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Fine structure of C_{60} photoionization cross-section oscillations

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Abstract

We have measured the angle-resolved photoemission spectroscopy of a C_{60} single crystal in the low photon energy region from 13.0 to 34.0 eV with small increments (0.5 or 1.0 eV). The ratios of partial photoionization cross-sections for the HOMO and HOMO-1 bands exhibit many fine structures. The energy positions of the fine structures agree well with the giant resonances of dipole transition between individual molecular orbitals, which were predicted by a quantum chemistry model. The magnitudes of the HOMO/HOMO-1 ratios, however, indicate further theoretical works are still needed. The important role of collective excitation in the photoionization cross-section of C_{60} is suggested.

1. Introduction

In an early photoemission study of C_{60} film [1], Benning *et al* observed that the spectral intensities of the highest-occupied-molecular-orbital- (HOMO-) derived feature and the HOMO-1 feature oscillated with the incident photon energies. Soon after, it became a consensus that the photoionization cross-section oscillations are intrinsic to the C_{60} molecule, since the oscillations were also observed on gas-phase C_{60} [2]. Since then, experimental measurements have observed the oscillations in a large energy region from ∼20 eV to the carbon K edge (290 eV) [3]. The oscillations were also observed on monolayer C_{60} on metal surface [4] and metal-intercalated fulleride [5]. On the theoretical side, some different models have been raised to describe the oscillations, such as the spherical-standing-wave final state model [6], the jellium or spherical jellium model [3, 7], the quantum chemistry model [8–10], and the multicentered photoemission model [11]. The quantum chemistry model [8–10] predicted fine structures of the cross-section oscillations in the energy region between the

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threshold and about 25 eV above it. As the fine structures do not exist in other models, making clear its existence by experimental measurements would be of great importance to understanding the cross-section oscillations of C_{60}.

No experimental data in the literature exhibited fine structures. However, we noted that the photon energy intervals (usually larger than 2 eV) in the published works were not small enough to observe the possible fine structures. We also noted that experimental data obtained with photon energies less than 20 eV were rather sparse. In this paper, we measure the photoemission intensity ratio of the HOMO band and the HOMO-1 band of solid C_{60} in the photon energy region from 13.0 to 34.0 eV with increments of 0.5 eV (13–30 eV) or 1.0 eV (31–34 eV) to study the fine structures.

2. Experimental details

We thought a single crystal sample and angle-resolved photoemission spectroscopy were needed to study the fine structures, since the scattering effect in the solid significantly modified the angular distribution of the HOMO/HOMO-1 intensity ratio [12, 13]. The sample of the present work was a C_{60} single crystal grown with the gas-phase method [14]. One of the free (111) surfaces with size $\sim 4 \times 6$ mm^2 was cemented to a metal post, which would be used to cleave the crystal. The other parallel (111) surface was cemented to the sample holder. To avoid the charging effect, the sample was fully covered by a silver film deposited before cleavage. The C_{60} single crystal was cleaved *in situ* at pressure of $\sim 2 \times 10^{-10}$ mbar, and a clean and flat (111) surface was obtained. The incident photons were induced from the 4B9B beam line of Beijing Synchrotron Radiation Facility. An angle-resolved spherical deflection analyzer was used to collect the photoelectrons at normal emission. The angle between the photon beam line and the direction of the normally emitted photoelectrons was 45°. The overall energy resolution was 0.15–0.3 eV, depending on the photon energies.

3. Results and discussion

Figure 1 shows the synchrotron radiation angle-resolved photoemission data. The spectral lines were normalized to the height of the HOMO band, and the photoemission intensity of the HOMO-1 band oscillates with photon energies. The spectral lines recorded with the photon energies of 29.0, 29.5 and 30.0 eV have unsatisfactory signal-to-noise ratios, indicating the cross-section minima around 29.5 eV for the HOMO and HOMO-1 bands in the energy region of this work.

To obtain the spectral intensities of the HOMO and HOMO-1 bands, we carried out a sophisticated fitting procedure. Figure 2 schematically illustrates the curve fitting for the spectrum recorded with the photon energy of 21.5 eV as representative. We used two Gaussian functions to simulate the HOMO-1 band, finding that only one Gaussian function could not fit the experimental data well. The HOMO band was also simulated with two Gaussian functions although it could be fitted fairly well with one Gaussian function for some spectral lines. These fitted curves only play the role of calculating the spectral intensities as accurately as possible, and we should not overemphasize their physical meaning. The dashed line in figure 2 represents the exponential extrapolation of the low binding energy side of the HOMO-2 band. The dotted line is a linear background. The linear background is simple but efficient. The spectral weight near 3.0 and 4.7 eV cannot be fitted satisfactorily without the background.

The determined HOMO/HOMO-1 intensity ratios are shown in figure 3(a). The ratios for the spectra acquired with photon energies from 29.0 to 30.0 eV or below 14.0 eV may have non-negligible uncertainties due to the bad signal-to-noise ratios or strong backgrounds.

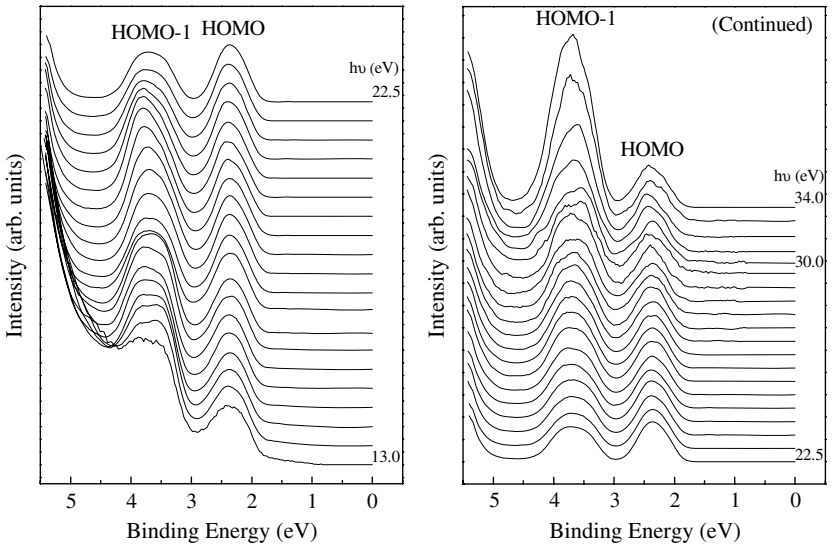

Figure 1. Synchrotron radiation angle-resolved photoemission spectra of C_{60} single crystal. The photoelectrons were recorded at normal emission. The angle between the incident photon beam and the analyzer direction was 45°. The increment of photon energy was 0.5 eV from 13.0 to 30 eV, and 1.0 eV from 30.0 to 34.0 eV.

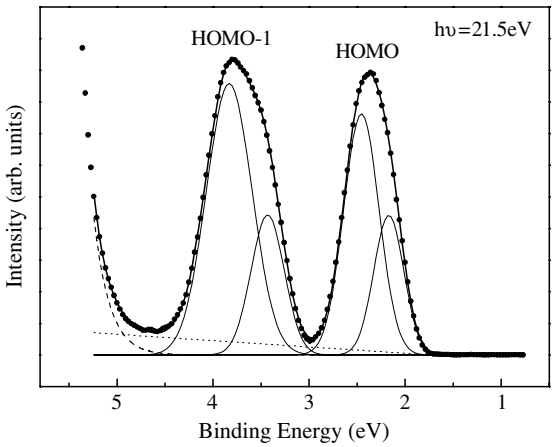

Figure 2. Illustration of the spectral intensity determination. The scattered dots are the experimental data recorded with the photon energy of 21.5 eV as representative, and the bold solid line is the fitted curve. Both the HOMO band and the HOMO-1 band are fitted with two Gaussian functions (thin solid lines). The low binding energy side of the HOMO-2 band is simulated with an exponential extrapolation (dashed line). The dotted line is a linear background.

For the remaining spectra, we believe the intensity ratios are rather accurate. Abundant fine structures can be seen in the figure. There are two distinct peaks located at 22.5 and 17.5 eV, a weak peak located at 15.5 eV, and a step around 27.0 eV. Two shoulders at 19.5 and 24.0 eV are also discernable. As for the abrupt change at 29.5 eV, we cannot be sure it is a fine structure due to the bad signal-to-noise ratio of the corresponding spectrum.

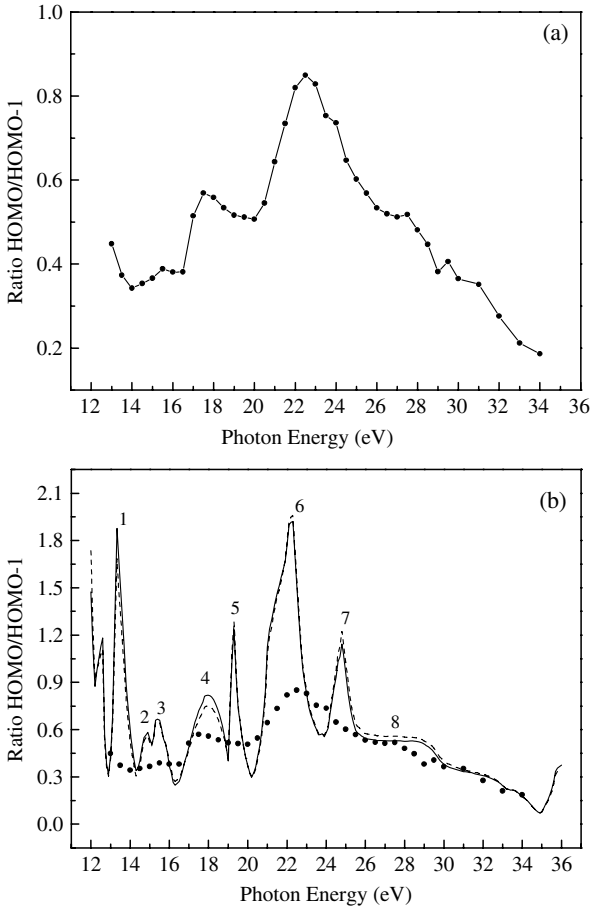

Figure 3. (a) Experimentally determined HOMO/HOMO-1 intensity ratio. (b) Comparison of the experimental data with the calculated photoionization cross-section ratios. The scattered dots are experimental data. The solid line is the ratios between the calculated partial cross-sections of the HOMO and HOMO-1 orbitals that were digitized from [8]. The dashed line is the emendation of the solid line by considering the asymmetry parameters. The calculated results have been homogeneously shifted towards higher binding energy by 1.5 eV.

To discuss quantitatively the fine structures, we compare in figure 3(b) our experimental data with the *ab initio* quantum chemistry results calculated by Venuti *et al* [8]. In the calculation of [8], the initial and final states were symmetry and angular-momentum specified occupied molecular orbitals and the antibonding valence orbitals (unoccupied molecular orbitals) respectively, and a series of giant resonances were predicted. The solid line in figure 3(b) was digitized from [8]. The predicted fine structures in the energy region of the present work are labeled with numbers from 1 to 8. The dashed line is the emendation of the solid line by considering the asymmetry parameters [8]. In our experimental setup (the angle between the photon beam and the direction of the analyzer entrance was 45°), the correction by the asymmetry parameters is inappreciable. For the comparison with the experimental data, the theoretical lines have been shifted towards higher photon energy by 1.5 eV. All the experimentally observed fine structures have their counterparts in the theoretical line with energy discrepancies less than 1 eV. So we can say that the giant resonance of the

dipole transition between occupied and unoccupied molecular orbitals is the main reason for the observed fine structures.

As for the magnitude of the photoionization cross-section, we observed the minima for the HOMO and HOMO-1 bands around 29.5 eV (see the discussion of figure 1). The calculated results (figure 7 in [8]) also exhibited the minima. The HOMO/HOMO-1 ratio also coincides with the experimental data fairly well from 30.0 to 34 eV in figure 3(b). However, the calculated results are greater than the experimental data by a factor of at least two in the photon energy region from ∼17.0 to ∼24.0 eV, and are drastically greater than the experimental data below 17.0 eV. The magnitude disagreement indicates that further theoretical development is needed to match the observed behavior. As one of the future theoretical works, we argue the collective excitation should be considered. Bertsch *et al* [15] predicted a collective excitation plasmon with energy of ∼20 eV, and the plasmon could decrease the oscillation strength by a factor of ∼2, which satisfactorily explains the magnitude discrepancy from ∼17.0 to ∼24.0 eV in figure 3(b). The remarkable magnitude deviations of the sharp features 5 and 7 may be because the photon energy increment (0.5 eV) in the measurements is not yet small enough, besides the effect of the plasmon. Another effect of the collective excitation, the screening effect, can more significantly decrease the strength of the cross-section oscillations at still lower photon energies [15], and can interpret the increased deviation of the calculated results from the experimental data below 17.0 eV. As we mentioned above, the photon energy of the calculated result in figure 3(b) was shifted to higher binding energy by 1.5 eV to fit the experimental data. The energy shift, together with some small energy discrepancies of the fine structures, can also find their physical origins in the collective excitation [15]. It should be very promising to carry out an improved calculation of [8] by considering the collective excitation.

The observed fine structures have important implications for some other theoretical models [6, 7, 11]. The models of [6, 7, 11] can only be applied to high photon energies, say, higher than about 40 eV, since they cannot explain the fine structures. All these models depended on certain adjustable parameters, such as the potential energy parameter U_m in [6], the thickness of the valence electron cloud in [7], and the inner potential V_0 in [11]. These parameters were adjusted in these references to fit experimental data that included the low photon energy data. We guess the inclusion of low energy data have blocked a thorough and accurate understanding of the photoionization cross-section oscillation in the high energy region, and suggest renewed works of these models to achieve more satisfactory results and/or evaluate the validity of different models.

4. Conclusions

In summary, we have observed the fine structures of the HOMO/HOMO-1 intensity oscillation. The fine structures verify the general rationality of a quantum chemistry model to describe the photoionization cross-section oscillation of C_{60} at low photon energies. Improvement of the model by taking into account the collective excitation is indicated. The present work also implies the photoionization cross-section oscillations of C_{60} have different origins for different photon energy regions. The thorough understanding of the oscillations from the photoionization threshold to the carbon K edge is still an open topic.

Acknowledgments

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