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ОРИГИНАЛЬНЫЕ НАУЧНЫЕ СТАТЬИ
ORIGINAL SCIENTIFIC PAPERS

STRONG ENHANCEMENT OF DOUBLE AUGER DECAY FOLLOWING PLASMON EXCITATION IN C_{60}

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FIELD: molecular physics, synchrotron radiation, photoelectron spectroscopy, fullerenes, dipole resonance, Auger decay, Plasmon, collective oscillation, localized excitation, delocalized relaxation
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Abstract:

One of the important characteristics of the C_{60} molecule is the collective response of its valence electron cloud to the electromagnetic radiation. This collective behavior gives rise to the occurrence of the giant dipole resonance (so called surface plasmon) in the absorption spectrum centered around 20 eV, which has also been analyzed theoretically by various authors. Concerning photoelectron emission, plasmonic excitation is characterized by a particular intensity behavior near the threshold. We present here a new series of the K-shell photoelectron spectra with particular emphasis on the qualitative analysis of all ionization with excitation and double ionization processes. Our measurements of the C_{60} plasmon excitation follow the so-called Thomas-Derrah law and are in good agreement with the corresponding behavior of satellite excitations in atoms such as neon.

Key words: molecular physics, photoelectron spectroscopy, plasmon excitation.

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Introduction

Since the discovery of C_{60} molecule (Kroto et al, 1985, pp.162-163), (Krätschmer et al, 1990, pp.354-358) many studies have been performed to investigate its fundamental properties. These properties are mainly driven by its unique molecular structure like a spherical shell (Electronic Properties of Fullerenes, 1993), (Korica et al, 2005, pp.132031-132035). C_{60} is known to have a plasmon excitation where 240 valence electrons contribute to a delocalized electron cloud that can oscillate relative to the carbon ion core forming the C_{60} molecular cage. This oscillation produces a giant resonance in the C_{60} photoabsorption (Hertel et al, 1992, pp.784-787) and electron-energy-loss spectra (Leiro et al, 2003, pp.205-213) at the excitation energy of about 20eV. It has also been observed in the photofragmentation experiments as an enhanced relative fragmentation of C_{60}^{+} ion at the same photon energy (Karvonen et al, 1997, pp.3466-3472). It has been interpreted by different theoretical models as a dipole collective giant resonance (Amusia & Connerade, 2000, pp.41-70), (Bertsch et al, 1991, pp.2690-2693), (Ekardt, 1984, pp.1925-1928), due to autoionization, which arises from collecting the strength of the individual one-electron transitions into a single collective excitation.

Experimental set-up

The measurements were performed at the HASYLAB undulator beam line BW3 in Hamburg using monochromatized synchrotron radiation whose wavelength can be scanned with a resolution set to an appropriate value. The photon beam crosses an effusive beam of C_{60} molecules, provided by an oven heated to 500 °C. Outgoing electrons are detected in time-of-flight (TOF) electron spectrometers at two different angles with respect to the electric vector of the ionizing radiation (Fig. 1). Appropriate voltages can be applied to the TOF-analysers to keep a constant resolution of the electron spectra for different photon energies.

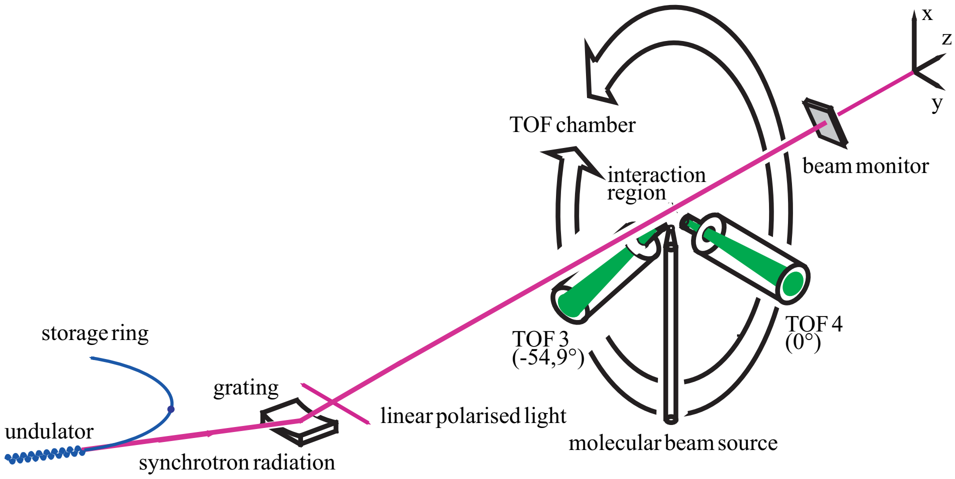

Figure 1 – The experimental set-up
Рис. 1 – Экспериментальная аппаратура
Слика 1 – Експериментална апаратура

Results and Discussion

Plasmon excitation in C_{60} molecule

Figure 2 shows an example of the K-shell photoelectron spectrum of C_{60}, recorded at 390 eV photon energy, covering the whole range of kinetic energies down to zero kinetic energy. The spectrum is converted to the binding energy and the background has been subtracted.

The spectrum consists, besides the single narrow C(1s) main line (Lichtenberger et al, 1991, pp.203-208), of a variety of satellite lines and higher lying plasmon excitation (Weaver et al, 1991, pp.1741-1744), (Benning et al, 1992, pp.6899-6913), (Terminello et al, 1991, pp.491-496). The low binding energy side of the C1s (from 1.9 eV to 9.3 eV) is characterized by different dipole and monopole shake-up satellites, except the one at the 6.0 eV which relates to the π plasmon. The energy region between 10 eV and 20 eV does not have discrete dipole transitions for free molecules and collective resonances are the dominating effects here (plasmon like excitations). The broad peak at the high binding energy side is also caused by several plasmon excitations.

Such plasmons are supposed to originate from a collective motion of σ- and/or π-electrons in the electric hull of the C_{60} molecules following the ionization of a K-shell electron.

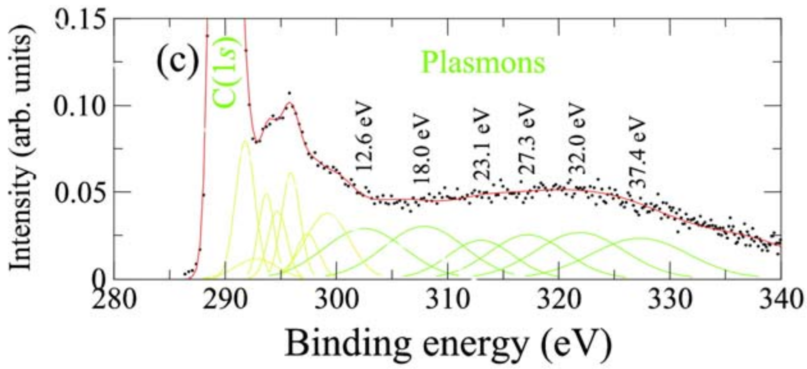

Figure 2 – A recorded spectrum of the 54.7°- analyser for a photon energy of 390eV
Рис. 2 – Анализатор спектра на 54.7°для энергии фотона 390eV
Слика 2 – Спектар анализатора на 54,7° за енергију фотона од 390 eV

We have also studied the dynamical behaviour of plasmon excitation by recording the photoelectron spectra as a photon energy function. This is illustrated in Figure 3 for several different photon energies.

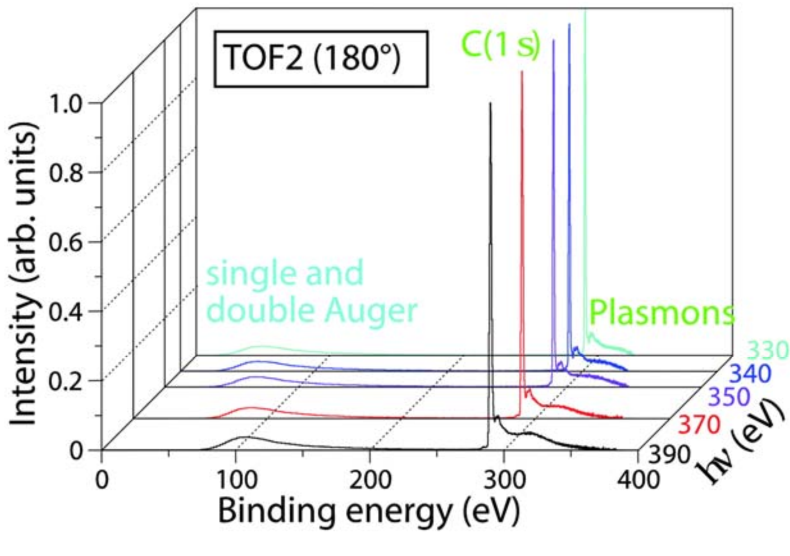

Figure 3 – Spectra as a function of the binding energy of the 180°-analyser for different photon energies
Рис. 3 – Спектр в функции связной энергии анализатора на 180° для различных уровней энергии фотона
Слика 3 – Спектар у функцији од енергије везе за анализатор на 180° за различите енергије фотона

Our results are in good agreement with the model of T. D. Thomas (Thomas, 1984, pp.417-420), a time-dependent model which describes the transition between adiabatic and sudden behaviour. It takes into account the interaction between the outgoing electron and the remaining electrons which leads to shake-up satellite electrons because the photoejected electron may emerge with less energy than in the adiabatic picture. In addition, multiple electron ejection is possible, in which case a continuous shake-off spectrum is observed since the discrete energy can be arbitrarily divided between the emitted electrons. In the frame of this model, the intensity ratio of the "shake-up" process and the C(1s) line is given by the expression:

$$\mu = \mu_\infty \exp\left\{ -\left(r\left[\overset{0}{A}\right]\Delta E\left[eV\right]\right)^2 / \left(15.32 E_{ex}\left[eV\right]\right)\right\}, \qquad (1)$$

where:
μ – intensity ratio of the "shake-up" process and the C(1s) main line,
μ_∞ – asymptotic value of μ (taken from Leiro et al, 2003, pp.205-213),
r – the distance until the electrons are separated from the molecule,
$r \approx 0.4Å$, note: $r << r(C_{60})$,
ΔE – the excitation energy of the "shake-up" process,
E_{ex} – the kinetic energy of the outgoing electrons.

Figure 4 shows a comparison of the experimental results with the results of the model of T. D. Thomas (Thomas, 1984, pp.417-420). With increasing energy, the plasmon intensity reaches its sudden limit faster than expected pointing to the localized excitation processes rather than to a delocalized relaxation in response to core-hole creation. The sudden limit intensity is as large as 30% of the total K-shell ionization events. Our measurements are in good agreement with the corresponding behavior of the satellite excitations in atoms such as He, Ne and Ar (Holland et al, 1979, pp.2465-2484) where electron correlation effects are supposed to enhance various cross sections.

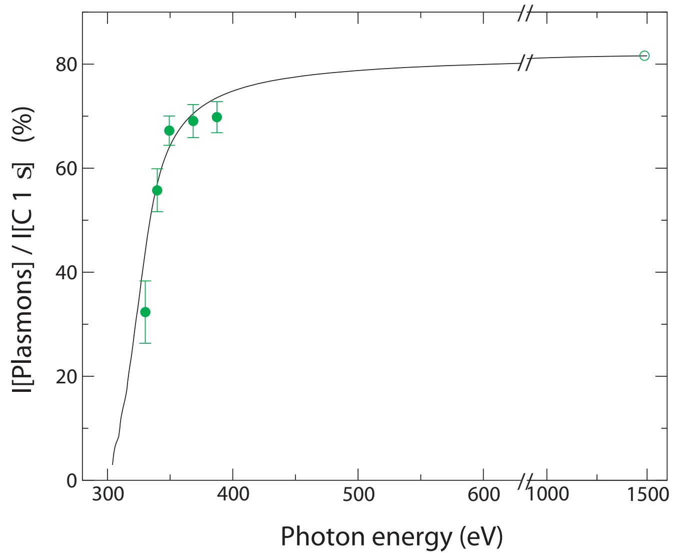

Figure 4 – Experimental and calculated values of the ratio of the intensity of all plasmon peaks and the intensity of the C(1s) main line as a function of excitation energy.
Рис. 4 – Экспериментальные и расчетные значения отношений интенсивности всех плазмонных пиков и интенсивности C(1s) главной линии в функции энергии возбуждения.
Слика 4 – Експериментална и израчуната вредност односа интензитета свих пикова плазмона и интензитета C(1s) главне линије у функцији енергије ексцитације

Double Auger decay of the excited C60

The strength of the shake-off processes contributes also significantly to total K-shell ionization rate. The relative fraction of this shake-off rate has been, however, unknown so far, although the complete photoelectron spectra exhibit a large fraction of continuously distributed photoelectron intensity which could either result from shake-off photoelectron emission or double Auger decay (Fig.5). The quality of the former K-shell photoelectron measurements was insufficient to disentangle these two contributions experimentally (Aksela et al*,* 1995, pp.2112-2115), (LeBrun et al*,* 1994, pp.3965-3968), (Brühwiler et al*,* 1993, pp.3721-3724), (Krummacher et al*,* 1993, pp.8424-8429).

The contribution of different excitation events can by separated with the *ansatz* (Fig.5):

$$\begin{aligned} Total\ Auger &= Auger_{single} + Auger_{double} \\ &= C(1s) + Satellites + Plasmons + e_{shakeoff} \end{aligned}$$

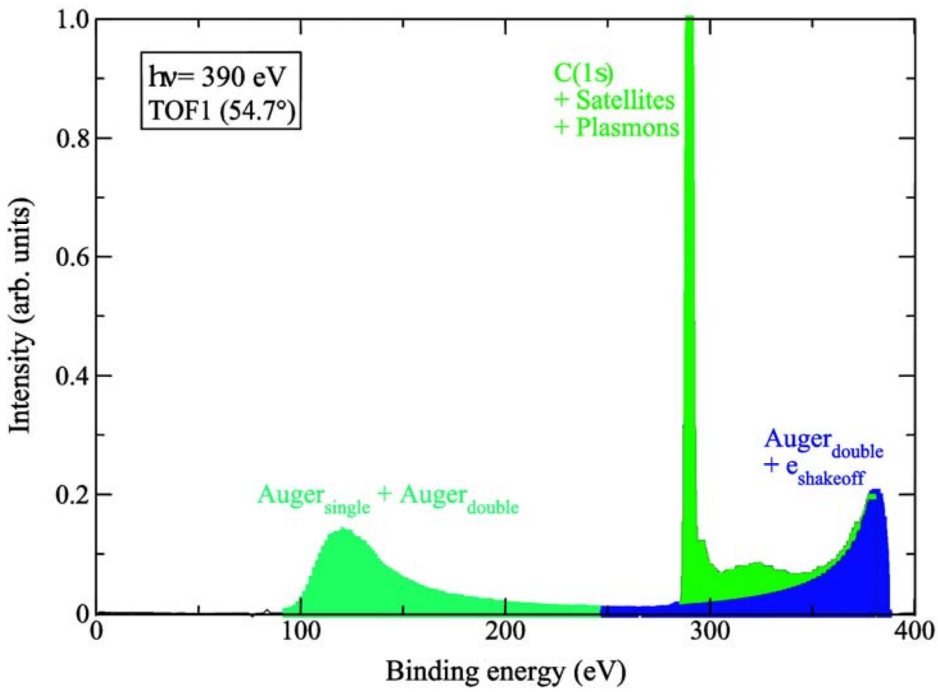

Figure 5 – Photoelectron spectrum recorded with a photon energy of 390eV. Different types of contributions are marked with colours. The intensity of the single and double Auger process can be deduced from the coloured areas.
Рис. 5 – Фотоэлектронный спектр, записанный для энергии фотона 390eV. Различные виды влияния обозначены разными цветами. Интенсивность Оже-процессов можно определить по обозначенным частям.
Слика 5 – Фотоелектронски спектар снимљен за енергију фотона 390eV. Различите врсте доприноса означене су различитим бојама. Интензитети Ожеових процеса могу се одредити из обојених области.

Performing a spectral analysis, which takes all primary and secondary ionization events into account, yields a double Auger rate as high as 60% of the total Auger yield. This is an extremely high value, raising the question of its origin. Assuming that the main line and the related shake-off emission result predominantly in single Auger decay, the K-shell photoionization associated with satellite and plasmon excitations remain the only plausible source for such a high double Auger rate.

The only reason for this highly unusual behaviour may be the fact that satellite and plasmon excitations both populate LUMO states which are strongly delocalized and may be completely in the continuum for the double charged C_{60}^{2+} ion resulting from the K-shell ionization and the subsequent core-hole refilling process (Maxwell et al, 1994, pp.10717-10725), (Wästberg et al, 1994, pp.13031-13034). The excited electron cannot survive in this unstable situation and will consequently leave the C_{60} ion along with the Auger electron in a form of an Auger shake-off transition. These arguments, however, have to be validated by more sophisticated calculations.

Conclusion

We have studied the C_{60} molecule photoionization above the C(1s) threshold, in the photon energy range hv=(330-390)eV. A careful analysis of the spectra yielded two surprising and unexpected results:

(i) With energy increase, the plasmon intensity reaches its sudden limit faster than expected pointing to localized excitation processes rather than to a delocalized relaxation in response to core-hole creation. The sudden limit intensity is as large as 30% of the total K-shell ionization events.

(ii) Performing a spectral analysis taking all primary and secondary ionization events into account yields a double Auger rate as high as 60% of the total Auger yield.

The double Auger processes are probably linked to the plasmon excitation in the C_{60} molecules.

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УСИЛЕНИЕ ДВОЙНОГО ОЖЕ-РАСПАДА, СОПРОВОЖДАЮЩЕГО ВОЗБУЖДЕНИЕ ПЛАЗМОНОВ В C_{60}

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ОБЛАСТЬ: молекулярная физика, синхротронное излучение, Фотоэлектронная спектроскопия, фуллерены, дипольный резонанс, Оже-распад, плазмон, коллективные колебания, локализованное возбуждение, делокализованная релаксация
ВИД СТАТЬИ: оригинальная научная статья
ЯЗЫК СТАТЬИ: английский

Резюме:

Одной из самых значительных свойств молекулы C_{60} является коллективная реакция ее валентных электронов на электромагнитные излучения. Вследствие коллективной реакции в спектре поглащения возникает огромный дипольный резонанс (так называемый поверхностный плазмон), приблизительно на 20 eV, который был неоднократно представлен различными авторами в их теоретических исследованиях. В случае фотоэлектронной эмиссии, наблюдаются характерное поведение плазмонов при возбуждении на пороге ионизации. В работе представлена новая серия фотоэлектронных спектров К-оболочки, а также подробный квалитативный анализ всех ионизаций с возбуждениями в процессе двойной ионизации. На основании проведенного анализа и измерений плазмонного возбуждения C_{60} при применении так называемого закона Томас-Дерраха можно утверждать, что они полностью совпадают с соответствующим поведением сателлитного возбуждения атомов в неонах.

Ключевые слова: молекулярная физика, фотоэлектронная спектроскопия, возбуждение плазмонов.

ЈАКО ПОЈАЧАЊЕ ДВОСТРУКОГ ОЖЕОВОГ РАСПАДА КОЈИ ПРАТИ ПЛАЗМОНСКУ ЕКСЦИТАЦИЈУ У C_{60}

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ОБЛАСТ: физика молекула, синхротронско зрачење, фотоелектронска спектроскопија, фулерени, диполна резонанца, Ожеов распад, Плазмон, колективна осцилација, локализована ексцитација, делокализована релаксација
ВРСТА ЧЛАНКА: оригинални научни чланак
ЈЕЗИК ЧЛАНКА: енглески

Сажетак:

Једна од значајних карактеристика C_{60} молекула је колективни одговор његових валентних електрона на електромагнетно зрачење. Ово колективно понашање доводи до појаве огромне диполне резонанце (тзв. површински плазмон) у апсорпционом спектру на око 20 eV, који су различити аутори и теоријски анализирали. Када је у питању фотоелектронска емисија, плазмонску ексцитацију карактерише посебно понашање на прагу јонизације. Приказана је нова серија фотоелектронских спектара К-љуске са тежиштем на квалитативној анализи свих јонизација са ексцитацијама и процесима двоструке јонизације. Мерења плазмонске ексцитације C_{60} прате тзв. Томас-Дирахов закон и у великој су сагласности са одговарајућим понашањем сателитских ексцитација у атомима као што је неон.

Кључне речи: физика молекула, фотоелектронска спектроскопија, плазмонска ексцитација.

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