Theory of highly charged ion energy gain spectroscopy of molecular collective excitations

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Abstract. This paper discusses the physical mechanism by which a highly charged, energetic ion partly neutralized by electron transfers from a target—a large molecule, a cluster or a solid surface—can create target collective excitations in the process. We develop an analysis for the system of a highly charged ion flying by a fullerene molecule. Our analysis offers a new explanation for the periodic oscillations observed in the high-resolution energy gain spectra of energetic Ar$^{q+}$ ions ($q=8, 13, 14, 15$) flying by C$_{60}$ molecules. For the Ar$^{q+} \rightarrow$ Ar$^{(q-s)+}$ spectra with $q=13–15$ and $s=1$ or $2$, the observed oscillations of 6 eV periodicity are assigned to energy losses due to multiple, Poissonian excitations of C$_{60}$ $\pi$-plasmons (6 eV quantum). The excitation energy quanta are subtracted from the kinetic energy gained by the ion when one or at most two electrons are transferred to increasingly deep Rydberg states of the ion. The observed 3 eV periodicity for $q=8$ arises from the specific Rydberg energy levels of Ar$^{\text{VIII}}$ (Ar$^{7+}$). The first few shallow levels of this ion are separated by about 3 eV, while some of the pairs of adjacent, deeper levels are also separated.

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by 3 eV. Each deep-level pair produces two interdigitated, Poissonian series of 6 eV $\pi$-plasmon excitation peaks resulting in an apparent periodicity of 3 eV throughout the spectra. The broad $\sigma$-plasmons (25 eV quantum) are found to contribute a background continuum to the medium- and high-energy regions of the observed spectra. The physical model analyzed here indicates that electronic collective excitations in several other systems could be studied by highly charged ion energy gain spectroscopy at sufficient resolution.

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1. Introduction

Colliding probe particles (photons, neutrons, electrons, neutral atoms, ions, etc) with atoms, molecules, nanoclusters, solid surfaces, etc have been the universal method for investigating the microscopic properties of the target. In particular, energetic, highly charged ions colliding with gaseous or bulk materials have been in great use in recent decades to determine such properties as the stopping power of matter for charged particles [1]–[3] or the multiple ionization and fragmentation of molecules [4]–[7]. In this field, since the discovery of fullerenes, the giant molecule C$_{60}$ has been an ideal reference system of study because, being intermediate between a small molecule and bulk material, it displays individual excitations typical of the molecular state as well as collective excitations characteristic of condensed matter. In particular, the role of the giant dipole resonance of C$_{60}$ above 20 eV in various collision phenomena has been the centre of attention of early works [6, 7] as well as more recent works [5].
In a series of beautiful experiments, Selberg et al [8] have measured the kinetic energy gain spectra of energetic Ar\(^{d+}\) \((q = 8, 13, 14, 15)\) flying by \(C_{60}\) molecules at distances close enough to cause partial neutralization of the ion by electron transfers from the molecule. The unusually high resolution of the experiment (of the order of 1 eV) allowed the detection of spectacular fine structures in the gain spectra consisting of many intensity oscillations repeating regularly every few eV.

In this paper, these periodic oscillations, which so far have defied interpretation, are given a full explanation thanks to a new model for the molecule–ion interactions that, like in the recent work of Kelkar et al [5], takes into account internal excitations of the plasmon degrees of freedom of \(C_{60}\).

The experimental spectra of Ar\(^{d+}\) ions of initial energy \(E_0 = 3.3q\) keV [8] are reproduced in figures 3–6 of section 4, along with the results of the present study. All of the spectra show a few sharp, intense peaks followed, at higher gain energies, by a decaying, oscillatory tail. To interpret their observed spectra, Selberg et al [8] used the over-the-barrier model (figure 1).

The process of one-electron transfer from the molecule to the ion is assumed to become possible when the ion reaches the distance \(R\) from the \(C_{60}\) centre determined by the crossing of the molecular potentials before and after transfer [8],

\[
U_{in}(R) = -\frac{\alpha_0 q^2 e^2}{2 R^3},
\]

\[
U_{out}(R) = -\frac{\alpha_1 (q - 1)^2 e^2}{2 R^3} + \frac{(q - 1) e^2}{R - R_0} - E_n,
\]

where \(R_0\) is the \(C_{60}\) radius. In these expressions, the dipole polarizations \((l = 1)\) of \(C_{60}\) induced by the incoming Ar\(^{d+}\) ion and by the outgoing Ar\(^{(q-1)+}\) ion are treated classically; \(\alpha_0 = 80\) Å\(^3\) and \(\alpha_1 = 57\) Å\(^3\) are the \(C_{60}\) and \(C_{60}^*\) dipole polarizabilities used in [8], respectively. In these relations, multipolar interactions \((l > 1)\) are ignored. The second term in (2) is the repulsion energy between the outgoing \(q - 1\) ion and the hole created at a distance \(R_0 \sim 3.5\) Å from the \(C_{60}\) centre on the ion side. In the spectrum, discrete energy gain peaks of Ar\(^{(q-1)+}\) are expected to be generated by the transfer to the ion kinetic energy of the electronic energies \(E_n = |E_{nl}| - I_1\), where \(E_{nl}\) are the ion Rydberg energy levels and \(I_1 = 7.6\) eV is the first ionization potential of \(C_{60}\). Figure 1 illustrates the energetics of the process for Ar\(^{15+}\) for which the Rydberg levels can be approximated by hydrogenic energy levels.

According to equations (1) and (2), the first, threshold peak of the one-electron spectrum will occur for a transfer occurring at the over-the-barrier distance \(R \approx R_1\) given by \(U_{in} = U_{out}\) and for a minimum of energy transfer \(E_n\). This threshold energy gain has to be at least equal to the Coulomb repulsion energy between \(C_{60}\) and Ar\(^{(q-1)+}\) at the critical distance \(R_1\), plus the difference between the polarization self-energies of the ion in its incoming and outgoing paths. For Ar\(^{15+}\), the threshold gain peak (indicated in figure 1(a)) occurs at \(E_{12} = 13.5\) eV [8].

Thumm et al [9] have proposed a theory that also assumes ‘over-the-barrier’ transfer conditions. The theory is based on classical rate equations for the occupation of ion energy levels by multiple electron transfers from \(C_{60}\), one-electron transfer per peak in the spectrum. The first few peaks obtained in this theory thus correspond to an increasing number of electron transfers, up to five in the calculation [9]. See [9] for details of this theory and for a comparison with the experiments.

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Figure 1. (a) Representation to scale of the electron Coulomb potentials (in eV) around non-interacting $C_{60}$ and $Ar^{15+}$. $E_{n}^{\text{Ryd}} = -13.6/n^2$ (eV) designates the energy level of the $n$th ion Rydberg state $|n\rangle$ and $I_1$ is the first ionization potential of $C_{60}$ separating the $|\text{homo}\rangle$ level from the vacuum level. The electronic energy gains available from one-electron transfer events are given by $E_n = |E_{n}^{\text{Ryd}} - I_1|$. The first, threshold energy gain is $E_{12} = 13.5$ eV (see text). (b) The Coulomb potentials for the ‘over-the-barrier’ model for one-electron transfer. The transfer state marked $E_{12}^{\text{Ryd}}$ is a hybrid resonant state admixing the $|\text{homo}\rangle$ molecular state with the threshold ion Rydberg state $|n_0\rangle$ ($n_0 = 12$). The value of the ‘over-the-barrier’ distance of approach $R_1 \approx 18.7$ Å is consistent with the experimental total cross section of one-electron transfer for this ion $\sigma_{\text{tot}} = 10 \pm 3.1 \times 10^{-14}$ cm$^2$ written as $\sigma_{\text{tot}} = \pi R_1^2$ [8].
There are several features of the observed spectra (shown in section 4) that were not explained by Thumm et al [9] and that have so far not received any convincing interpretation:

1. In their overall shape, all of the gain spectra look remarkably similar. For one-electron transfer, the spectra begin with a few intense peaks at low gain energies followed, at medium and high energies, by a long tail decaying in an oscillating manner.

2. For two-electron transfer, the spectra occur at high gain energies and are bell-shaped with very many oscillations on top.

3. All one-electron spectra with $q = 13, 14$ and $15$ show the same oscillation period of $6 \text{ eV}$.

4. By contrast, the oscillation period in the one-electron spectrum for $q = 8$ is $3 \text{ eV}$ rather than $6 \text{ eV}$.

5. For each of the four ions, the oscillations in the one- and two-electron spectra have the same oscillation period ($6 \text{ eV}$ for $q = 13–15$ and $3 \text{ eV}$ for $q = 8$).

In this paper, we propose a new mechanism for the formation of spectra that explains quantitatively all of the observations listed above. The basic idea of our model is that the energy exchange events taking place between the ion and $C_{60}$ consist of an interplay between the process of one- or two-electron transfer to discrete ion Rydberg levels and the simultaneous multiple excitations of the $C_{60}$ plasmons. The oscillation period is identified as the $6 \text{ eV}$ $\pi$-plasmon energy quantum of $C_{60}$.

As we shall see, one notable merit of the plasmon model developed here is that it shows satisfactory agreement with experiment for all spectra with the same values of just a single pair of physical parameters for the description of the coupling between $C_{60}$ and the ion during the charge transfer event. The first parameter is an effective coupling constant for the interactions between the multipolar plasmons and the transfer electron and its hole on $C_{60}$; the second parameter is a transfer rate factor that measures the probability of the transferring electron to occupy a threshold ion state, namely that ion Rydberg state that becomes resonant with the highest occupied molecular orbital (HOMO) state of $C_{60}$ at the over-the-barrier distance $R_1$ (see figure 1(b)). That the theory is able to explain the spectra for all $q$s with just these two fixed parameters is consistent with the fact mentioned above that the four observed spectra are strikingly similar. Clearly, the physical mechanism by which the $C_{60}$ plasmons are involved in charge transfer must be identical for the four ions, the latter displaying no specificity other than the distribution of final capture states accessible to the transferred electrons.

The validity of the present model would be further reinforced by finding similar periodic oscillations (with the same $6 \text{ eV}$ quantum) in the gain spectra of other ions of the $\text{Ar}^{q+}$ series, or of highly charged ions of other elements, flying by $C_{60}$ molecules. Also, finding the same $6 \text{ eV}$ quantum in the spectra of fullerene targets other than $C_{60}$ would add confirmation to the present assignment and would further support our theoretical model.

2. Quantum treatment of $C_{60}$ polarization

2.1. The $\pi$-plasmons and $\sigma$-plasmons

Various electric fields involved in the experiment give rise to $C_{60}$ polarization, which is the collective response of the $\pi$- and $\sigma$-electron states known as $\pi$-plasmons and $\sigma$-plasmons. Ultraviolet absorption spectra and electron energy loss spectra of $C_{60}$ and other fullerenes indicate that the relatively sharp $\pi$-plasmons have the energy quantum $\hbar \omega_{\pi} = 6 \pm 1 \text{ eV}$,
while the broad $\sigma$-plasmons have $\hbar \omega_\sigma = 25 \pm 5$ eV [10]. Such collective excitations are common to all sp$^2$-bonded carbons (graphite [11], graphene [12], fullerenes [10, 13], carbon onions [14], carbon nanotubes [15], polyaromatic hydrocarbons [16], etc). The total linear, dipolar polarization of C$_{60}$ can be represented by the model dynamical polarizability [17],

$$\alpha(\omega) = \frac{1}{3} \frac{\alpha_0 \omega_{\pi}^2}{\omega_{\pi}^2 - \omega^2 - i \omega \delta_{\pi}} + \frac{2}{3} \frac{\alpha_0 \omega_{\sigma}^2}{\omega_{\sigma}^2 - \omega^2 - i \omega \delta_{\sigma}},$$  \hspace{1cm} (3)

where the $\delta$s are plasmon frequency widths. The static dipole polarizability $\alpha_0$ consists of one-third $\pi$ and two-thirds $\sigma$ contributions, proportional to the number of participating bonds, one p$_z$ radial bond and three trigonally hybridized sp$^x$p$^y$ tangential bonds, respectively.

2.2. Mechanisms

The gain spectra of the ions result from energy transfer processes between C$_{60}$ and the ion. As explained above, the source of gain energy is ultimately the energy $E_n$ liberated by the process of electron capture from C$_{60}$ into a shallow or deep Rydberg state of the ion (figure 1(a)). In the present interpretation, this released energy is assumed to be apportioned between the kinetic energy gain of the ion and energy losses caused by multiple excitations of the quantized polarization of C$_{60}$. Momentum and angular momentum conservation in these processes is ensured by the heavy C$_{60}$ molecule acting as a sink. Thus the gain spectrum is seen as resulting from atomic energy gain processes accompanied by energy losses from C$_{60}$ plasmon shake-up processes.

During the incoming Ar$^{q+}$ ion trajectory, the C$_{60}$ plasmons are ‘prepared’ in a coherent state by the highly charged ion acting as a classical, time-dependent electric field. This coherent state is a Poissonian superposition of virtually excited plasmon energy states. The average excitation energy is equal and opposite to the classical self-energy of the ion given in equation (1) (see below). In the outgoing trajectory, the polarization amplitude and the average self-energy of the $q-1$ ion in equation (2) are progressively reduced. The net deceleration energy of the outgoing ion is smaller that the net acceleration energy in its incoming path. Hence, the abrupt change of ion charge contributes a net polarization energy gain equal, as indicated in equations (1) and (2), to the difference of polarization energies in the incoming and outgoing trajectories. This difference is supplied by the electronic energy $E_n$. In the quantum treatment, because of the discreteness of the plasmon energy spectrum, this gain must occur in an oscillatory manner. However, as will be shown below, the effect of the abrupt change of ion charge on the real plasmon excitations turns out to be small, due to the large impact parameter $R_1 (>10 \text{ Å})$ and to the fourth-order dependence on $1/R_1$ of this mechanism (see equations (1) and (2)). Thus the change in ion charge and molecular polarizability alone cannot explain the observed high energy gains.

A far more potent source of energy gain and real plasmon excitations is the process of electron transfer itself towards deep ion Rydberg levels, combined with the coupling of the plasmons to the transferring electron and to its hole left behind on C$_{60}^+$. The electron capture is necessarily a fast process, occurring on a time scale $\hbar/E_\alpha$, which, for deep Rydberg capture states, can be much shorter than the plasmon period $2\pi/\omega_\pi$. This sudden perturbation can cause real, multiple plasmon excitations. In the present theory, the overall spectrum then consists of an oscillatory loss spectrum trailing each gain peak associated with the electron transition to successively deeper ion Rydberg states.

In the sections that follow, we present a quantitative implementation of these ideas.

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2.3. Model Hamiltonian

For simplicity, we begin by assuming that all of the multipolar polarization modes of C\textsubscript{60} for different angular momenta can be lumped into a single effective plasmon degree of freedom. Later on, when necessary, we shall somewhat relax this simplification by introducing explicitly distinct $\pi$- and $\sigma$-plasmon classes of modes but still treating all multipolar modes of each class as a single effective oscillator.

In order to bring about the main, qualitative features of the model, we adopt a semi-classical approach in which the plasmon degree of freedom is treated fully quantum mechanically, while all three monopole charges (ion, electron and hole) are treated classically for what concerns their interaction with the plasmon. This means that the plasmon field ‘sees’ the monopole charges as tracing rigid trajectories and ‘feels’ the polarization force of the monopoles as a time-dependent perturbation to which it responds quantum mechanically. As is well known, in such a model, the evolving plasmon quantum state can be described exactly in terms of the coherent states of a harmonic oscillator. We shall see that knowledge of that exact plasmon state along with the ion Rydberg spectrum allows us to infer, via energy conservation, the energy gain spectrum of the ion probe. Such a semi-classical method has been applied with quantitative success to several problems of charge scattering by collective excitations of solid surfaces or of fullerenes [12, 13, 18]. Moreover, a problem of charge transfer in field ion spectroscopy, similar to the present one, has been successfully treated in the same semi-classical approach by one of us [19]–[20].

Our model Hamiltonian is

$$H = H_p + H_{ip} + H_{hp} + H_{ep},$$

where $H_p$ is the bare plasmon Hamiltonian of C\textsubscript{60} where $a$ and $a^+$ annihilate and create a plasmon energy quantum $\hbar \omega$, respectively. The other terms in (4),

$$H_{ip} = \gamma_i(t)(a + a^+),$$

$$H_{hp} = \gamma_h(t)(a + a^+),$$

$$H_{ep} = \gamma_{en}(t)(a + a^+),$$

are the linear, time-dependent interactions of the ion ($\gamma_i$), the hole ($\gamma_h$) and the electron ($\gamma_{en}$) with the plasmon, respectively. More precisely, the latter is the interaction between the plasmon and the ‘active’ electron leaving the C\textsubscript{60} state $|\text{homo}\rangle$ and ending in the ion Rydberg state $|n\rangle$. In this term, the phenomenological dependence on $n$ will be made explicit later.

For obtaining an order of magnitude estimate of the effect of the various terms, we shall first use the dipole part of the C\textsubscript{60} or C\textsubscript{60}+ polarization. In this dipolar approximation, the coupling coefficients for one-electron transfer are

$$\gamma_i(t) = e q \sqrt{\frac{\hbar \omega \alpha_0}{2 R^4(t)}} [1 - \theta(t)] + e (q - 1) \sqrt{\frac{\hbar \omega \alpha_1}{2 R^4(t)}} \theta(t),$$

$$\gamma_h(t) = e \sqrt{\frac{\hbar \omega \alpha_1}{2 R^4_0}} \theta(t),$$

where $\theta(t)$ is the Heaviside step function.
\[
\gamma_{en} = -e \frac{\hbar \omega \alpha_1}{2 R_{en}^4(t)} \theta(t).
\] (11)

In equation (9), \(R(t)\) is the ion distance to the \(C_{60}\) centre and \(\theta(t)\) is the Heaviside unit step function effecting the sudden change of ion charge from \(q\) to \(q-1\) at time \(t=0\). The ion–plasmon coupling \(\gamma_1(t)\) involves the \(C_{60}\) polarizability \(\alpha_0\) in the incoming path \((t < 0)\) and the \(C_{60}\) polarizability \(\alpha_1\) in the outgoing path \((t \geq 0)\). The hole–plasmon coupling \(\gamma_h(t)\) is turned on when the active electron leaves \(C_{60}\) at time \(t = 0\). We assume that the hole stays at \(R_0\) for at least several plasmon periods (the slow dynamics of the hole could easily be included in a refined version of the semi-classical theory by giving a parameterized time dependence to the hole position on \(C_{60}\), but here we will ignore this for simplicity). Finally, in the coupling \(\gamma_{en}(t)\) of the active electron to the plasmon, \(R_{en}(t)\) is the distance between the electron and the \(C_{60}\) centre whose dependence on \(n\) will be made clear below. This interaction is turned on simultaneously with that of the hole (but with opposite sign), and is turned off over a short time via the rapid increase of \(R_{en}(t)\) as the electron leaves the molecule and lands in the final capture state \(|n\rangle\). At \(t = 0\), at the onset of the transfer, \(R_{en}(0) = R_0\), so that the hole and the electron couplings exactly cancel each other, as they should.

The square-root form of the coefficients in equations (9)–(11) is justified as follows. If a quantum oscillator is stretched by a \textit{time-independent} amplitude, its Hamiltonian \(H = \hbar \omega a^+a + \gamma (a^+a)\) is diagonalized by the substitution \(b = a + \gamma / \hbar \omega\), with the result \(H = \hbar \omega b^+b - \gamma^2 / \hbar \omega\). The constant, negative term is the classical stretching energy. In equations (9)–(11) the indicated coupling strengths \(\gamma\) give the correct classical, electrostatic energies of the three monopoles in the \textit{dipole approximation} of the \(C_{60}\) polarization. Indeed for static monopoles, the total stretching energy is \(-(\gamma_1 + \gamma_h + \gamma_{en})^2 / \hbar \omega\). The three square terms are the self-energies of the three monopoles, each interacting with its own image in \(C_{60}\), while the three cross terms are the energies of the three monopoles, each interacting with the images of the other two monopoles. Images do not interact with each other in the present linear plasmon response.

2.4. Effects of the change of ion charge

In order to see how the semi-classical method works, we first study the quantum mechanism of \(C_{60}\) polarization by the ion. In the incoming trajectory \((t < 0)\), the Hamiltonian reduces to

\[
H_{in} = \hbar \omega a^+a + \gamma_1(t)(a^+a).
\] (12)

This time-dependent problem is exactly solved by using the coherent states, which are eigenstates of the destruction operator \(a\). If \(|0_p\rangle\) is the initial ground state of the plasmon, its exact state at time \(t\) is

\[
|\Psi_p(t)\rangle = e^{-(i/\hbar)H_p t} D |0_p\rangle = e^{-(i/\hbar)H_p t} |I^*(t)\rangle,
\] (13)

where \(|I^*(t)\rangle\) is a coherent state of eigenvalue \(I^*\) and where

\[
D(I) = \exp [I^* (t)a^+-I(t)a]
\] (14)

is the displacement operator that stretches the plasmon ‘half-field’ \(a\) by the coherent amplitude \(I^*(t)\) according to

\[
D^*(I^*)aD(I^*) = a + I^*(t).
\] (15)

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The stretching amplitude is given by
\[ I(t) = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \gamma_i(t') e^{-i\omega t'}. \]  

We want to know what will be the coherent plasmon amplitude just prior to the electron transfer at time \( t = 0 \), when the ion is at distance \( R_1 \) to the \( C_{60} \) molecule. One finds
\[ I_{in} = i \frac{\hbar \omega_0 e^2 q^2}{2} \frac{1}{R_1^2} \int_{-\infty}^{0} dt' e^{-i\omega t'}. \]  

Using the uniform trajectory of ion velocity \( v \),
\[ R_2(t) = R_2^0 + v^2 t^2, \]  
the integral in (17) could be performed exactly. However, we can take the adiabatic limit \( v \ll \omega R_1 \) appropriate for a slowly moving ion (in the experiment [8], the ions of kinetic energy 3.3 \( q \) keV move at velocity \( v \approx 1.26 \times 10^{14} \) \( \sqrt{q} \) nm s\(^{-1} \approx 4.87 \times 10^{14} \) nm s\(^{-1} \) for \( q = 15 \); this is 18 times smaller than \( \omega R_1 \approx 0.9 \times 10^{16} \) nm s\(^{-1} \) for the \( \pi \)-plasmon frequency \( \omega = 0.9 \times 10^{16} \) s\(^{-1} \) and \( R_1 \approx 1 \) nm). The result is
\[ I_{in} \approx i \frac{\hbar \omega_0 e^2 q^2}{2} \frac{1}{R_1^2} \int_{-\infty}^{0} dt' e^{-i\omega t'}. \]  

The integral is obtained from
\[ \lim_{\epsilon \to 0} \int_{-\infty}^{0} dt' e^{-i(\omega t' + \epsilon t')} = \frac{1}{-i\omega}, \]  
and hence
\[ I_{in} = -\sqrt{\alpha_0 e^2 q^2 / 2\hbar \omega R_1^2}. \]  

The plasmon is in a coherent superposition of energy states following a Poisson distribution of strength \( I_{in}^2 \). If an energy measurement was carried out on the molecule at time \( t = 0 \), the probability of finding the plasmon excited to its \( n \)th energy state would be \( \exp(-\alpha_0 e^2 q^2 / 2R_1^2) / n! \). The average, virtual excitation energy is \( \hbar \omega I_{in}^2 \), which is just the opposite of the classical ion polarization self-energy of equation (1). Inserting numbers from the Ar\(^{8+} \) case, one obtains \( \hbar \omega I_{in}^2 = 1.2 \) eV. Due to the large impact parameter \( R_1 \), this is small compared to the \( \pi \)-plasmon quantum \( \hbar \omega = 6 \) eV. Therefore the initial plasmon field is close to remaining in its ground state. The corresponding negative work, \(-1.2 \) eV, serves to give a slight acceleration to the incoming ion towards the \( C_{60} \) molecule [8].

The expression for potential energy will be different on the outgoing path where molecular polarization and ion charge have changed. The plasmon displacement due to the outgoing ion is
\[ I_{out} = \frac{i}{\hbar} \sqrt{\frac{\hbar \omega_1 e^2 q}{2} \frac{1}{R_1^2}} \int_{0}^{\infty} dt' e^{-i\omega t'}, \]  
or
\[ I_{out} = \sqrt{\frac{\alpha_1 e^2 q}{2\hbar \omega} \frac{1}{R_1^2}}. \]
The average, virtual excitation energy is now \( \bar{h}\omega I_{\text{out}}^2 = \alpha_1 e^2 (q - 1)^2 / 2R_1^4 \) \( \approx 0.67 \) eV, for \( q = 8 \), which is the opposite of the classical polarization energy of equation (2). The total average ion potential energy difference due to a change in C\(_{60}\) polarization and ion charge is \( h\omega (I_{\text{out}}^2 - I_{\text{in}}^2) \approx 0.53 \) eV. This difference gives a slight energy gain to the ion that must be supplied, along with the Coulomb repulsion between the hole and the \((q - 1)\) ion, by the electronic energy \( E_n \), according to equation (2).

To obtain an evaluation of the real plasmon excitation caused by the partial neutralization of the ion, the probability amplitudes before and after electron transfer must be coherently added before squaring. The net average plasmon excitation energy is then

\[
\bar{h}\omega (I_{\text{in}} + I_{\text{out}})^2 = \frac{e^2}{2R_1^4} \left[ \sqrt{\alpha_0 q} - \sqrt{\alpha_1 (q - 1)} \right]^2.
\]

This amounts to 0.08 eV for \( q = 8 \). It might be objected that, since the plasmon of the neutral C\(_{60}\) molecule does not coincide with that of the C\(_{60}^+\) ion (the latter having one less participating electron), the procedure of adding up the amplitudes of two different plasmon fields in equation (24) is not quite rigorous. In spite of this, equation (24) does indicate that the real plasmon excitation caused by a mere change in ion charge is expected to be small. In what follows, the term in equation (9) will therefore be neglected.

### 2.5. Combined effects of the hole–plasmon and the active electron–plasmon couplings

We now turn to the interaction of the hole and of the transferring electron with the plasmon, i.e. to the effect of the combined terms in equations (10) and (11). We ask for the probability of an electron transition from the initial state \( |0\rangle \) of the system at \( t = 0 \) to a deeper Rydberg state \( |n\rangle \) with simultaneous excitation of \( m \) plasmons. By energy conservation, the excess energy released \( E_n - m\bar{h}\omega \) must be transferred to the ion kinetic energy. The outgoing kinetic energy spectrum of the ion is therefore conceived as an inelastic loss spectrum trailing the discrete atomic transition peaks.

We begin by evaluating the plasmon excitation probability with the semi-classical method used so far in previous estimations. The hole–plasmon and the electron–plasmon excitation amplitudes must be coherently added together, giving

\[
I_n = i \frac{\bar{h}\omega \alpha_1 e^2}{2R_0^4} \left[ \int_0^\infty dt' e^{-i\omega t'} - \int_0^\infty dt' e^{-i\omega t'} f_n(t') \right],
\]

where

\[
f_n(t) = \frac{R_0^2}{R_{\text{en}}^2(t)}.
\]

The first term in the square brackets of equation (25) comes from the hole–plasmon coupling of equation (10) turned on at \( t = 0 \). In the second term that comes from equation (11), \( f_n(t') \) turns off the electron–plasmon coupling over an appropriate transit time \( \tau_n \), which is the time taken by the electron to leave C\(_{60}\) and land on the final ion state \( |n\rangle \) with energy release \( E_n = \bar{h}\omega_n \). A lower bound of the transfer time \( \tau_n \) can be estimated from the uncertainty principle

\[
\omega_n \tau_n \geq 1.
\]
The turn off or transfer rate $\tau_{\alpha}^{-1}$ is thus at most $\omega_n$. For calculation convenience and on physical grounds, we shall represent the time dependence of $R_n(t)$ in equation (26) by an exponential increase with time, i.e. $R_n(t) = R_0 \exp(f \omega_n t/2)$ and hence

$$f_n(t) = e^{-f \omega_n t},$$

(28)

where $f \omega_n$ is the actual transfer rate in which $f$ is a transfer factor whose significance is discussed below. The swiftness of transfer and hence the electron decoupling rate $f \omega_n$ depend on the liberated energy $\hbar \omega_n$: the larger the energy, the faster the decoupling.

An exponential for the ‘trajectory’ $R_n(t)$ would be found by solving Newton’s equation of motion for the transfer electron travelling over the Coulomb barrier approximated as an inverted parabola. However, classical mechanics cannot justify the phenomenological dependence of the transfer rate $f \omega_n$ on the final state $|n\rangle$, as represented in equation (28).

In order to clarify the physical meaning of the $f$ parameter in equation (28), we note that the capture of the electron by the ion is a two-step process consisting of a slow, adiabatic electron transfer followed by a sudden transition: first, as the ion slowly approaches the molecule and reaches the capture distance $R$, two dimensionless factors, $|\text{resonant state}\rangle$ provide a good empirical reference point for judging the quality of a future calculation of the effective theory. Its numerical work that follows, the factor $f$ may be viewed as the probability of finding the electron located on the ion where it occupies the initial resonant state $|\text{initial resonant state}\rangle$. Equivalently, $f$ and $1 - f$ are the fractions of time that the electron spends on the ion and on $C_{60}$, respectively, while the ion is in the vicinity of the molecule, prior to dropping to the final state. The overall capture rate is then clearly the product of the probability $f$ and the atomic transition rate $\omega_n$.

Formally, if the initial resonance is written as $|0\rangle = \cos \alpha |\text{homo}\rangle + \sin \alpha |n_0\rangle$, then $f = \sin^2 \alpha$. The corresponding mixing angle $\alpha$ would have to be calculated from a non-perturbational, quantum treatment of the resonant state. We note that the dynamics of electron transfer for a similar system, namely a Na metallic cluster and a highly charged Xe$^{25+}$ flyby ion, has been described theoretically by Plagne and Guet [21]. A similar treatment is required for the determination of the transfer rate factor $f$ appropriate for the present $C_{60}/Ar^{10+}$ system. However, such a calculation clearly lies outside the scope of the present paper. Instead, in the numerical work that follows, the factor $f$ will be treated as the first adjustable parameter of the theory. Its unique value, chosen to fit all of Selberg et al’s [8] experiments, will be found to be $f \approx 0.1$ corresponding to a mixing angle $\alpha \approx 0.3$. This numerical fit to experiment should provide a good empirical reference point for judging the quality of a future calculation of the resonant state $|0\rangle$.

Introducing equation (28) into (25), the plasmon amplitude now becomes the product of two dimensionless factors,

$$I_n = \sqrt{\frac{\alpha_1 e^2}{2\hbar \omega R_0^3}} (1 - i \int_0^\infty dx \ e^{-ix - i\omega_n x}) \equiv g F_n,$$

(29)

where $g$ is the square-root prefactor and $F_n$ is the function in parentheses,

$$F_n = \frac{v_n}{i + v_n},$$

(30)
Figure 2. (a) The distribution of energies available from one-electron transfer to hydrogenic Rydberg $s$-states $|n\rangle$ for $\text{Ar}^{15+}$. The relative peak intensities (left ordinates) are proportional to $n$. The continuous S-shaped curve (red line, right ordinates) shows the energy dependence of the strength function $|F_n|^2$ defined in equation (30). (b) The gain spectrum for one-electron transfer calculated with coupling to the $\pi$-plasmons only with a coupling constant $g = 1.5$. The intensity of each of the original peaks in (a) is now spread over a Poisson distribution (strength $g^2|F_n|^2$) of plasmon peaks on the energy loss side of the zero-plasmon peak. Note the intensity gaps at high energies.

and

$$v_n = f\omega_n/\omega.$$ (31)

The transfer function $|F_n|^2 = v_n^2/(1 + v_n^2)$ is an S-shaped function of the transfer energy $E_n = h\omega_n$; for shallow ion states, $v_n < 1, |F_n|^2 \ll 1$, whereas for deep states, $v_n > 1$ and $|F_n|^2 \approx 1$ (see figure 2(a)).

2.6. Adjusting the coupling constant $g$

In equation (29), $g$ measures the dimensionless dipole coupling strength. For further evaluation, we will not keep the explicit expression for $g$ in equation (29), for this expression holds only
for the $l = 1$, dipole approximation appropriate for the plasmon coupling to distant charges such as the ion. The dipole coupling surely underestimates the electron–plasmon and hole–plasmon interactions because both the hole and the departing electron are initially embedded in, and indeed are part of, the $\pi$- and $\sigma$-electron distributions of C$_{60}$. When the electron leaves the C$_{60}$ electron shell, couplings to all of the multipole plasmon modes of the molecule are turned on. Ideally one should couple each multipolar mode separately to the electron–hole pair. Instead, to keep the theory simple, we want to continue working with one single effective plasmon but we will upgrade $g$ to an effective coupling constant and treat it as the second adjustable parameter.

Thus,

$$S_n = |I_n|^2 = g^2 |F_n|^2$$

(31’)

is now the overall, variable strength of the Poisson distribution trailing the gain peak for each of the Rydberg energy transfer $E_n$. The key feature of our model is that the strength $S_n$ is not constant throughout the spectrum but depends on the quantum number $n$, i.e. the depth of the capture Rydberg level (see figure 2(a)). Due to the variable transfer rate $f_{\omega_n}$ in (31), the S-shaped function $S_n$ decreases when $n$ increases from the deep Rydberg states towards the shallower states close to the gain threshold. Physically, the transitions toward deep ion states take place so fast that the electron in effect disappears suddenly from the molecule and a wave of C$_{60}$ plasmon 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 molecule more slowly, giving time to the plasmon to cover the hole quasi-adiabatically. Hence one expects that in the vicinity of the threshold the gain spectrum will reflect mainly the bare ionic Rydberg states, while for medium- and high-energy gains the final states will be ‘dressed’ more strongly by the plasmon shake-up process.

3. Gain spectra

3.1. One-electron spectrum with $\pi$-plasmon only

We are now in a position to write down the quantum mechanical formula for the energy gain spectrum. The overall energy gain spectrum for one-electron transfer, with simultaneous multiple excitations of $\pi$-plasmon quanta $\hbar \omega_{\pi}$, can be written as

$$G_1^\pi (E) = \sum_n |\langle 0 | V | n \rangle|^2 e^{-S_n} \sum_m \frac{S_n^m}{m!} \delta (E - E_n + m\hbar \omega_{\pi}).$$

(32)

The matrix element squared measures the quantum mechanical probability for the transferred electron to reach the final state $|n\rangle$ of energy $E_n^\text{Ryd}$, in the absence of plasmon excitation. In that matrix element, as stated before, the initial state $|0\rangle$ is an admixture of the $|\text{homo}\rangle$ state of C$_{60}$ with the resonant Rydberg state $|n_0\rangle$ of the ion. $V$ stands for all the relevant electron interactions in the Hamiltonian leading to the transition (e.g. the electron–hole Coulomb attraction, not written explicitly in the plasmon Hamiltonian of equation (4), the electron–ion image repulsion, etc). Further factors in equation (32) express the Poissonian quantum probability of simultaneously exciting any integer number $m$ of plasmon quanta. The only semi-classical element in this formula is the way we compute the strength $S_n$ of the Poisson distribution. The $\delta$-functions express energy conservation. The Rydberg energies appropriate for the $q = 13$–$15$ ions will simply be taken as the degenerate hydrogenic levels $E_n^\text{Ryd} = -13.6q^2/n^2$ eV, whereas
those of the \( q = 8 \) ion will be taken from the National Institute of Standards and Technology (NIST) table of energy levels for \( \text{Ar}^{\text{VIII}} \) [22].

The measured spectra have a finite energy resolution and the plasmon has a finite lifetime, so that the delta functions in equation (32) will be suitably broadened to Lorentzians.

### 3.2. The role of \( \sigma \)-plasmons

When the electron transfer involves a deep enough Rydberg level, the possibility arises for the transition to cause excitations of one or more quanta of the high-energy \( \sigma \)-plasmon \( (\hbar \omega_{\sigma} = 25 \text{ eV}) \). Additional terms representing the \( \sigma \)-plasmon need to be added to the model Hamiltonian of equation (4). Again, we will assume that all the multipolar \( \sigma \)-modes are lumped into a single oscillator, distinct from the \( \pi \)-mode oscillator.

Now the model has two independent plasmon degrees of freedom separately coupled to the transferring action. Being independent of each other, the probability of exciting one mode will multiply the probability of exciting the other mode (see e.g. [19, 20, 23, 24] for similar situations where a continuum of plasmons is involved). We can then immediately generalize our expression (32) for a single mode in the following way,

\[
G_{\pi,\sigma}^{1}(E) = \sum_{n} |\langle 0 | V | n \rangle|^2 e^{-S_{\pi,n}} \sum_{m_{\pi},m_{\sigma}} \frac{S_{\pi,n}^{m_{\pi}} S_{\sigma,n}^{m_{\sigma}}}{m_{\pi}! m_{\sigma}!} \delta \left( E - E_{n} + \hbar(m_{\pi} \omega_{\pi} + m_{\sigma} \omega_{\sigma}) \right),
\]

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

\[
S_{\mu,n} = g_{\mu}^{2} |F_{\mu,n}|^{2}, \quad F_{\mu,n} = \frac{v_{\mu,n}}{i + v_{\mu,n}}, \quad v_{\mu,n} = f \omega_{n}/\omega_{\mu}.
\]

The transfer fraction \( f \) being a one-electron property of the \( \text{C}_{60} \)-ion complex, the same value must be used for the two kinds of collective plasmon modes. Because of the S-shape of the \( S_{n} \) Poissonian strengths (see figure 2(a)), it is clear that the \( \sigma \)-plasmons will affect only the medium- and high-energy parts of the gain spectrum, where \( E_{n} = \hbar \omega_{n} > \hbar \omega_{\sigma} = 25 \text{ eV} \).

### 3.3. Two-electron spectrum

In the present model and semi-classical theory, the two-electron transfer spectrum with multiple excitations of \( \pi \)-plasmon can be written as

\[
G_{2}^{\pi}(E) = \sum_{n \leq n'} |\langle 00 | V | nn' \rangle|^2 e^{-S_{n,n'}} \sum_{m} \frac{S_{n,n'}^{m}}{m!} \delta \left( E - E_{n} - E_{n'} + m\hbar \omega_{\pi} \right),
\]

where

\[
S_{n,n'} = g^{2} |F_{n} + F_{n'}|^{2},
\]

where \( S_{n,n'} \) is the coupling strength for the excitation of plasmon quanta by the simultaneous transfer of two electrons, the first to the capture state \( |n \rangle \) and the second to the state \( |n' \rangle \). In the semi-classical approach, it is mandatory that the two amplitudes in equation (36) be added before squaring, just as the hole and electron amplitudes were coherently added in equation (29) to obtain the strength \( S_{n} \). The plasmon amplitude is coherently driven by the two time-dependent forces exerted independently by each of the two departing electrons, or more precisely by the two electron–hole pairs. The prefactors in equation (35) are double.

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electron transition probabilities. The transfer processes can be uncorrelated if the two electrons are treated independently or correlated to each other if one takes into account the exchange-correlation effects of their Coulomb repulsion. Again working out the corresponding matrix elements in equation (35) is a complex problem outside the scope of this paper. For simplicity, but consistent with our one-electron transfer description, we shall assume here that the processes are uncorrelated and that the matrix elements are proportional to the product of two independent single-electron transfer probabilities. As we shall see, this assumption appears to be borne out by the success of the theoretical simulation of the two-electron spectra of the high-\( q \) ions (\( q = 13–15 \)). The energies in equation (35), \( E_n'' = |E_{n''}^{\text{Ryd}} - I_2| \), now involve the second ionization potential \( I_2 = 11.6 \text{ eV of C}_{60} \) [8].

In the calculations for the high-\( q \) ions, we have assumed that the energy levels accessible to the first electron are the hydrogenic levels \(-13.6 q^2/n^2 \text{ eV}\) of the \( q \) ion, while those of the second electron are the hydrogenic levels \(-13.6(q-1)^2/n'^2\) of the \((q-1)\) ion. There is a threshold gain energy for the two-electron spectra that is approximately given by (ignoring polarization terms) \( E_n + E_{n''} = 2e^2(q-2)/R_2\), where \( R_2 \) is the ion impact parameter for the double transfer. The observed threshold is about 20 eV. Finally, if the two electrons transferred land on the same ion level, the exclusion principle forbids them from having parallel spins. Thus, in the calculation of the spectrum (35), we reduce the contributions of the \( n = n' \) terms by a factor of \( 1/4 \), corresponding to one allowed final singlet state and three forbidden triplet states.

With the high energies liberated by the two-electron transfer events, it is likely that the \( \sigma \)-plasmon modes will also be excited. Then the spectrum is a product similar to equation (33) between the \( \pi \)- and the \( \sigma \)-excitation probabilities, each with a coherently added amplitude as in equation (36). The formal expression is rather cumbersome and need not be written explicitly here.

### 3.4. The \( \text{Ar}^{8+} \) spectrum

The apparently anomalous 3 eV peak separation of the \( \text{Ar}^{8+} \rightarrow \text{Ar}^{7+} \) or \( \text{Ar}^{6+} \) spectra requires a specific explanation. The reduced separation is in fact not an anomaly at all but a consequence of a specific energy level scheme of \( \text{Ar}^{\text{VIII}} = \text{Ar}^{7+} \) whose \( \text{Ar}^{8+} \) core is large enough to split the normally degenerate hydrogenic energies according to their angular momentum \( l \). It turns out that the actual level scheme shows a repeated occurrence of a separation of about 3 eV between several of the split Rydberg levels \( E_{nl}^{\text{Ryd}} \) of this ion. Subtraction of multiples of the \( \pi \)-plasmon 6 eV quanta from these levels will obviously produce a persistent 3 eV oscillation throughout the spectrum.

The NIST level scheme [22] of \( \text{Ar}^{\text{VIII}} \) is given in table 1. The configurations of multiplet levels are indicated in the first line of the table. The configurations have been grouped into boxes when their slightly different energies fall within a width of 1.5 eV around their mean values, corresponding to the width of the \( \pi \)-plasmon and the instrumental resolution. In each box, these neighbouring energy levels have been averaged (the second line in the table). Inspection of the spectrum reveals the presence of several 2.5–3.5 eV level separations between the groups. The average energies \( E_n \) indicated for each group have been used as input in the theoretical formula (33) for the one-electron spectra of this ion.

We did not attempt to compute the two-electron spectrum (35) for this ion. The reason is that this calculation requires the numerous two-electron excitation levels of \( \text{Ar}^{\text{VII}} \) for
Table 1. Energy transfers $E_n = |E_{nl}^{\text{Ryd}} - I_1|$ for Ar$^{\text{VIII}}$ where the $E_{nl}^{\text{Ryd}}$ energy levels are tabulated in [22] and where $I_1 = 7.6$ eV is the first ionization energy of C$_{60}$. The $(n, l)$ manifolds are binned together when their energies differ from their mean (number line) by less than an energy width of 1.5 eV.

| Configurations   | Energy transfers $E_n$ (eV) for Ar$^{\text{VIII}}$ |
|------------------|--------------------------------------------------|
|                  | 10.5 13 16.5 19.5 21.5 27.5 32.5 35.7 47 49.5 58 64.5 |

the configurations $1s^22s^22p^6n'n'$ with $n' \geq n \geq 3$, while unfortunately only the one-electron excitation levels $1s^22s^22p^63n'$ are known and tabulated [22].

4. Results

4.1. One-electron gain spectra for $q = 13–15$

In figure 2(a), we begin by showing the energy gain spectrum that would be expected from the hydrogenic levels $E_n^{\text{Ryd}}$ of an Ar$^{15+}$ ion with no coupling to the C$_{60}$ plasmons.

The evaluation of the intensities of the successive peaks in figure 2(a), namely the relative transfer probabilities $|\langle 0 | V | n \rangle|^2$ in equation (33), is a complicated problem in quantum chemistry and, as already stated, a detailed calculation falls outside the scope of this paper. However, for this purpose, the dependence of $|\langle 0 | V | n \rangle|^2$ on $n$ is all that matters. An evaluation of this dependence can be made by noting that the major part of the matrix element is between the $|n\rangle$ state and the threshold ion Rydberg state $|n_0\rangle$ into which the electron is resonantly transferred from the C$_{60}$[homo] state. The contribution of the latter to the matrix element is negligible due to its small spatial overlap with $|n\rangle$. Then in $\langle n_0 | V | n \rangle$, $V$ can be expanded in powers $r^k$ of the electron radial distance $r$ to the ion centre. The corresponding hydrogenic matrix elements $\langle n_0 | r^k | n \rangle$ have been studied by Badawi et al [25]. For the large values of $n_0$ appropriate for the shallow initial Rydberg states involved here, the matrix elements are seen to be roughly proportional to $n$ [26]. It has been gratifying to see that by assuming a power-law dependence $|\langle 0 | V | n \rangle|^2 \sim n^\gamma$ with $1 \leq \gamma \leq 3$, the present theory yielded a good representation of the rate of decay in intensity of the observed high-energy tails in the spectra. For the numerical work to be reported, we have used $\gamma = 1$ for $q = 13–15$ (figures 2–5) and $\gamma = 3$ for $q = 8$ (figure 6).

The transfer function $|F_n|^2$ is also plotted in figure 2(a) to indicate the dependence on energy transfer of the Poissonian strength $S_n = g^2 |F_n|^2$ for the coupling of the electron–hole pair to the plasmon.

Figure 2(b) is the calculated gain spectrum for the reaction Ar$^{q+} + C_{60} \rightarrow$ Ar$^{(q-1)+} + C_{60}^{+}$ coupled to the $\pi$-plasmon only. The coupling constant used, $g_{\pi} = 1.5$, is about twice the value in the dipolar approximation ($g = 0.7$), consistent with the expected role of the higher multipolar polarization. Each of the hydrogenic peaks of figure 2(a) is seen to be depressed.
Figure 3. (a) The experimental energy gain spectra for Ar$^{15+}$ for one-electron transfer (black curve) and two-electron transfer (blue curve) [8]. (b) The theoretical one- and two-electron gain spectra including coupling to $\pi$- and $\sigma$-plasmons. In the calculated one-electron spectrum $G_1$, the $\sigma$-plasmon contribution fills the intensity gaps at high energies of figure 2(a) with a quasi-continuous intensity toppled by $\pi$-plasmon oscillations. The two-electron spectra $G_2$ are discussed further in figure 7.

and replaced on its loss side by a Poissonian distribution of multiple loss peaks separated by 6 eV. The original intensity of each hydrogenic peak is spread over the associated Poisson spectrum. As noted before, the Poisson strength $S_n = g^2|F_n|^2$ that regulates this intensity spreading (figure 2(a)) decreases when approaching (from the right) the spectrum threshold where the original hydrogenic peaks are less reduced by plasmon losses. Now one understands the unexplained observation noted in the introduction, namely that the observed spectra at intermediate and high gain energies consist of a decreasing, quasi-continuous tail with 6 eV oscillations superposed: the original, sharp Rydberg states (figure 2(a)) are reduced and replaced on their loss side by an extended Poissonian spectrum of equivalent strength.

In the calculated spectrum of figure 2(b) there are intensity gaps appearing on the loss side of the highest Poisson spectra originating at $E_5 = 115$ eV and $E_4 = 185$ eV levels. This is an energy region where the $\sigma$-plasmon is likely to be strongly excited. In the calculated one-electron spectrum of figure 3(b), the broad $\sigma$-plasmon has been turned on according to

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Figure 4. (a) The experimental energy gain spectra for $\text{Ar}^{14+}$ [8]. Note that the black, experimental curve is the sum of the one- and two-electron transfer curves. (b) The theoretical one- and two-electron gain spectra including coupling to $\pi$- and $\sigma$-plasmons.

equation (33) with a coupling constant set at $g_{\sigma} = 2.5$. This value, higher than the $\pi$-plasmon coupling constant ($g_{\pi} = 1.5$), is consistent with the larger oscillator strength of the $\sigma$-plasmon (see equation (3)).

Now, with both couplings present, the previous gaps have disappeared. They have been replaced by a broad continuous intensity background of $\sigma$-plasmon on top of which the 6 eV oscillations of the $\pi$-plasmon are superposed.

Figure 3(b) also shows the broad two-electron spectrum extending from 20 to 180 eV (see below for a discussion of this spectrum). Finally, the calculated spectra of figure 3(b) can be compared to the observed one-electron and two-electron data for $q = 15$ shown in figure 3(a) [8]. The overall resemblance between the observed and theoretical spectra is astounding quantitatively in peak positions and even, qualitatively, in intensities.

The calculated $\pi$- and $\sigma$-plasmon spectra for $q = 14$ and 13 are compared to the corresponding experimental spectra in figures 4 and 5, respectively. Unfortunately, for these two ions, Selberg et al [8] do not provide the one-electron transfer spectrum separately from the two-electron spectrum. Nevertheless, it is clear that the overall agreement between theory
Figure 5. (a) The experimental energy gain spectra for Ar$^{13+}$ [8]. Note that the black, experimental curve is the sum of the one- and two-electron transfer curves. (b) The theoretical one- and two-electron gain spectra including coupling to $\pi$- and $\sigma$-plasmons.

and experiment is very satisfactory for the peak positions and even for the intensities when the two-electron intensities are subtracted visually from the combined one- plus two-electron curve.

4.2. One-electron gain spectrum for Ar$^{8+}$

Table 1 shows the energy transfers $E_n$ obtained from the Rydberg spectrum of energy levels of Ar$^{8+}$ according to NIST tabulated data [22]. In the calculation of the spectrum, the strength of the bare peaks $|\langle n_0|V|nl\rangle|^2$ has been tested as being proportional to $n^\gamma$ with either $\gamma = 1$, 2 or 3, independent of the value of $l$. Here it was found that better agreement is obtained with $\gamma = 3$. The capture $s$-states ($l = 0$) were given unit weight, while all other states ($l > 0$) were assigned the weight 0.5.

Figure 6 compares the calculated spectrum for one-electron transfer to the experimental one that, for this ion, has also been given in [8] separately from the two-electron transfer data.
Figure 6. (a) Experimental [8] one- and two-electron energy gain spectra for Ar$^{8+}$. Note the change of gain energy scale compared to that used for the higher charge ions in figures 3–5. (b) Theoretical one-electron spectrum for this ion including coupling to $\pi$- and $\sigma$-plasmons. The medium- and high-energy gain peaks are separated by about 3 eV rather than 6 eV, due to the specific Rydberg energy spectrum of this ion (see the text and table 1).

The first noticeable feature of the calculated spectrum is the presence of a peak separation of about 3 eV throughout the spectrum. As stated before, this is due to the peculiar distribution of Rydberg energies of this ion, namely the presence of several 2.5–3.5 eV differences between adjacent levels shown in table 1.

On the high energy tail, one observes, as in the previous spectra, the spreading of the peak intensities over Poissonian distributions of $\pi$- and $\sigma$-plasmons on the loss side of the peaks. For example, one recognizes clearly the 3 eV oscillations on the loss side of the nominal position of the 2p$^6$4d level at 49.5 eV. The latter level, in combination with the 2p$^6$4f level at 47 eV, produces a series of overlapping loss peaks separated by approximately 3 eV, down to 39 eV. The peak around 40 eV (where table 1 shows no level) is clearly a first-order $\pi$-plasmon loss peak of the Rydberg level at 47 eV, etc. What is seen in the energy range between 58 and 27.5 eV are several series of interdigitated 6 eV $\pi$-plasmon loss peaks generated by the ion Rydberg spectrum.
Figure 7. Detailed comparison between the theoretical two-electron gain spectrum and the observed spectrum for Ar\textsuperscript{15+}. The oscillations on top of the bell-shape continua are separated by about the $\pi$-plasmon quantum of 6 eV. Irregularities of the oscillations are caused by the overlap of Poissonian plasmon series originating from combined Rydberg energy transfers $E_n + E_{n'}$ in equation (35).

Well below 30 eV, the peak intensities are less affected by plasmon excitation processes and become dominated by those of the original Rydberg levels that are themselves separated by intervals of 2.5–3.5 eV (see table 1). On the threshold side, according to the present calculation, the Rydberg 2p\textsuperscript{6}7s7p manifold gives the highest peak of the spectrum at 13 eV. The observed left shoulder at 10.5 eV of this major peak corresponds to the 2p\textsuperscript{6}7d-7h Rydberg manifold (see table 1). The right shoulder at 16.5 eV corresponds to the 2p\textsuperscript{6}6d-6h Rydberg states. The assignment of these three major peaks is also that of Selberg et al [8]. However, their intensities receive weak contributions from the $\pi$-plasmon excitation phenomenon. A weak shoulder appearing at 7 eV in the theoretical spectrum is due to the first-order loss $\pi$-plasmon satellite of the major 13 eV peak and could account for the weak shoulder at that energy in the observed spectrum.

4.3. Two-electron gain spectra

Figure 7 compares the computed and experimental two-electron transfer spectra for the $q = 15$ argon ion in greater detail.

Both spectra consist of a broad, bell-shaped continuum extending from about 20 to 180 eV. This arises from two-electron transitions toward a dense forest of capture states corresponding to all possible pairs $(n, n')$ of combined energies $E_n + E_{n'}$ above an energy threshold of 20 eV. The continuum is obtained by broadening these numerous peaks with the instrumental resolution. The continuum is skewed in intensity towards low energies, as one might expect, since the combinations of shallower states have higher weight proportional to $n \cdot n'$. To obtain good
agreement between the two continuous spectra of figure 7, it was essential to take into account the Pauli exclusion principle, which reduces the \( n = n' \) transitions by a factor of 4, as discussed previously. It was also necessary to introduce the \( \sigma \)-plasmons that, due to the high energies involved, contribute throughout the spectrum.

Superposed on the continuum are many intensity oscillations due to multiple \( \pi \)-plasmon excitations of 6 eV quanta. Note that in both the calculated and experimental spectra, there are irregularities in the peak separations. This is because the 6 eV oscillation series do often overlap phase shifted. We emphasize here that the calculated spectrum does not involve either any new parameter adjustment or any arbitrary alignment with the observed spectrum. The calculation uses the same coupling constant parameters \( (g_\pi = 1.5, g_\sigma = 2.5) \) and transfer rate factor \( (f = 0.1) \) as for the one-electron spectra. The agreement is astonishing, taking into account the simplicity of the theoretical model.

The results of the calculations of the two-electron spectra for the other high-\( q \) ions \( (q = 14, 13) \) are shown, in figures 4 and 5, simultaneously with the calculated results for the one-electron spectra. All spectra were found to conform to the same general shape and to the same interpretation as that of figure 7. As stated before, we did not attempt to calculate the two-electron transfer spectrum of \( \text{Ar}^{8+} \) for lack of data on the double excitation levels of \( \text{Ar}^\text{VII} \). However, we are confident that the 3 eV oscillation period would also show up there because of its strong presence in the one-electron spectrum of this ion.

5. Conclusions

We have elaborated a new plasmon model for the interpretation of spectacular but ill understood kinetic energy gain spectra of highly charged \( \text{Ar}^{q+} \) ions scattered and partially neutralized by \( \text{C}_{60} \) [8]. Thanks to its exceptionally good energy resolution, the experiment was able to detect what we believe to be the role played in the neutralization events by the quantized collective excitations characteristic of the giant molecule. The model that we have proposed in this paper is based on an interplay between molecular plasmon excitations and the energetics of the electron transfer to the ions. In spite of its several simplifications, the model seems to embody the essential physics of the problem and explains, in a unified way, all of the remarkable features of the spectra, particularly the occurrence of regular intensity oscillations extending to very high gain energies in both the one-electron and two-electron spectra. In effect, all spectra bear witness to the strong shake-up of molecular plasmons caused by the sudden electron transfers to discrete ion Rydberg energy levels.

Our theory used the powerful semi-classical approach to evaluate the role of multiple plasmon excitations. The model Hamiltonian contains just two disposable parameters whose values are not arbitrarily adjusted but are chosen on physical grounds: (i) an effective coupling constant \( g \) between the \( \text{C}_{60} \) multipolar plasmons and the electron–hole pair of the charge transfer and (ii) a parameterized transfer rate \( f \omega_n \) reflecting the swiftness of the overall electron transfer. The latter consists of an adiabatic, ‘horizontal’ transfer of the electron from \( \text{C}_{60} \) to a resonant Rydberg state (transfer factor \( f \)) followed by a sudden, ‘vertical’ transition to the final state (rate factor \( \omega_n \)). We emphasized here that the present theory gives satisfactory agreement with experiment for all four ions \( q = 8 \) and 13–15 by using the same coupling constants (whose chosen values are consistent with the known polarizability properties of the \( \text{C}_{60} \) molecule) and the same transfer factor \( f = 0.1 \) for all spectra. We did not find it necessary or useful to attempt an optimization of the values of these parameters to best fit the spectra individually. This
gives credence to the theory and reflects the obvious fact that the mechanism of involvement of $C_{60}$ plasmons in the charge transfers must be identical for the four ions, notwithstanding their different capture state energies.

The success of the present theory entails that if one were to use other heavy, highly charged ions (e.g. $Ar^{16+}$, $Kr^{q+}$, etc), with the exquisite energy resolution of Selberg et al [8] experiments, similar oscillatory gain spectra ought to be observed with the unique periodicity of the 6 eV $\pi$-plasmon quantum of $C_{60}$. Also, other fullerenes in the vapour phase ($C_{70}$, $C_{84}$, etc) or other sp$^2$ targets in the solid state (such as thin graphite films, graphene sheets, carbon onions, etc, assuming that experimentally suitable methods can be developed for such targets) should reveal the same behaviour. Although sp$^2$ carbons, with their remarkable $\pi$ resonance, are specially suited to this kind of experiment, they are by no means the only target that could be used to observe the effect of collective excitations on the partial neutralization of highly charged ions. Grazing incidence scattering experiments of energetic ions on metallic clusters [21], or surfaces of various metals such as Al, Mg, Ag and Au, which all have well-defined surface plasmon modes [22, 23], could be used. The glancing incidence geometry enables us to discriminate gentle scattering encounters, involving charge transfer and inelastic processes similar to those studied here, from the flurry of destructive events occurring in head-on collisions [27, 28].

A preliminary, short report on the present work has appeared in [29].

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