Effects of partial cross sections on the energy distribution of slow secondary electrons

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The shapes of the energy distribution of secondary electrons can be predicted for fast incident charged particles by using dipole oscillator strengths in conjunction with the Born formula. Target atoms or molecules may have one or more ionization potentials close to the first one and the corresponding partial photoionization cross sections are sometimes large. Allowance must then be made for the differences in kinetic energies of photoelectrons which leave alternative ionic states. This produces a significant change in the expected secondary electron spectrum at low energies. The photoionization data for NO are analyzed and the predicted shape of the secondary electron energy distribution agrees well with that of the experimental distribution at those secondary electron energies where a comparison is possible. Predicted low energy results from a preliminary analysis for N2 are also reported.

I. INTRODUCTION AND THEORY

In previous papers1–3 a method was given for testing the consistency of experimentally determined energy distributions of secondary electrons produced by the impact of fast charged particles on atoms or molecules. The method is based on the formula for the differential cross section in the first Born approximation which for incident particles of charges ze and velocity v is given by

\[
\frac{\partial^2 E}{\partial E} = \frac{4\pi a_0^2 e^2}{E} \left\{ A(E) \ln \left( \frac{4TRCE(E)}{E^2} \right) + B(E, T) \right\}, \tag{1}
\]

where \( T = \frac{1}{2}mv^2 \), \( m \) being the electronic mass, \( a_0 \) is the Bohr radius, \( R \) is the Rydberg unit, and \( E \) is the energy transfer. The function \( C(E) \) is the square of the maximum momentum transfer at which the dipole interaction dominates, \( A(E) \) is related to the dipole oscillator strength \( df/dE \) through the relation

\[
A(E) = \frac{R^2}{E} \frac{df(E)}{dE}, \tag{2}
\]

and \( B(E, T) \) contains the contributions to \( d\sigma/dE \) from "hard" collisions, i.e., those with large momentum transfers. If the target electrons have binding energy \( B \), then the secondary electron energy is \( W = E - B \). If there are several binding energies, then there will be summations over the contributions from different orbitals in Eq. (1).

For the production of fast secondary electrons, hard collisions dominate, and the main features of the differential cross section can be obtained from the Mott formula for incident electrons or the Rutherford formula for other particles.4 At low and intermediate secondary energies where "soft" collisions (i.e., those with small momentum transfers) are more prevalent, the characteristics of \( d\sigma/dE \) as a function of \( E \) are mainly determined by those of \( df/dE \). The above approach has been verified for many collision systems, e.g., for proton and electron impact data for He,5 and electron impact data for Ar.1,6 H2,7 and Ne.8 Some workers have, in fact, introduced "empirical" scaling functions to weight the hard and soft collision contributions in the Born formula.5,7,8

It has proved valuable to present secondary electron data by means of a Platzman plot in which the quantity

\[
Y(E, T) = \frac{d\sigma(E, T)}{dE} \frac{TE^2}{4\pi a_0^2 R^2} \tag{3}
\]

is plotted against the inverse of the energy transfer in Rydbergs. The quantity \( Y(E, T) \) is, in fact, the ratio of the differential cross section to that given by the Rutherford formula. The advantages of presenting the data in such a fashion are (1) the range of the independent variable \( (R/E) \) is finite, (2) the low and intermediate energy parts of the spectrum are emphasized, and (3) the area under the curve is proportional to the total ionization cross section. In particular, (2) and (3) enable one to test the consistency of the data in the way described in previous articles.1–3

Thus, if one inserts the Born formula1 in Eq. (3), the dipole contribution appears as \( Edf/dE \). Since low and intermediate energy secondaries are produced (for high incident energy \( T \) mainly by the dipole interaction, part (2) of the consistency test can be performed by comparing the shape of \( Y(E, T) \) with that of \( Edf/dE \) in the Platzman plot. Values of the latter can be obtained from measured total photoionization cross sections \( \sigma_{\text{ph}}(E) \) through the relation

\[
\sigma_{\text{ph}}(E) = 4\pi a_0^2 R [df(E)/dE], \tag{4}
\]

where \( \alpha \) is the fine structure constant.

In all the previous applications of the above approach, the formulas (2) through (4) have been used without taking into account the various ionization potentials of the target atom or molecule. In secondary electron spectra only the kinetic energy of the electrons is taken into account, not the energy transfer. That is, electrons with a given kinetic energy could have come from various orbitals with different binding energies. Photoionization cross sections, on the other hand, are usually reported as functions of the photon energy \( E \) (or wavelength) which is the actual energy transferred in the ionization process. Since we are interested in comparing the continuum oscillator strength with the secondary electron energy distribution, we have to recast the former as a function of the kinetic energy of the ejected electrons.

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Suppose an atom or molecule has a sequence of ionization potentials \( B_j \), for \( j = 1, 2, \ldots, n \). We distinguish the corresponding partial oscillator strengths for ionization, \( df_j/dE \), where \( E_j = W + B_j \), from the total oscillator strength for ionization, \( df/dE \). When summation over different orbitals is taken into account in the Born formula (1), it is apparent that the dipole contribution to \( YE(T) \) comes from

\[
F(W) = \frac{Edf}{dE} + \sum_{j=2}^{n} \frac{E_j}{E} \frac{df_j(E_j)}{dE_j},
\]

where \( E = W + B_1 \). It is the shape of \( F(W) \) in the Platzman plot which should indicate the shape of \( YE(T) \) for low and intermediate values of \( E \). [Note that the total areas under the curves \( F(W) \) and \( Edf/dE \) are identical in the Platzman plot providing one neglects multiple ionization.]

Let \( \Delta_j = B_j - B_1 \) for \( j = 2, \ldots, n \). When the \( \Delta_j \) are large and the corresponding partial photolization cross sections are small in comparison with the total cross section, the partitioning of \( df/dE \) is not important, as illustrated by the previous analyses\(^8\) for Ne, etc. For atoms of large atomic number and for most diatomic molecules other than \( \text{H}_2 \), the first few \( \Delta_j \) may be quite small, and the partial cross sections for transitions leading to the first few excited ionic states are often quite large, in which case the quantity \( F(W) \) departs significantly from \( Edf/dE \). This will be illustrated for the molecule NO for which a substantial amount of data is available concerning ionization potentials and partial cross sections. A brief qualitative report of our analysis for \( \text{N}_2 \) will also be given.

| TABLE I. | Ionization potentials of NO. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| M.O. of NO \( \text{vacated} \) | State of NO \( \text{\textsuperscript{\text{\textbullet}}} \) | Ionization potential \( \text{\textsuperscript{\text{\textbullet}}} \) (eV) | Group |
| \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) |
| \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) | \( \pi^2p \) |

**FIG. 1.** Branching ratios versus photon wavelength for production or states of groups of states of NO\( \text{\textsuperscript{\text{\textbullet}}} \) by photoionization of NO. For details of the groups of states, see Table I.

II. APPLICATION TO NO

The diatomic molecule NO has several ionization potentials within 10 eV of the first ionization potential (9.26 eV) and the partial cross sections for photoionization leading to excited states of NO\( \text{\textsuperscript{\text{\textbullet}}} \) have high branching ratios. Hence, this molecule is one for which re-casting the \( Edf/dE \) curve according to Eq. (5) should be important. This is also expected to be the case for large atoms such as \( \text{Xe} \), the diatomic molecules \( \text{N}_2 \), \( \text{O}_2 \), and \( \text{CO} \), as well as polyatomic molecules such as \( \text{H}_2\text{O} \), \( \text{CH}_4 \), and \( \text{NH}_3 \). For many of these, however, there are insufficient data on partial cross sections to carry out the necessary computations. For NO, the reconstitution of \( Edf/dE \) produces significant changes well into the energy region of the measured secondary electron spectrum and a direct test of the importance of the use of Formula (5) is possible.

The ground state of NO has the electronic structure which can be written\(^10\) (though the \( g \) and \( u \) symmetries are not strict)

\[
X^2\Pi: KK(c_2 \text{~2s} \text{~2p} \text{~2p}) \text{~(c_2 \text{~2s} \text{~2p})} \text{~(c_2 \text{~2p})} \text{~(c_2 \text{~2p})}.
\]

Table I shows the 13 states of NO\( \text{\textsuperscript{\text{\textbullet}}} \) which result when various orbitals higher than the \( K \) shells (denoted by \( Kk \)) are vacated, together with the corresponding ionization potentials. The values are taken from Turner et al.,\(^15\) Edqvist et al.,\(^11\) Samson,\(^12\) and Siegbahn et al.\(^13\) The Turner et al. values are given when they are close to the values given by Edqvist et al. If there is a large discrepancy, then the Edqvist et al. value is given in parentheses. The next ionization potential below those given in Table I is 40.6 eV\(^13\) corresponding to a wavelength of 305 Å.

Partial photoionization cross sections for NO have been measured from 584 to 782 Å by Bahr et al.,\(^14\) but some ionic states are not resolved when their ionization potentials are close. Groups of such close-lying final states for which partial cross sections are not resolved are classified as \( A \), \( B \), \( C \), and \( D \) in Table I. The only other available partial cross section data are at 462 Å\(^12\) and at 304 Å.\(^11\) These three sets of data were used to construct the branching ratio curves for production of states or groups of states of NO\( \text{\textsuperscript{\text{\textbullet}}} \) shown in Fig. 1. It
can be seen that contributions to the total cross section from groups A and B become larger within a few eV of their appearance thresholds. Though there are uncertainties in the details of these curves below 584 Å, the most important effects in the reconstituted oscillator strength density come from energies where the branching ratios are known.

The partial cross sections \( \frac{df}{dE} \) to be used in Eq. (5) should be independent of the angular distribution of photoelectrons since we are interested only in the energy distribution of secondary electrons. Unfortunately, most data on partial cross sections determined from photoelectron analysis, including those in Refs. 11 and 14, are deduced from photoelectrons ejected at 90° to the incident light beam direction. Partial cross sections obtained by integration over the photoelectron angles may be somewhat different from those at 90°. Hence, our results on \( F(W) \) presented below may require slight modification if data on partial cross sections that are angle-independent become available (e.g., by measurements at the “magic angle”).

In Fig. 2(b) is shown the \( E df/dE \) curve obtained from the photoionization data compiled by Berkowitz.\(^{15} \) In the wavelength range from first threshold to about 680 Å, the photoionization cross section is characterized by a large number of autoionization peaks corresponding to Rydberg series converging to excited states of NO.\(^{\ast} \) An estimate of the direct photoionization contribution was made by drawing a smooth curve through the lowest points (long dashed curve).

The branching ratios of Fig. 1 were applied to values of the total \( df/dE \) and \( F(W) \) [Eq. (5)] was computed at various values of the energy transfer up to \( E = 2.5 \) R. The results are indicated by the (mainly) solid curve in Fig. 2(b). Extrapolation of known branching ratios was necessary for a few high \( E \) values when calculating the contributions from transitions which lead to highly excited states of NO,\(^{\ast} \) but the uncertainties in the final results should not be more than 10%. Some of the pronounced autoionization peaks have been included in the term \( E df/dE \), but there are so many in the region from \( E = 0.95 \) to 1.35 R that a dashed curve has been used in Fig. 2(b) for most of that energy region. Furthermore, when autoionization could leave the ion in either the ground or excited states (i.e., when \( E \) is greater than the appearance potential of NO\(^{\ast} \) (\( \epsilon \) \( \Sigma^\ast \)))\(^{\ast} \), the kinetic energies of the ejected electron can be determined only when branching ratios are known. The correct magnitudes and energies of the autoionization peaks for \( E > 1.15 \) R are thus uncertain, but the details of those peaks which have been included are accurate.

The outline of the theory in Sec. 1 indicated that the differential cross section for production of secondary electrons should consist of soft and hard collision components. The version of the Mott formula previously employed\(^{3-8} \) was used to compute the curve marked "MOTT" in Fig. 2(a). For NO one must take into account the degeneracy in the final states which result when an electron is removed from \( \pi_2p \) orbitals. Also shown in Fig. 2(a) is the Platzman plot of the secondary electron data of Opal et al.\(^{15} \) for impact of 500 eV electrons on NO.

It can be seen that “adding” the original \( E df/dE \) value in Fig. 2(b) to the Mott curve of Fig. 2(a) would lead to a sharper rise of \( Y(E, T) \) at \( R/E = 0.85 \) R than that of the Opal et al. data.\(^{18} \) Furthermore, the peak would be at the wrong secondary electron energies. The result of adding the calculated \( F(W) \) to the Mott cross section, on the other hand, leads to a shape which is in agreement with the secondary electron data where this is known. Also, \( Y(E, T) \) for the experimental data begins to turn upward at the lowest secondary energies for which the cross section was measured. One can see that this is not the beginning of an overall trend, but probably a superposition of autoionization peaks. Further confirmation of this is obtained by extrapolating \( Y(E, T) \) from the Opal et al. data to zero secondary kinetic energy according to the shape of \( F(W) \). This is indicated by the dashed curve in Fig. 2(a). That this extrapolated \( Y(E, T) \) is basically correct is obtained by determining the value of the total ionization cross section \( \sigma_i \) from the relation

\[
\sigma_i(T) = \frac{\sigma_{i0}}{T} \int_{R/E_{\text{max}}}^{R/B_1} Y(E, T) d(R/E),
\]

where \( \sigma_{i0} \) is the total ionization cross section at a reference temperature \( T_0 \).
where $E_{\text{max}} = (T - B_{2})/2$. From the Opal et al. data and the extrapolated $Y(E, T)$ in Fig. 2(a), one obtains $\sigma_{1} = 1.95 \text{ sr}$ (without autoionization peaks) which agrees well with the experimental value of $\sigma_{1} = 2.10 \text{ sr}$ obtained by Rapp and Engander-Golden.\(^{17}\)

The results we have given for NO show that when there are ionization potentials close to the first and the partial photoionization cross sections for production of the corresponding excited Ionic states are large, then it is important to recast the $E df/dE$ curve to allow for the different kinetic energies of the ejected electrons. The method employed previously for light rare gas atoms and H\(_{2}\), using the Born formula (1) in conjunction with oscillator strength data and a hard collision cross section (Mott or Rutherford), can then be applied to more complex atomic or molecular systems, providing partial cross sections are known over a sufficient range of energies. More experiments on partial cross sections, for $E$ up to 100 eV, are clearly desirable. Although the branching ratios for NO below 584 Å in Fig. 1 have been interpolated using the few known data points, the gross features of $F(W)$ are expected to be basically correct. The use of correct partial cross sections in the calculation of average energy spent per ion pair, for example, would lead to a higher value than that obtained from the total $E df/dE$.

Finally, we make some remarks about our investigation for N\(_{2}\). Though the partial cross section data are not as well known for this molecule as NO, we used the available data to calculate the quantity $F(W)$ from the measured total photoionization cross sections of Cook and Metzger\(^{18}\) and the values given by Berkowitz\(^{15}\) in conjunction with the partial cross sections obtained by Blake and Carver\(^{19}\) and by Gardner and Samson.\(^{20}\) The most significant differences between $E df/dE$ and $F(W)$ occurred between first threshold ($E = 1.15 \text{ R}$) and $E = 1.55 \text{ R}$, where a comparison with the value $Y(E, T)$ of the Opal et al. data\(^{18}\) is not possible. Our computed $F(W)$ values indicate that $dn/dE$ should have a peak for secondary electron energies of about 1.1 eV and a minimum at about 2.9 eV. The data of Stolterfoht\(^{21}\) for proton impact on N\(_{2}\) show the predicted peak at the correct secondary energy. The minimum, however, is not discernible in the experimental results, which could be due to its being filled in by closely spaced autoionization peaks. Additional data are needed to completely resolve the discrepancy.

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\begin{itemize}
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