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Highly charged ion energy gain spectroscopy of molecular excitations

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ABSTRACT

We show that the measurement at high resolution of the kinetic-energy gain spectrum of a highly charged ion (HCI) scattered and partly neutralised by a molecule, a nanocluster or a surface can reveal the excitation spectrum of the target. As a first application of the analysis, we demonstrate that the periodic oscillations in the measured energy gain spectra of energetic Ar^{q+} ions flying by C_{60} molecules arise from the coherent multiple excitations of C_{60} plasmons.

Highly charged ions (HCI) have been frequently used to probe the properties of various targets such as the stopping power of matter for charged particles [1–3], the multiple ionisation and fragmentation of molecules [4–7], etc. In particular the C_{60} molecule has been a favourite target for many works [4–8]. One very promising technique has been the measurement[9] of the spectrum of kinetic energy increase of slow HCI upon their partial neutralisation by collisions with C_{60}. The experiment was performed with such high energy-resolution as to allow detection of a spectacular fine structure in the gain spectra of Ar^{q+} ions ($q = 8, 13, 14, 15$) consisting of very many intensity oscillations repeated regularly every 6 eV and extending to very high gain energies. Here we show that these periodic oscillations arise from the multiple excitations of 6 eV π-plasmons of C_{60} accompanying the charge-transfer events. Our interpretation implies that HCI gain spectroscopy at high resolution could be a powerful new tool to investigate electronic excitations of other large molecules, nanoclusters or solid surfaces. For the latter we point out that HCI gain spectroscopy would be a technique of *extreme surface sensitivity*, the transferred electrons necessarily originating from the very first atomic layer of the target.

In a series of beautiful experiments, Selberg et al. [9] have measured the kinetic-energy gain distributions for net one- and two-electron transfers in distant collisions of slow Ar^{q+} ions with C_{60} molecules. The measured energy gains of detected $Ar^{(q-1)+}$ and $Ar^{(q-2)+}$ ions extend to very high energies (>100 eV) and display numerous intensity oscillations regularly separated by 6 eV.

Thumm et al. [10] have developed a theory which attributes the first few oscillations in the measured $Ar^{(q-1)+}$ spectra to an increasing number of neutralisation events, up to five electrons transferred. By contrast the new analysis proposed here assigns the gain energies in all spectra to the transfer of only one or at most two electrons to deep Rydberg states of the HCI and the many intensity oscillations to multiple π-plasmon excitations of C_{60} occurring simultaneously with neutralisation events. The new model explains quantitatively all the observations which have so far remained ill understood.

The source of both the energy gain of the ion and the target plasmon excitation is the energy $E_n = |E_n^{\mathrm{Ryd}}| - I_1$, where E_n^{Ryd} is the nth Rydberg state energy of the ion and I_1 is the first ionisation energy of the target. The various electric fields involved in HCI gain spectroscopy cause a target polarisation which is dominated by the *collective response* of the electrons known as plasmons. π-Plasmons at $\hbar\omega_\pi = 6 \pm 1$ eV and σ-plasmons at $\hbar\omega_\sigma = 25 \pm 5$ eV are characteristic collective excitations of C_{60} [11,12], other fullerenes [13] as well as all forms of sp^2 bonded carbon in bulk or in clusters [14–18].

Let a_μ^+ and a_μ be the creation and destruction operators of one energy quantum $\hbar\omega_\mu$ of plasmon of μ-type in the target. The quantized polarisation Hamiltonian of the target is

$$H_p = \sum_\mu \hbar\omega_\mu \left(a_\mu^+ a_\mu + \frac{1}{2} \right). \tag{1}$$

The three monopoles appearing in a charge-transfer experiment are the HCI (i), the transferred electron (e) and its hole (h) left behind on the target. While the plasmons are quantized, the monopoles will be treated here as classical, time-dependent sources of electric fields linearly driving the polarisation of the target. Such a semi-classical treatment has been quantitatively successful in several other instances of charged particle scattering spectroscopy [19–21]. The Hamiltonian coupling the plasmons to the monopoles is then

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$$H_{pm} = \sum_{\mu} (\gamma_{i\mu} + \gamma_{h\mu} + \gamma_{e\mu})(a_\mu + a_\mu^+). \quad (2)$$

The time-dependence of the ion coupling coefficients $\gamma_{i\mu}(t)$ is that of an ion moving so slowly on the time scale of one plasmon period that the plasmons are able to respond adiabatically to this perturbation. These terms are responsible for a small change in quasi-static polarisation energy upon charge transfer, but do not cause significant, real excitations of the plasmons themselves.

The plasmon shake up processes arise mainly from the electron and hole terms in Eq. (2). The partial neutralisation of the ion is assumed to begin at time $t = 0$ by the creation of an electron–hole pair on the target and the removal of the electron. Then the combined, time-dependent coupling coefficients of the electron–hole pair can be represented as

$$\gamma_\mu(t) = \gamma_{h\mu} + \gamma_{e\mu} = \hbar\omega_\mu g_\mu [1 - \rho(t)]\theta(t), \quad (3)$$

where $\theta(t)$ is the Heaviside unit step function which initiates the transfer event. The first term in the r.h.m. represents the plasmon coupling to the hole while the second term is the coupling to the transferring electron where $\rho(t)$ is a function rapidly decaying in time from 1 to 0 as the electron moves away from the hole position at R_0. When the interactions are limited to the dipole approximation, the coupling strength g_μ is $g_\mu = (\alpha e^2/2\hbar\omega_\mu R_0^4)^{1/2}$, where α is the static dipole polarizability of the target and $\rho(t) = R_0^2/R_e^2(t)$ where $R_e(t)$ is the instantaneous electron position. This coupling indeed generates the classical dipole image self-energies $-|\gamma_\mu|^2/\hbar\omega_\mu$ for a fixed hole and a fixed electron. However, since the electron is initially embedded within the electron density of the target, the dipole approximation surely underestimates the coupling strength. Therefore g_μ will be upgraded and treated as a first disposable parameter in the theory to take account, in an effective way, of all the multipolar interactions between the electron–hole pair and the μ-plasmons.

At $t = \infty$, the plasmons will have been driven into a coherent state which is a Poissonian distribution of energy states [19–21]. The probability of finding the μ-plasmons excited to the mth energy state is given by $\exp(-I_\mu^2)I_\mu^{2m}/m!$, where

$$I_\mu = \frac{i}{\hbar}\int_0^\infty dt\gamma_\mu(t)e^{-i\omega_\mu t}. \quad (4)$$

From energy conservation, the multiple plasmon energy quanta are subtracted from the ion kinetic-energy gain. On physical grounds and for calculation convenience the electron coupling function is taken as $\rho(t) = \exp(-t/\tau_n)$, where τ_n is a short transit time of the electron from the C_{60} HOMO to the nth Rydberg state of $Ar^{(q-1)+}$. It is argued that from the uncertainty principle $\tau_n E_n \geqslant \hbar/2$, say $\tau_n\omega_n = 1/f$ with $\omega_n = E_n/\hbar$ and $f(\leqslant 2)$ a decoupling rate factor. The decoupling rate $f\omega_n$ is proportional to the transition energy $\hbar\omega_n$: the deeper the Rydberg level, the faster the decoupling. In the numerical work to follow, f will be treated as the second adjustable parameter of the theory.

The integral in Eq. (4) is now

$$I_{n\mu} = g_\mu \frac{f\omega_n}{i\omega_\mu + f\omega_n} \quad (5)$$

$S_{n\mu} = |I_{n\mu}|^2$ is thus the variable strength of the Poisson distribution of energy losses to the μ-plasmons. The key feature of our model is that the strength $S_{n\mu}$ is not constant throughout the spectrum: $S_{n\mu}$ decreases when n increases from the deep Rydberg states towards the shallower states. Physically, the transitions toward deep ion states take place so fast that the electron in effect disappears suddenly from the target and a wave of plasmons rushes in, tsunami-like, to screen the naked hole. This violent action creates several plasmon quanta. For transitions to shallow states, the electron leaves the target more slowly, giving time to the plasmons to cover the hole quasi adiabatically. Hence one expects that the first few peaks in the spectrum will reflect mainly the weakly perturbed ionic Rydberg spectrum while the medium and high-energy parts of the spectrum will be affected progressively more strongly by the plasmon shake up processes.

In view of applying the general theory to the Ar^{q+}/C_{60} system, we shall assume here that there are just two plasmon types, the π- and σ-plasmons of C_{60}. The overall energy gain spectrum for one-electron transfer, with simultaneous excitations of m_π plus m_σ plasmon quanta, can be written as

$$G_1(E) = \sum_n |\langle 0|V|n\rangle|^2 e^{-(S_{n,\pi}+S_{n,\sigma})} \sum_{m_\pi m_\sigma} \frac{S_{n,\pi}^{m_\pi}}{m_\pi!}\frac{S_{n,\sigma}^{m_\sigma}}{m_\sigma!}\delta[E - E_n + \hbar(m_\pi\omega_\pi + m_\sigma\omega_\sigma)]. \quad (6)$$

The matrix element squared measures the probability for the electron to transfer from its initial state |0> to the ion capture state $|n>$ of energy E_n^{Ryd}, in the absence of any other phenomenon. Actually |0> is a superposition, created by the adiabatic approach of the HCI, between the C_{60} HOMO and a threshold $Ar^{+(q-1)}$ Rydberg state. The terms of V causing the electron transfer are, besides the HCI perturbing potential, the electron–hole coupling and the indirect coupling between the electron and the C_{60} polarisation induced by the HCI. The transfer probability $|\langle 0|V|n\rangle|^2$ is a complicated, approximately linear function of n for small n's (i.e. intermediate and deep Rydberg states). Further factors in Eq. (6) express the product of independent Poissonian probabilities of exciting any integer number of plasmon quanta of any kind. The last factor is the energy-conserving delta function expressing that the plasmon excitation energies are subtracted from the Rydberg energy gain E_n.

The two-electron transfer spectrum is obtained by replacing the one-electron strengths $S_{n,\mu}$ in Eq. (6) by two-electron strengths $S_{nn',\mu}$:

$$G_2(E) = \sum_{n\leqslant n'} |\langle 00'|V|nn'\rangle|^2 e^{-(S_{nn',\pi}+S_{nn',\sigma})} \times \sum_{m_\pi m_\sigma} \frac{S_{nn',\pi}^{m_\pi}}{m_\pi!}\frac{S_{nn',\sigma}^{m_\sigma}}{m_\sigma!}\delta[E - (E_n + E_{n'}) + \hbar(m_\pi\omega_\pi + m_\sigma\omega_\sigma)], \quad (7)$$

where for $\mu = (\pi, \sigma)$

$$S_{nn',\mu} = g_\mu^2 |I_{n\mu} + I_{n'\mu}|^2 \quad (8)$$

The prefactors in Eq. (7) are double electron transition probabilities which, for consistency with the one-electron simulations, will be taken to be proportional to the product of the probabilities of one-electron transfers. The energies for the second electron transfer $E_{n'} = \left|E_{n'}^{Ryd}\right| - I_2$, involve the Rydberg levels of the $q-1$ ion and the second ionisation potential I_2 of the target. The measured spectra have a finite energy resolution and the plasmons have a finite lifetime, so that the delta functions in Eqs. (6) and (7) must be broadened to Lorentzians.

We now apply the theory to the Ar^{q+}/C_{60} system [9]. We limit ourselves here to the spectra for $q = 15$ for which the Rydberg levels can be approximated to the hydrogenic formula $E_n^{Ryd} = -13.6q^2/n^2$ eV. A full account of all the observed spectra will be given elsewhere. In Fig. 1a, we begin by showing the spectrum of transition energies E_n for Ar^{15+}. The probability $|<0|V|n>|^2$ has been taken to be proportional to n. Fig. 1a would be the one-electron energy gain spectrum with zero plasmon excitation. Fig. 1b is the calculated gain spectrum for the $q \to q-1$ reaction coupled to the π-plasmons only ($S_{n,\sigma} = 0$). The coupling strength, $g_\pi = 1.5$, is substantially larger than it would be in the dipolar approximation ($g_\pi = 0.8$). The decoupling rate factor was taken as $f = 0.1$. In Fig. 1b, the original hydrogenic peaks of Fig. 1a are seen to be reduced and replaced on their loss side by a Poissonian distribution of multiple loss peaks separated by the π-plasmon quantum of 6 eV. The

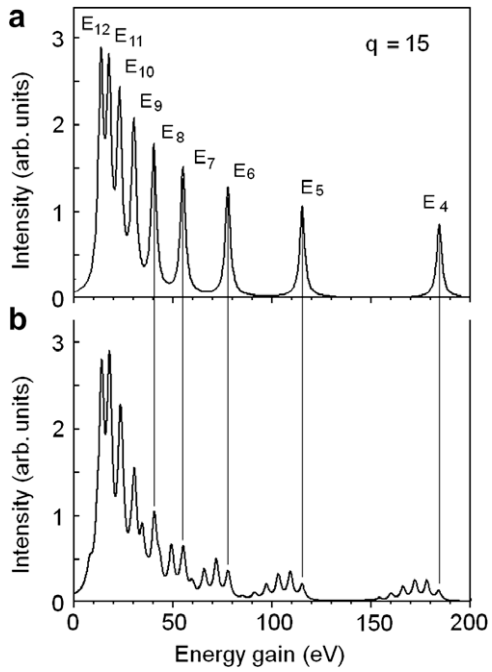

Fig. 1. (a) The distribution of hydrogenic Rydberg states E_n for Ar^{15+}. (b) The energy gain spectrum for one-electron transfer calculated with coupling to the π-plasmons only. Notice the intensity gaps at high energies.

original intensity of each hydrogenic peak is conserved but is now spread over the associated Poisson spectrum. As noted before, the Poisson strengths $S_{n\pi}$ decrease when approaching the spectrum threshold E_{12} where the original hydrogenic peaks are less reduced by plasmon losses. In the calculated spectrum of Fig. 1b one notes that there are *intensity gaps* appearing on the loss side of the highest Poisson series at E_5 and E_4. This is an energy region where the C_{60} σ-plasmons are likely to be strongly excited. In the calculated one-electron spectrum of Fig. 2b, the broad σ-plasmons have been turned on according to Eq. (6), with a coupling strength $g_\sigma = 2.5$. This value, higher than the π-plasmon strength g_π, is consistent with the expected larger oscillator strength of the σ-plasmons [12]. With both couplings present, the previous gaps have virtually disappeared. They are replaced by a broad continuous intensity background of σ-plasmons on top of which the 6 eV oscillations of the π-plasmons are superposed. Now one understands the unexplained fact that the observed spectrum at intermediate and large gain energies consists of an oscillating, continuously decaying tail. Fig. 2b also shows the broad two-electron spectrum calculated from Eq. (7) (see below for a discussion of this spectrum). The results of Fig. 2b are compared to the observed one-electron and two-electron data [9] shown in Fig. 2a. The overall resemblance between the observed and theoretical spectra is astounding both quantitatively in peak positions and even qualitatively in intensities.

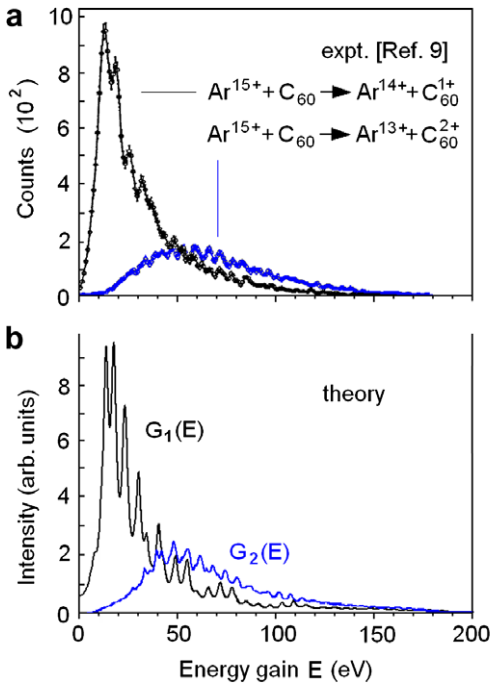

Fig. 2. (a) Theoretical one-electron and two-electron energy gain spectra including coupling to π- and σ-plasmons. (b) Experimental gain spectra for Ar^{15+} [9].

Fig. 3 compares the computed and experimental *two-electron* spectra in greater detail. Both spectra consist of broad, bell shaped continua extending from about 20 to 180 eV. These arise from two-electron transitions toward a dense forest of peaks corresponding to all possible pairs (n, n') of combined energies $E_n + E_{n'}$ in Eq. (7). Each of these peaks is depressed and its intensity is spread, on its loss side, over Poisson distributions of plasmon peaks of 6 and 25 eV separations. The spectrum is obtained by adding up the many Poissonian spectra and broadening with the instrumental resolution. There are irregularities in the peak separations in both observed and calculated spectra, due to the fact that the 6 eV oscillation series often overlap. The calculation uses the same coupling strength parameters ($g_\pi = 1.5$, $g_\sigma = 2.5$) and decoupling rate factor ($f = 0.1$) as for the one-electron spectrum. The agreement is striking, taking account of the simplicity of the theoretical model.

In conclusion, we have presented a new plasmon model for the calculation of kinetic-energy gain spectra of HCI partially neutralised by flying by a polarisable target at 'glancing incidence' (i.e. at small deflection angles for gas phase molecules or at grazing incidence in surface scattering). A successful application of the general theory was made to the spectacular but ill understood gain spectra for the system Ar^{q+}/C_{60} [9]. The model explains in a unified way all the remarkable features of both the one-electron and two-electron spectra, particularly the occurrence of very many intensity oscillations extending to very high gain energies.

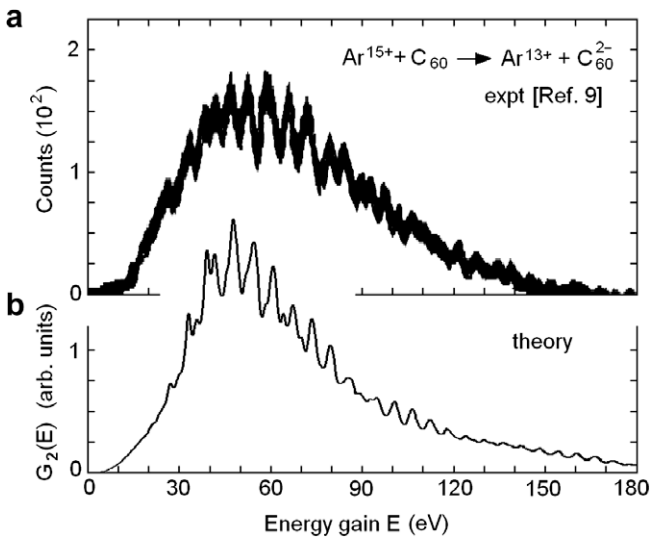

Fig. 3. Detailed comparison between the observed two-electron spectrum (a) and the theoretical spectrum (b) for Ar^{15+}. The oscillations are separated by about the π-plasmon quantum of 6 eV. Series of multiple plasmon peaks derived from combined Rydberg levels $E_n + E_{n'}$ overlap and cause irregularities in the spectrum.

The present interpretation allows predicting that if one were to use other HCI or other large molecules with the exquisite energy resolution of Selberg et al. [9], similar inelastic gain spectra would be observed, characteristic for the electronic excitations of the target molecules. For example other fullerenes (C_{70}, C_{84}, ...) or other sp^2 carbon targets would be expected to reveal the same 6 eV oscillatory spectra. Grazing incidence scattering experiments on various metals such as Al, Mg, Ag, Au, which all have well defined surface plasmon modes [20,21] could be used for further testing the concepts developed here. The glancing incidence geometry enables one to discriminate relatively gentle scattering encounters from the flurry of violent events occurring in head-on collisions [22,23].

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