Diffraction effects in the photoionization of clusters

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Abstract

In many atomic or molecular clusters an electron cloud exists which is delocalized over a volume of well defined shape. It is shown that the total and partial photoionization cross sections of those clusters oscillate on a scale of energy typically reached by synchrotron radiation. The frequencies of the oscillations are related to geometrical properties of the electron cloud, such as its thickness and the diameter of the cluster. These properties can in principle be extracted from the experimental photo cross section. As specific examples we discuss an alkali-metal cluster (Na_{40}) and the fullerene C_{60}. © 1997 Published by Elsevier Science B.V.

Most properties of a cluster X_N consisting of N atoms or molecules of type X can be traced back either to the single-particle limit $N = 1$ or to the solid-state limit $N \to \infty$. Among such properties, as they have been observed in photoabsorption spectra, are isolated atomic/molecular resonances ($N = 1$ limit) and collective excitations whose name *plasmon resonances* points to their origin in the solid phase ($N \to \infty$) [1,2]. Much effort has been invested to understand the collective effects which are strongest close to the classical Mie resonance (typically a few eV above the ionization threshold for alkali-metal clusters) [3]. Hence, the region of a few eV photon energy, conveniently reached by conventional dye lasers, has been investigated carefully and theory and experiment are in good agreement [4]. No experiments on alkali clusters have been performed at higher energies which can be reached by synchrotron radiation. Theoretical considerations are also lacking well beyond energies of collective excitations.

Here, we discuss an interesting diffraction effect which occurs for higher energies in the photoioniza-

tion cross section. Since this effect is intimately related to the geometrical shape of the cluster, it is a unique cluster property, neither present in the atomic nor in the solid-state limit. Moreover, the effect allows in principle a determination of those geometrical properties (such as the cluster diameter) directly from the photo cross section.

Our theoretical approach is based on the jellium approximation in combination with a density-functional-theory (DFT) description of the delocalized electron cloud [3]. Within the effective single-particle picture of the jellium model we calculate dipole matrix elements for each ionized electron between bound and continuum states in the jellium potential. To uncover the origin of the diffraction we represent the dipole operator in the *acceleration gauge*,

$$D_a = \frac{1}{i\omega} \nabla_r V(r). \tag{1}$$

The single-particle approach is justified at energies high enough so that no collective motion of the electrons occurs. Pictorially, we have to consider photon frequencies which are so high that the charged

cloud of electrons is not able to follow those rapid oscillations of the electromagnetic field vector. The total photo cross section

$$\sigma(\omega) = \sum_{\{i: E_i + \hbar\omega = E_f > 0\}} \sigma_{fi}(\omega) \qquad (2)$$

may be written as a sum over partial cross sections

$$\sigma_{fi}(\omega) = \int d\Omega |D_{fi}|^2, \qquad (3)$$

where each σ_{fi} describes the ionization of one electron from a bound state ψ_i into the accessible final continuum states ψ_f integrated over all angles Ω. The final states are restricted by energy conservation and dipole selection rules which govern the transition amplitude $D_{fi} = \langle \psi_f | D | \psi_i \rangle$.

For a simple analytic derivation, we concentrate on a spherical shape of the electron cloud, i.e. on closed-shell clusters [1]. Since in this case states are characterized by angular momentum quantum numbers, in general the dipole selection rule allows ionization from an initial state l_i into two final states $l_f = l_i \pm 1$.

A typical jellium potential is shown in Fig. 1a. As we can see, the electrons, although delocalized over the ionic cores of their mother atoms, form a charged cloud whose spherical boundary is relatively sharp, here for Na_{40}. We define the edge at $r = L$ as the cluster radius. The sharp edge makes the cluster potential different from soft molecular (Morse-type) or atomic (Coulombic) potentials and leads to oscillations in the photoionization cross section (Fig. 1b) calculated from Eq. (2). This type of oscillation is not observed in a generic molecular [5] or atomic [6] photoionization cross section of valence electrons. To understand the diffraction phenomenon in clusters we consider for the moment a box potential with an infinitely sharp edge (see Fig. 1a). For the dipole operator we obtain in this case a δ-function in the radius, $D_a \propto (r/r)\delta(r - L)$. Hence, for a given initial state ψ_i the partial cross section is proportional to

$$\sigma_{fi} \propto |\psi_f(L)\psi_i(L)|^2 \propto 1 + \cos(2kL - 2\eta), \qquad (4)$$

where $k = \sqrt{\hbar\omega + E_i}$. In Eq. (4) we have assumed

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[1] Large clusters come close to a spherical shape even for open shells.
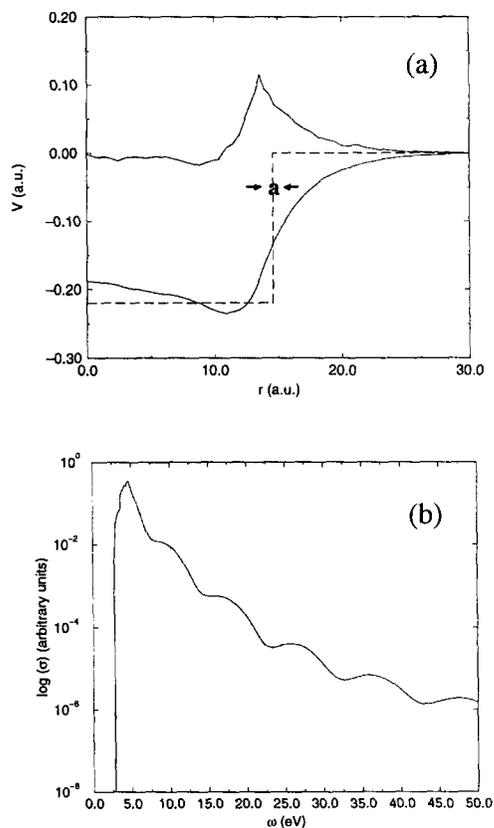

Fig. 1. (a) The jellium potential from a density functional calculation [15] for Na_{40} (solid). The "softness" parameter a of the potential edge is indicated. A box potential with the same edge L is shown with a dashed line; (b) the photoionization cross section of Eq. (2) for Na_{40}.

that E_i is small compared to $\hbar\omega$ so that we can describe the continuum electron in the final state roughly by a free (spherical) wave, i.e. a spherical Bessel function, whose asymptotic form for $kL \gg 1$ is a cosine. The phase shift η expresses the deviation from the free wavefunction due to the short-range interaction. For free motion it is solely caused by the centrifugal potential $l(l + 1)/2mr^2$ and has the value $\eta_l = l\pi/2$. Hence, a spherical box potential with radius L leads to an oscillation of the photo cross section with a frequency of $2L$ in k, or again for $|\hbar\omega/E_i| \gg 1$ in $\sqrt{\hbar\omega}$. If the edge of the potential is softened in a way that corresponds to the real situation in clusters, the dipole operator is no longer a delta-function, but it is still strongly peaked about $r = L$ so that the oscillations in the photo cross
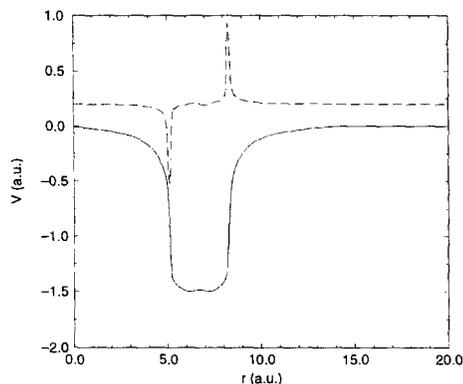
Fig. 2. The jellium potential for C_{60} from [9] (solid), and its derivative $dV(r)/dr$ (dashed) entering the dipole operator of Eq. (1).

Fig. 3. The photo ionization cross section for the HOMO (solid) and the HOMO-1 (dashed) electronic level of C_{60}, see text.

section are preserved for a softened edge (see Fig. 1b). The main effect of the "width" of the edge is to introduce an exponential decay in the cross section $\sigma(\omega) \propto \exp(-ak)$ compared to the purely algebraic decay $\sigma \propto k^{-7}$ caused by a box potential.

Here, however, we are mainly concerned with features of the photo cross section induced by the geometry of the cluster and in the light of the diffraction mechanism as sketched above, the structure of the C_{60} cluster promises interesting effects in the photoionization cross section. The carbon atoms of C_{60} form the surface of a sphere on which they are distributed uniformly. Since each C atom supplies its 4 valence electrons we have a cloud of 240 electrons in a hollow sphere centered about the cage of the carbon ions. It has been established [8] that properties of this electron cloud, which has spherical geometry to a good approximation, can be described by a radial jellium potential [9] shown in Fig. 2. A more recent model potential [10] with softer edges is probably more realistic. However, we have checked that there is no qualitative difference in the diffraction effects when calculated from a potential with softer edges (see also the remark in Ref. [21] of [10]).

In contrast to the charged sphere of alkali-metal clusters (Fig. 1a) which has one edge, the hollow sphere of the valence electron distribution of C_{60} has two edges with $L_> > L_<$ (see Fig. 2). Hence, the dipole operator of Eq. (1) now has two peaks (Fig. 2) which lead to an oscillation with two different fre-
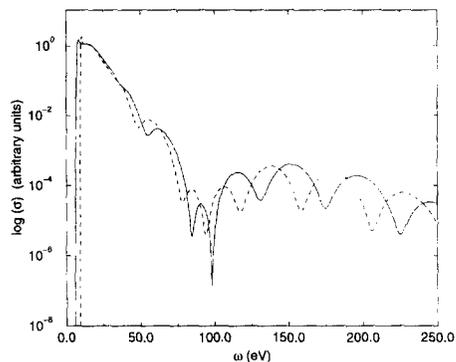
quencies of the dipole transition *amplitude* D_{fi} (see Eq. (3)). The partial cross section Eq. (3) will then oscillate with four frequencies, $2L_<$, $d = 2L_>$ and additionally with $\Delta_+ = L_< + L_>$ and $\Delta_- = L_> - L_<$. In Fig. 3 we show partial cross sections for the ionization of the bound states with radial quantum number $\nu = 2$ and angular momentum $l = 4$ (also referred to as the $2g$ state) and for the $2h$ state. These states correspond to the HOMO and the level below the HOMO level. At first glance one can see oscillations at a frequency which is close to the diameter of the cluster, $d = 2L_>$, and a beat with a much lower frequency. The Fourier transform of the cross section (Fig. 4) reveals the presence of all four frequencies. However, due to the magnitude of $L_>$
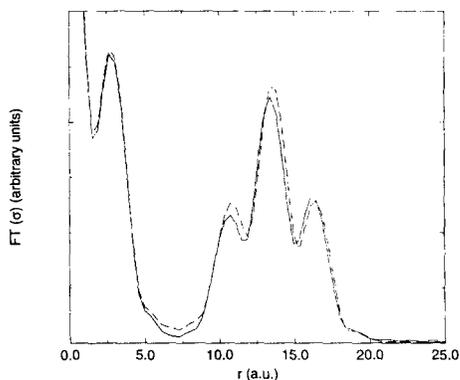

Fig. 4. Fourier transform of the scaled cross section of Fig. 3 as a function of photon wavenumber $k = \sqrt{\hbar\omega}$. A scaling $\exp(-ak)$ has been chosen to compensate the exponential decay of $\sigma(k)$ before the Fourier transform was applied.

and $L_<$ only the frequency of the beat Δ_- differs significantly from the other three which might be collectively taken as the cluster diameter d (see Fig. 4). These partial cross sections have actually been measured and display the expected oscillations at a frequency of the cluster diameter d [11–13]. In a recent model [14] the frequency of the oscillations has been linked to our frequency Δ_+.

If the beating frequency Δ_- could be seen experimentally it would provide the possibility to determine the *thickness* of the electron layer. To uncover a full period of the beat one would need to measure the photo cross section over roughly twice the photon energy range (250 eV) that has been measured so far. It is not clear if the jellium approximation holds at these high energies. However, even at lower energies (100–150 eV), where the diameter-related oscillations are clearly present and indicate a delocalized electron density, it should be possible to identify a relative minimum in the cross section caused by the beat frequency (in Fig. 3 at roughly 100 eV).

Fig. 5 gives a pictorial interpretation of the diffraction effect. The crucial point is that the recoil momentum must be absorbed and therefore a free electron cannot absorb photons. This aspect of photoabsorption is most clearly expressed in the acceleration gauge of the dipole operator Eq. (1) which is zero in regions where the potential is flat (e.g. inside the cluster), i.e., where the electron is quasi free and cannot absorb photons. Hence, the ionized electron is

only created at the edges of the potential where dV/dr is large. Under this constraint it is easy to explain the interference pattern by the difference of the path lengths of electron waves starting at the cluster edge (Fig. 5).

Note that the diffraction effect observed in EXAFS spectra is created from a single ionized wave of an *inner shell* electron. Interferences are due to the scattering of that wave from different (atomic) centers [16]. In a jellium cluster two (or more) waves of ionized *valence* electrons are created coherently during photoabsorption from the delocalized electron cloud. Well defined frequencies of the oscillations are due to the constraint that photoabsorption is restricted to the potential edges.

We would like to point out another interesting detail which is easily understood in our picture of photoionization of jellium clusters. In Fig. 3 one sees that the two partial cross sections for the $2g$ and the $2h$ level oscillate almost perfectly out of phase, at least for higher energies. This property is supported by the experimental cross sections (Fig. 7 in [13]). We recall from Eq. (4) that the final state wavefunction is approximately a spherical Bessel function with asymptotic behavior $(kL \gg 1)$ for an angular momentum l_f of $\psi_f \propto \cos(kL - l_f \pi/2)$. Due to the dipole selection rule, the initial $2g$ state $(l_i = 4)$ connects only with final angular momenta $l_f = 3$ and $l_f = 5$. Hence, the phase difference between the two contributions in the *squared* transition matrix element is $2\Delta l_f \pi/2 = 2\pi$ which means both partial cross sections oscillate in phase. The same is true for the final states $l_f = 4$ and $l_f = 6$ which arise from the initial $2h$ level. For this reason the relative phase Δ_{gh} of the cross sections $\sigma_{fi=g}$ and $\sigma_{fi=h}$ is exclusively determined by the angular momentum difference $\Delta l_i = 1$ of the *initial* states. Hence, for the partial cross sections, we have again twice the phase difference of the respective wavefunctions, namely $2\Delta l_i \pi/2 = \pi$, i.e. the observed out-of-phase oscillation.

To summarize, we have identified a diffraction effect which leads to oscillations in the partial and total photoionization cross section of jellium clusters. We have shown, by representing the dipole operator in the acceleration gauge that this diffraction effect caused by the sharp edge of the cluster potential is directly related to the geometrical shape of the clus-
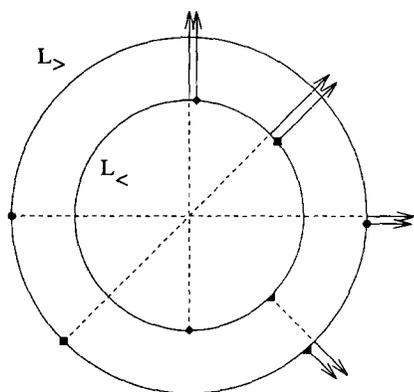

Fig. 5. The paths of the radial electron waves created by photoabsorption at the cluster edge. The different symbols for the point of creation indicate the four possible combinations which lead to interference with a respective path difference shown dashed.

ter. Taking an alkali-metal cluster (Na_{40}) and the fullerene C_{60} as examples we have demonstrated that from the frequency of the oscillations it is possible in principle to determine the cluster size (Na_{40}, C_{60}) and eventually even the thickness of the electron cloud (C_{60}) experimentally. We hope that this work will stimulate such experiments although we are aware of the numerous difficulties, from the question of mass selection in the alkali-metal case to the necessity of a good procedure for subtracting the background in order to uncover the possible beat frequency, for instance in C_{60} photoionization.

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