Proportionality of Electron-Impact Ionization to Double Photoionization

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A comparison is made between the cross section σ_e^+ for electron-impact ionization of singly charged ions and the ratio $\sigma^{2+}/\sigma_t(\text{abs})$ of double photoionization to the total photoionization cross section for N, O, and Ne. The photon- and electron-impact data were found to be proportional to each other to within about 9% for the first 70 eV above threshold. A study of the literature data shows that this proportionality between photon- and electron-impact data is a general phenomenon. The limits of the proportionality are unknown.

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During our recent studies of direct double photoionization of Ne, O, and N,[1-3] we observed a strong similarity between the shapes of the branching-ratio curves [i.e., the ratio of the double to total photoionization cross section $\sigma^{2+}/\sigma_t(\text{abs})$] and σ_e^+, the cross section for single ionization of an ion by electron impact.[4-7] A comparison of our data with the recommended experimental values[8,9] of σ_e^+ for Ne^+, O^+, and N^+ showed that the branching ratios were proportional to σ_e^+ over a considerable energy range above the double-ionization threshold. It is the purpose of this Letter to present experimental evidence of this proportionality and to show that it can be explained if we consider double photoionization to be a two-step process.

Consider direct double photoionization as a two-step process where the absorbed photon produces a single energetic photoelectron (from the outer shell of an atom) which then interacts with the remaining $(N-1)$ electrons to produce a secondary electron. From this model we can see a striking similarity with the external electron-impact process for ionization of an ion. This is shown schematically in Fig. 1. When the total energy ε of the two escaping electrons is the same in each case, then the final stages are identical in both collisional processes, with the exception that the total angular momentum carried off by the electrons will differ, in general, between the two cases. The intermediate stages differ only in that the external electrons are all directed into the ion and can interact with the valence electrons as they enter and leave the interaction zone, whereas the photoelectrons are created within the interaction zone with some moving out and others into the atom. Thus, there may be different interaction path lengths. However, the electron-electron correlations effects must be similar in both intermediate stages.

For photon impact at low gas pressures the total absorption cross section $\sigma_t(\text{abs})$ is defined by the equation $\Delta I = I_0 n L \sigma_t(\text{abs})$, where I_0 is the number of photons incident upon a gas of number density n and traversing a path length L. For atoms $\sigma_t(\text{abs})$ is identical to the total photoionization cross section. The number of doubly charged ions $\mathcal{N}^{2+}$ produced is determined by the partial cross section σ^{2+} defined by the equation $\mathcal{N}^{2+} = I_0 n L \times \sigma^{2+}$.

For electron impact on an ion we must consider an absorption cross section $\sigma_e(\text{abs})$ that determines the number of electrons Δn_e that enter the interaction volume of the ions. We define this cross section by the equation $\Delta n_e = n_e n_i L \sigma_e(\text{abs})$, where n_e is the number of electrons incident on an ion beam of number density n_i. The partial cross section σ_e^+ for single ionization of an ion is defined by the equation $\mathcal{N}^{2+} = n_e n_i L \sigma_e^+$.

We hypothesize that for electron or photon impact on an ion or atom, respectively, we will have a free energetic electron within an ion trying to escape along an effective path length l' or l, respectively, through $(N-1)/V$ electrons per unit volume, where V is the volume of the interaction zone. The cross section $\sigma_e^+(\text{int})$ for producing single ionizing events caused by the internal electron interactions can be defined by the equation $\mathcal{N}^{2+} = \Delta I (N-1)(l/V)\sigma_e^+(\text{int})$ for photon impact and a similar equation for external electron impact where Δn_e and l' are substituted for ΔI and l, respectively. All possible electron correlation processes are embodied in $\sigma_e^+(\text{int})$. The above equations can be summarized as follows:

Photon impact on atoms	Electron impact on ions	
$\Delta I = I_0 n L \sigma_t(\text{abs})$	$\Delta n_e = n_e n_i L \sigma_e(\text{abs})$	(1)
$\mathcal{N}^{2+} = I_0 n L \sigma^{2+}$	$\mathcal{N}^{2+} = n_e n_i L \sigma_e^+$	(2)
$\mathcal{N}^{2+} = \Delta I (N-1)(l/V)\sigma_e^+(\text{int})$	$\mathcal{N}^{2+} = \Delta n_e (N-1)(l'/V)\sigma_e^+(\text{int})$	(3)
$\therefore\ \sigma^{2+}/\sigma_t(\text{abs}) = \sigma_e^+(\text{int})(N-1)l/V$	$\sigma_e^+/\sigma_e(\text{abs}) = \sigma_e^+(\text{int})(N-1)l'/V$	(4)

$$\therefore\ \sigma^{2+}/\sigma_t(\text{abs}) = \sigma_e^+/[\sigma_e(\text{abs})\, l'/l]. \quad (5)$$

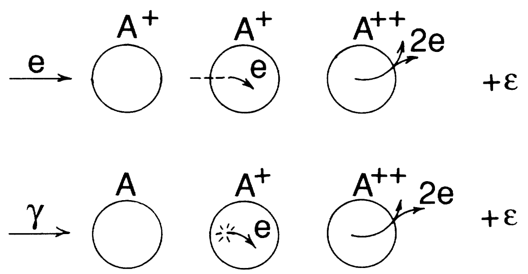

FIG. 1. Comparison for the production of A^{++} by electron-impact ionization of an ion A^+ and by photon-impact ionization of a neutral atom A.

Within our proposed model, Eq. (5) predicts the relationship that we might expect between photon and electron impact. This equation has a similar form to that used by Amusia *et al.*[10] who used the relation $\sigma^{2+}/\sigma^+ \sim \sigma_{ee}$, the cross section for internal scattering, in their calculation of the He^{2+} cross section. In our study of N, O, and Ne we observed that the branching ratio $\sigma^{2+}/\sigma_t(\text{abs})$ was proportional to σ_e^+ from 0 to 60 eV above the double-ionization threshold. This implies that the term in square brackets, Eq. (5), is constant for this energy range.

The magnitude of $\sigma_e(\text{abs})$ can be obtained by calculating the value of the impact parameter b such that the distance of nearest approach of the electron to the center of the ionic charge is equal to r_0, the average radius of the ion. Then, $\sigma_e(\text{abs}) = \pi b^2$. If this is done for the lowest electron energy that can ionize the ion then we get a maximum value for $\sigma_e(\text{abs})$. The values for r_0 used in the calculation were 0.063, 0.057, and 0.048 nm for N^+, O^+, and Ne^+, respectively.[11] We find that the ratio $b/r_0 = 1.32$ for N^+, O^+, and Ne^+ when $\varepsilon = 0$ and is about 14% smaller when $\varepsilon = 60$ eV. That is, $\sigma_e(\text{abs})$ will decrease as ε increases until $b \sim r_0$. However, we might expect the average value of l' to increase as b decreases. Whatever internal mechanism takes place, it appears experimentally that the energy dependence of the terms in the square brackets, Eq. (5), is such that they essentially cancel each other.

We present our branching-ratio results in Fig. 2 for N, O, and Ne, and compare them to the published σ_e^+ data normalized to give a good fit between 0 and 50 eV above threshold. The normalizing factors are 0.250×10^{16}, 0.292×10^{16}, and 0.375×10^{16} cm^{-2} for N, O, and Ne, respectively. Very good proportionality is found over the first 50–60 eV for each atom.

It is interesting to equate our proportionality constants with the square brackets in Eq. (5). At threshold ($\varepsilon = 0$) $\sigma_e(\text{abs}) = 5.47 r_0^2$. Inserting the values of r_0 for N^+, O^+, and Ne^+ into $\sigma_e(\text{abs})$ we find that the ratio l'/l is approximately constant for each of the elements and is ~ 2. For higher energies, when $b \sim r_0$, $\sigma_e(\text{abs}) = 3.14 r_0^2$ and l'/l is ~ 3.4. Thus, for the term in the square brackets to remain constant as ε increases requires l'/l to increase as expected.

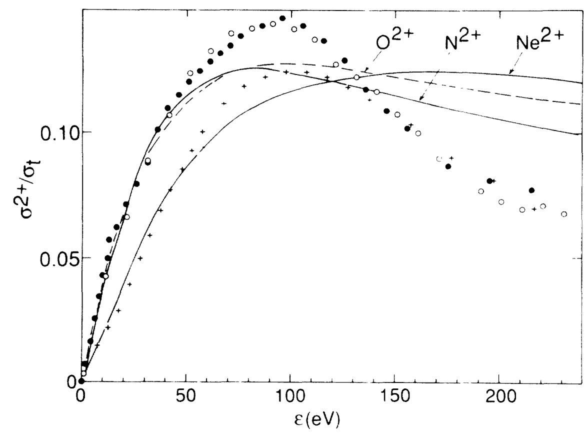

FIG. 2. Branching-ratio data for O^{2+}, ○ (Ref. 2); N^{2+}, ● (Ref. 3); and Ne^{2+}, + (Ref. 1) compared to the normalized σ_e curves for O^{2+}, --- (Ref. 5); N^{2+}, —— (Ref. 4); and Ne^{2+}, —— (Ref. 7).

We have also found that our proportionality constants given above can be replaced by a single Z-dependent factor, namely, $(Z-1)0.0417 \times 10^{16}$ cm^{-2}. Because r_0^2 appears in the denominator in Eq. (5) we looked for a Z dependence in the ionic radii used in this work and found $(Z-1)r_0^2 = (2.24 \pm 0.14) \times 10^{-16}$ cm^2, which is consistent with the experimental data. However, this may be fortuitous because the calculated values of the radii are uncertain by about $\pm 20\%$.

At higher photon energies the experimental branching ratios decrease more rapidly than do the electron-impact data. However, this may be an experimental problem. We note that there is poor agreement experimentally on the absolute value of the Ne double-ionization cross section and branching ratio at the higher photon energies.[1,12–15] Most of the published branching-ratio data, when normalized, follow the σ_e^+ curve for the first 50 eV and hold together with respect to each other over the first 80–90 eV. This gives us confidence in the correctness of the shape of the photoionization branching ratios in this energy region. Towards higher energies the published ratios begin to diverge from each other. The data of Wight and Van der Wiel[15] show an increase with energy whereas the present data[1] decrease rapidly with energy. Only the data of Holland *et al.*[14] and the calculations of Chang and Poe[16] show a plateau beyond 100 eV. The large deviation between the present high-energy data and that of Holland *et al.* may be caused partly by incomplete corrections for the effect of higher-order spectra and scattered light in the present results. If this turns out to be the case then from the data of Holland *et al.* Eq. (5) is valid between 0 and 200 eV. Clearly, new measurements should be made in this energy range.

We can find further evidence of the proportionality of

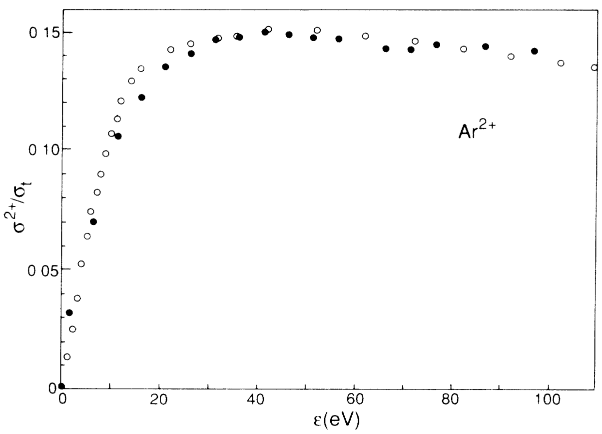

FIG. 3. Branching-ratio data for Ar^{2+}, ● (Ref. 17), compared to the normalized σ_e^+ data, ○ (Ref. 6).

the photoionization results to the electron-impact data by comparing the published data for Ar and He. In Fig. 3 we compare the branching ratios for Ar^{2+} obtained by Kossmann and Schmidt[17] (solid data points) to the values of σ_e^+ reported by Man, Smith, and Harrison[6] (open circles). The σ_e^+ values were normalized at about 35 eV to the branching-ratio data using a proportionality factor of 0.133×10^{16} cm^{-2}. The agreement is almost perfect over the entire range from 0 to 100 eV. Numerous measurements of the branching ratios have been made[13-15,18] and all are in general agreement with the data in Fig. 3.

Numerous measurements have also been made for the He^{2+} branching ratios.[13-15,19] We compare, in Fig. 4, the recent data of Kossmann and Schmidt[17] (crosses) and that of Bizeau *et al.*[19] (open circles) to the electron-impact ionization cross-section data for He^+.[20] We normalized the σ_e^+ curve (solid line) to fit the data of Bizeau *et al.* using a proportionality constant of 1.02 $\times10^{16}$ cm^{-2}. We have also included the data from the high-energy calculations of the photoionization branching ratios by Amusia *et al.*[10] The experimental results agree with the σ_e^+ curve to within a few percent. The largest deviation between σ_e^+ and the calculated branching ratios is only about 10% at 360 eV otherwise the calculated data fit the σ_e^+ curve between 200 and 600 eV. Amusia *et al.* estimate that shake-off accounts for 40% of the double-ionization cross section and that the remaining 60% is caused by inelastic scattering of the initial photoelectron on the remaining electron. We note that σ_e^+(int) in Eq. (3) includes both the inelastic-scattering and shake-off contributions. We believe that the observed proportionality will continue to higher photon energies. Thus, with our constant of proportionality we can use the electron-ion impact data of Peart, Walton, and Dolder[20] at 10 keV to predict that the ratio σ^{2+}/σ_t(abs) for He at 10 keV is ~0.32%, considerably less than the limit currently predicted by theory.[10]

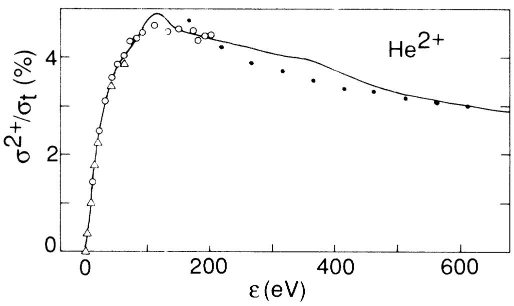

FIG. 4. Branching-ratio data for He^{2+} [experimental: ○ (Ref. 19), △ (Ref. 17); theoretical: ● (Ref. 10)] compared to the normalized σ_e^+ data, —— (Ref. 20).

Further justification of our model is obtained if we consider the photon-impact process given in Eq. (4). Bringing σ_t(abs) over to the right-hand side of the equation and integrating both sides with respect to frequency ν from zero to infinity we find that the oscillator strength for double photoionization is proportional to $N(N-1)$, where N is the total number of electrons in the atom. This is in agreement with our previous experimental results.[1]

A simple model for double photoionization involving an internal electron-impact process thus appears to account for the surprising result that the branching ratios for double ionization are proportional to the electron-impact ionization cross sections for single ionization of the corresponding ion. In addition, it appears that this is a general mechanism where the released photoelectron can cause excitation (satellite states) as well as multiple ionization of molecules. We have compared our branching-ratio data for "simultaneous" production of He^+ excited into the 2*s* level[21] with the external electron-impact data for excitation of He^+ into the 2*s* level.[22] Good proportionality exists between the two sets of data. We have compared the double-photoionization branching ratios measured by Dujardin *et al.*[23] and Kossmann *et al.*[24] for H_2 with the electron-impact ionization cross sections of Peart and Dolder[25] for $H_2{}^+$ and again find good proportionality.

Finally, on the basis of the above proportionality a clarification of the comparison of Wannier's threshold law[26] to double photoionization is necessary. From the Wannier threshold law we note that the number of doubly charged ions $\mathcal{N}^{2+}$ produced by electron impact of a singly charged ion is given by

$$\mathcal{N}^{2+} \propto \sigma_e^+ \propto \varepsilon^{1.056}. \qquad (6)$$

But from the observed proportionality between σ^{2+}/σ_t(abs) and σ_e^+ we see that for double photoionization, $\mathcal{N}^{2+} \propto \sigma^{2+} \propto \sigma_t(\text{abs})\sigma_e^+$. Thus, to test the Wannier law by the use of double-photoionization results, we should use the relationship

$$\sigma^{2+}/\sigma_t(\text{abs}) \propto \varepsilon^{1.056}. \qquad (7)$$

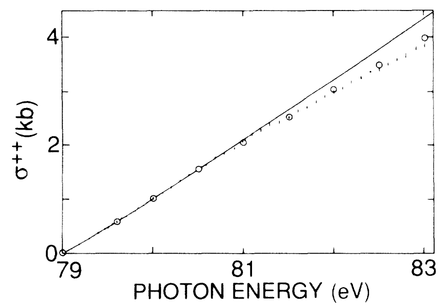

FIG. 5. He^{2+} photoionization cross-section data of Kossmann, Schmidt, and Andersen (Ref. 28) plotted as a function of photon energy. The solid line represents $\sigma^{2+} \propto \varepsilon^{1.056}$ and the open circles represent $\sigma^{2+} \propto \sigma_t(\text{abs})\varepsilon^{1.056}$.

Of course, exactly at threshold $\sigma_t(\text{abs})$ can be treated as a constant, and thus Eqs. (6) and (7) have the same energy dependence. But to test the extent of the validity of the law away from threshold, it appears that we should use Eq. (7).

Only two experiments have been performed to test the threshold law for double photoionization, namely, the studies of H^- by Donahue *et al.*[27] and of He by Kossmann, Schmidt, and Andersen.[28] Both groups compared the threshold law to σ^{2+}. In the H^- experiments the authors' noted that $\sigma_t(\text{abs})$ was essentially constant over their region of study. However, for He this is not the case and we find that the data of Kossmann, Schmidt, and Andersen are in better agreement with Eq. (7). We illustrate this in Fig. 5 by reproducing their figure along with the results for the product $\sigma_t(\text{abs}) \times \varepsilon^{1.056}$, which we normalized to their data at 80 eV.

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