sections of the HOMO and HOMO-1 bands, since the experimental data of solid C_{60}[1] and C_{60}-related materials[11, 12] were almost the same as that of gas-phase C_{60}[2]. On the other side, the photoionization cross-sections of the LUMO band (the conduction band of metallic K_3C_{60}) should be affected significantly by solid state effects, and might not be interpreted by the existing models[4—10]. The

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1) E-mail: phylihn@public.zju.edu.cn

present work affords the experimental data for further studies.

2 Experimental data

Sample preparation and PES measurements have been published elsewhere[13]. Briefly, a K_3C_{60} film with thickness of ~30 nm was prepared on the (111) surface of a C_{60} single crystal[14] by deposing K atoms onto the sample surface under room temperature. The synchrotron radiation angle-resolved photoemission spectra (SRARPES) were measured at normal emission with a sample temperature of 150 K. The angle between the photon beam line (the 4B9B Beamline of Beijing Synchrotron Radiation Facility) and the direction of the normally emitted photoelectrons was 45°. Fig. 1 shows the experimental data measured with photon energies from 14.5 eV to 27.5 eV and small increment of 0.5 eV (spectra measured with photon energies less than 14.5eV have too strong background to be analyzed, and are not shown here). Part of the experimental data was reported in [13] to study the LUMO band structure, whereas in this paper the spectra are used to study the photoionization cross-sections. Please note that a correction of the Fermi level (E_f) position has been carried out in Fig. 1 as compared with that in [13] (the spectra reported in [13] should have been shifted to lower binding energy by 0.2 eV).

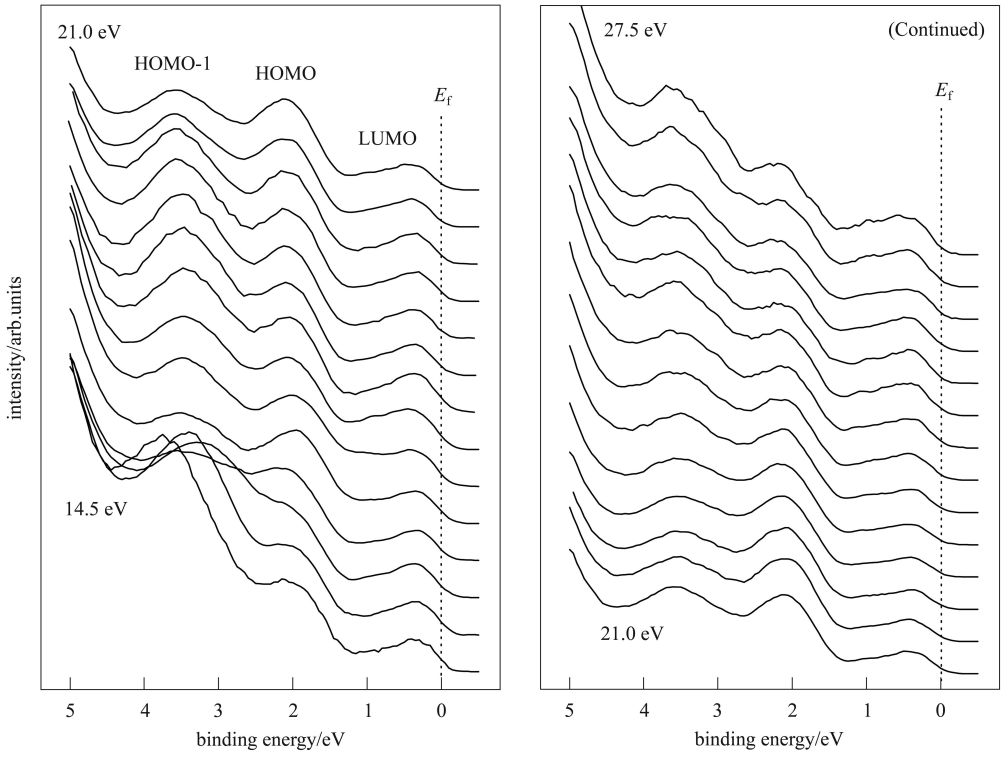

Fig. 1. Angle-resolved synchrotron radiation photoemission spectra of K_3C_{60} single crystal film. The increment of photon energy is 0.5 eV from 14.5 eV to 27.5 eV.

3 Analyses and discussion

The spectral lines in Fig. 1 are normalized to the height of the HOMO band, and the intensities of the HOMO-1 and LUMO bands vary with photon energies. For example, the HOMO/HOMO-1 ratio of the spectrum measured with $h\nu = 16.5$ eV is obviously larger than that of the spectrum measured with $h\nu = 19.5$ eV. To obtain the quantitative spectral intensities of the LUMO, HOMO and HOMO-1 bands, we carried out a rather sophisticated fitting procedure, as schematically illustrated in Fig. 2(a) for the spectrum recorded with the photon energy of 20.5 eV as representative.

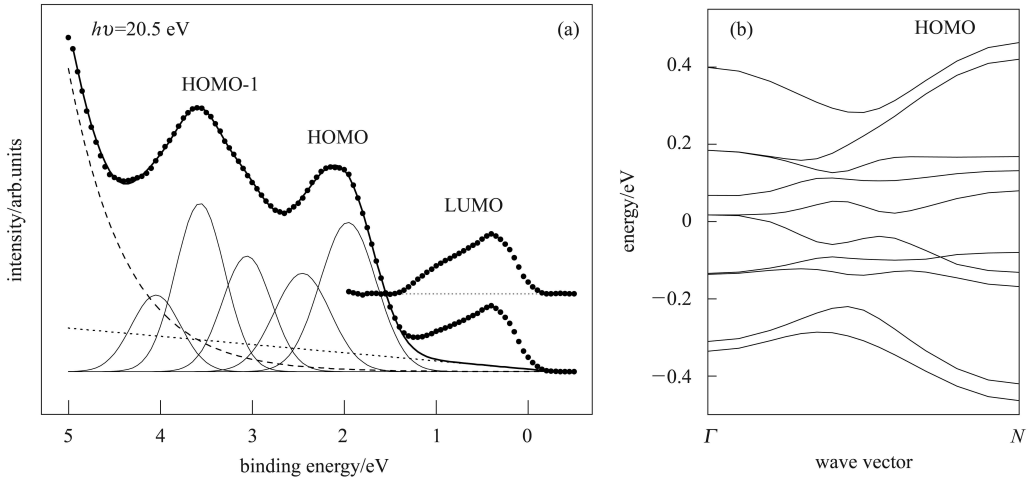

Fig. 2. (a) Illustration of the spectral intensity determination. The scattered dots are the experimental data. The bold solid line is the fitted curve to the HOMO, HOMO-1 bands and the background. The LUMO band is obtained by subtracting the experimental data by the fitted curve. (b) HOMO band structure along the Γ-N direction calculated with the tight-binding method. The zero of the vertical axis corresponds to the energy of the HOMO orbital before splitting.

We used two and three Gaussian functions to simulate the HOMO and HOMO-1 band, respectively. The number of the Gaussian functions is a compromise of the complicated band structures and the reliability of the mathematical simulation. Fig. 2(b) exhibits the HOMO band structure along the Γ-N direction (corresponding to the experimental measurements[13]), which was calculated with the same method as [13]. The HOMO band has a bandwidth of ∼0.9 eV that is made up of 10 subbands. The HOMO-1 band has 18 subbands (the band dispersions not calculated in this work) and should have an even broader bandwidth. The centroids of the HOMO and HOMO-1 bands are separated by only ∼1.5 eV (see Figs. 1 and 2(a)). Therefore, some subbands of the two bands may locate very near in the spectrum. This situation intrinsically limits the accuracy of the curve fitting. If we use too many Gaussian functions in the simulation, large number of adjustable parameters will make the simulation unreliable. On the other hand, a simulation with too few Gaussian functions can incorrectly ascribe some of the spectral weight near the dip (∼2.7 eV) to one of the two bands. We think the number of the Gauss components (thin solid lines) in Fig. 2(a) is appropriate although the simulation accuracy cannot be better than the case of pure C_{60}[3]. To further minimize the number of adjustable parameters, the simulation procedure was only applied to the HOMO and HOMO-1 bands. The LUMO band was then obtained by subtracting the experimental data (the scattered line) by the fitted curve (the bold solid line). The dotted line in Fig. 2(a) is a linear background. The background of K_3C_{60} sample is greatly stronger than the pure C_{60} sample[3], and the linear background underestimates the background for the higher binding energy part of the spectrum. However, this deficiency can be compensated by the dashed line in the figure that represents the exponential extrapolation of the low binding energy side of the HOMO-2 band and part of the background.

The determined LUMO, HOMO and HOMO-1 intensities (normalized to the summed intensities of the three bands) are shown in Fig. 3(a). Owing to the lack of absolute magnitudes of the cross-sections in this work, we show the LUMO/HOMO and HOMO/HOMO-1 intensity ratios in Fig. 3(b) that can be used to compare with the theoretical modes and be consulted by future work of other groups. For K_3C_{60}, there are 3, 10 and 18 electrons occupying the LUMO, HOMO and HOMO-1 bands (all the three bands are derived from C 2p state). If the cross-sections of these bands are identical, the LUMO/HOMO and HOMO/HOMO-1 ratios should be kept at 3/10 and 5/9, irrespective of photon energies. However, these ratios vary distinctly in Fig. 3(b). More significantly, abundant fine structures of the HOMO/HOMO-1 ratios for K_3C_{60} can be seen in Fig. 3(b), as we expected in the introduction. There are two distinct peaks located at 22.5 eV and 16.5 eV, a weak peak located at 19.0 eV, and two shoulders at 21.0 eV and 24.0 eV, which are labeled with numbers from 1 to 5. The LUMO/HOMO ratios also exhibit some fine structures.

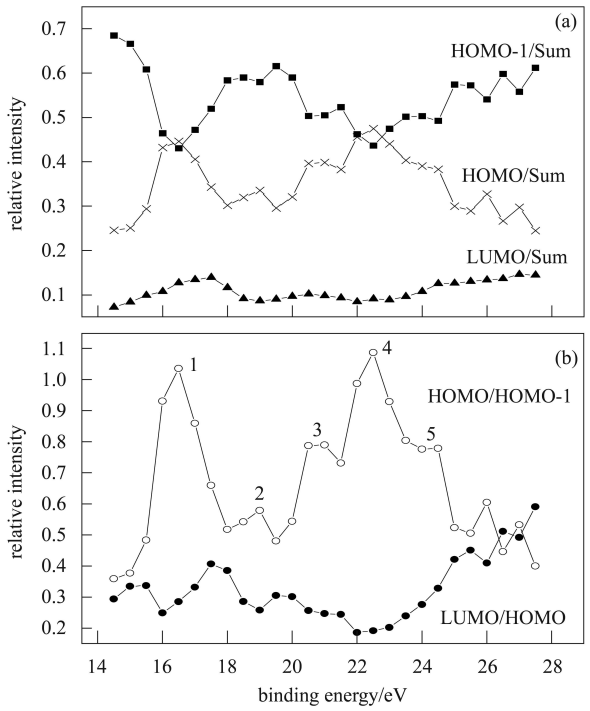

Fig. 3. (a) Experimentally determined LUMO, HOMO and HOMO-1 intensities relative to the summed intensity of the three bands. (b) LUMO/HOMO and HOMO/HOMO-1 intensity ratios.

Figure 4 compares the HOMO/HOMO-1 ratios of K_3C_{60} (open circles) with the corresponding experimental data[3] of pure C_{60} (crosses) and the ab initio quantum chemistry results calculated by Venuti et al[4]. The theoretical line in Fig. 4 has been shifted homogeneously towards higher photon energy by 1.3 eV to compare with the experimental data (the homogeneous shift is generally necessary because the absolute energy positions of the theoretical results have some uncertainties caused by calculation precision, although the precision is always good enough to assure that the relative energies between different features are converged). At the high photon energy side ($h\nu$ >20 eV), the two sets of experimental data coincide with each other fairly well (although some discrepancies exist in the HOMO/HOMO-1 magnitudes, which may be due to the simulation precision in Fig. 2.), and the energy positions of features 3 to 5 coincide with the theoretical results very well. This is what we have expected in the introduction. As the band filling does not change the symmetries and angular momenta of the HOMO and HOMO-1 orbitals, the photoionization cross-section oscillations of K_3C_{60} should be analogous with C_{60} to some extent. The HOMO/HOMO-1 magnitudes for both K_3C_{60} and C_{60} are apparently less than the calculated results, the reason for which has been already suggested in Ref. [3], and will be further discussed below. At the low photon energy side, however, the two sets of experimental data differ significantly from each other, in both magnitudes and energy positions. The comparison with the theoretical result is unsatisfactory yet. The magnitude of Feature 1 for K_3C_{60} is greater than the theoretical result, rather than the case of pure C_{60} in which this fine structure has a magnitude less than the theoretical result. The energy position of Feature 1 deviates from its theoretical counterpart by more than 1 eV (see the arrow in the figure), in comparison with the good consistence for pure C_{60}. These discrepancies reflect the different collective excitation behaviors of the two different samples, as also mentioned in the introduction.

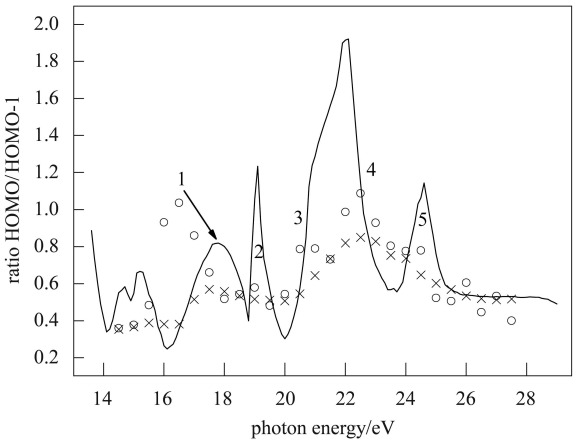

Fig. 4. Comparison of the experimental HOMO/HOMO-1 ratios with the quantum chemistry results. The scattered open circles are the experimental data of the present work (K_3C_{60}), while the crosses are the experimental data of C_{60} from Ref. [3]. The solid line is the ratios between the calculated cross-sections of the HOMO and HOMO-1 orbitals that were digitized from Ref. [4], which have been shifted homogeneously towards higher binding energy by 1.3 eV.

In Ref. [3], we verified the general validity of the quantum chemistry model (dipole transitions between the occupied and the unoccupied molecular orbitals)[4] in describing the photoionization cross-sections for low photon energy region. However, the quantum chemistry model does not cover all the physics of the photoemission process. We argued in Ref. [3] that the collective excitation plasmon and the screening effect predicted by Bertsch et al[15] can reasonably interpret the magnitude disagreement of the HOMO/HOMO-1 ratios for the pure C_{60} sample, which can also interpret the magnitude disagreement for K_3C_{60} on high energy side. Feature 1 of K_3C_{60}

in Fig.4 deviates substantially from the theoretical result and the experimental data of pure C_{60}. This reflects the fact that the number of valence electrons of K_3C_{60} differs from C_{60} and thus the collective excitation of C_{60} molecule in these two materials should have some differences. Besides, the theoretically predicted fine structures at 14.6 eV and 15.2 eV are not observed for both K_3C_{60} and C_{60}, which might be attenuated by the collective excitation, rather than the suspicion[3] that the increment of photon energy (0.5 eV) was not small enough. So, the present work adds new experimental reference to Ref. [3] for further theoretical developments.

As mentioned in the introduction, solid state effects (mainly the communization of the conduction electrons) should play an important role in the photoionization cross-sections of the LUMO band. This would be a profound topic concerning the foundational electronic structure of K_3C_{60}. K_3C_{60} is metallic. If the metallicity is mainly caused by a free electron-like band structure[13], the photon energy-dependent variations of the LUMO cross-sections in Fig.3 should be understood by usual final state effects (the initial state is the near free electron state). However, the LUMO band of K_3C_{60} is more probably a strongly correlated electron system. Only the electrons whose energy is very near the Fermi level are itinerant (the so-called coherent spectral weight in the photoemission of strongly correlated systems[16, 17]). Those electrons with relatively larger binding energy (say, between 0.5 eV and 1.3 eV) still belong to individual molecules (the so-called incoherent spectral weight in photoemission[16, 17]). Then, both the molecular property and solid state effects should play a role in the photoionization cross-sections of the LUMO band. At present, we cannot draw a definite conclusion about the origination of the remarkable photon energy-dependent variations of the LUMO/HOMO ratios in Fig. 3(b). We suggest that theoretical work ignoring the solid state effects be carried out, as the first step. After comparing the proposed theoretical results with the experimental data in Fig. 3, one may decide pertinently further research routines to thoroughly understand the photoionization cross-sections of the LUMO band.

4 Conclusions

The SRARPES data of K_3C_{60} are analyzed aiming at the photoionization cross-sections of the LUMO, HOMO and HOMO-1 bands. The HOMO/HOMO-1 intensity ratios exhibit some fine structures as the case of pure C_{60}, and thus support that the dipole transitions between the occupied and unoccupied molecular oribitals play an important role in understanding the photoionization cross-sections in low photon energy region. However, other physical processes, e.g., the collective excitation, are needed to interpret some discrepancies among the experimental data of K_3C_{60}, pure C_{60} and the quantum chemistry results. The experimental data reported in this paper can afford the reference for further theoretical development. The photoionization cross-sections of the LUMO band also show remarkable variations with photon energies, which can stimulate further work.

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