Contribution of the Metastable $E\,^3\Sigma_g^+$ State to the Population of the $C\,^3\Pi_u$ State of N_2 Following Electron-Impact Excitation*

L. Kurzweg, G. T. Egbert, and D. J. Burns
Behlen Laboratory of Physics, University of Nebraska, Lincoln, Nebraska 68508
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Following low-energy electron-impact excitation of molecular nitrogen, the method of delayed coincidence is used to separate the prompt and delayed radiation of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ transition. The emission function of the prompt radiation, due to direct C-state excitation, is seen to increase smoothly above threshold. The emission function of the delayed emission, due to collisional deactivation of metastable states, is composed of two sharp peaks at 12.0 and 12.7 eV as well as a broader peak at about 22 eV. The first of these peaks is recognized as the direct resonant excitation of the metastable $E\,^3\Sigma_g^+$ state. Evidence is found indicating that the other peaks, which may be associated with the excitation of the $a''\,^1\Sigma_g^+$ state, lead to indirect excitation of the E state.

I. INTRODUCTION

Experimentally observed excitation functions for the production of metastable states by low-energy electron impact on nitrogen display a sharply resonant feature at about 12 eV. This feature has been attributed to the resonant excitation of the $E\,^3\Sigma_g^+$ state of molecular nitrogen.

Electron-impact excitation of metastable nitrogen molecules has been studied primarily by quenching metastables in nitrogen beams using surface ionization[1–5] or Penning ionization.[6] Optical emission from excited molecular beams may, however, also be used to yield information on metastable behavior. Observing such a metastable beam, Freund[7] found the emission functions for the Herman-Kaplan bands ($E\,^3\Sigma_g^+ \rightarrow A\,^3\Sigma_u^+$) and for the (0, 0) band of the second positive system ($C\,^3\Pi_u \rightarrow B\,^3\Pi_g$) to have the same E-state resonant excitation peak. Since the observations were made on a segment of the beam in which all directly excited nonmetastable states had decayed, and since the C state is not metastable, Freund concluded that the E state was cascading into the C state.

Recently, Finn *et al.*[8] have observed structure near the thresholds of the second-positive-system emission functions. The nitrogen target in this experiment was excited by an electron beam with a 50-meV energy spread. Part of the structure observed using this narrow beam spread was found to be pressure dependent and was attributed to collisional processes in which the E state was quenched while exciting the C state.

In the present experiment, the emission from several bands of the second positive system is used to study the population of the C state after electron-impact excitation of a nitrogen-gas target. The method of delayed coincidence is used to separate prompt radiation, due to direct C-state excitation, from delayed radiation, due to collisional population of the C state from a metastable state.

It is found that the long-lived component of the radiation has an emission function consisting of two closely spaced peaks at 12.0 and 12.7 eV, as well as a broad maximum at 22 eV. The first of these peaks is identified as the direct resonant excitation of the E state.

II. EXPERIMENTAL ARRANGEMENT

In the present experiment, photons from the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ transitions are observed as they are emitted from a molecular-nitrogen-gas target which is excited by a square-wave-pulsed electron beam. The method of delayed coincidence is used to time-resolve the emission with respect to the start of each excitation pulse.

The experimental arrangement, which consists of a modulated electron gun, a gas target, a monochromator, a photomultiplier, timing circuits, and a multichannel analyzer, is shown in Fig. 1.

A multistage electron gun with a Soa immersion lens and an oxide-coated cathode is used. The gun is turned on and off by grounding the Soa lens and pulsing the cathode potential between ± 2.5 V, using a pulse generator with rise times less than 1 nsec. The gun is typically modulated at about 1 MHz with both on times and off times lasting for 0.5 μsec. The currents used are normally between 3 and 0.3 μA. The energy spread of the electron beam, measured using a parallel-plate energy analyzer, was found to be 0.3 eV full width at half-maximum.

The electron beam is directed into a gas cell through a circular entrance aperture with a 0.05-in. diameter. The excitation of the gas within the cell is observed at right angles to the beam through a 1-in. circular quartz disk located on the side of the cell. The beam is collected in a deep Faraday cup which forms part of the gas container but is electrically insulated from the gas cell. Gas pres-

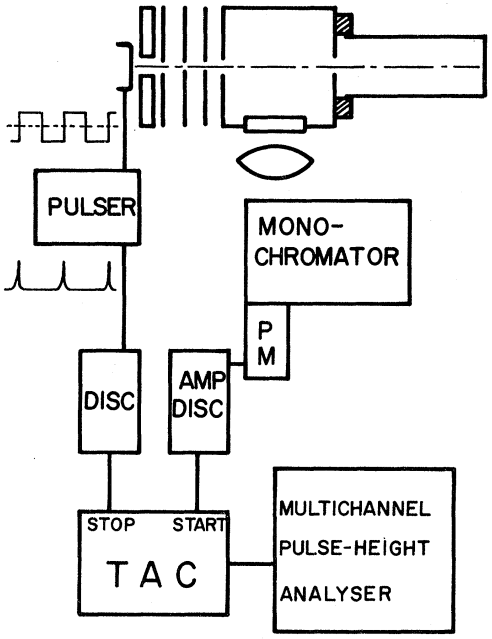

FIG. 1. Experimental arrangement showing the electron gun, gas cell, optics, and electronics (see text).

sure is maintained by flowing untrapped nitrogen into the cell through a needle valve from a tank of 99.9% pure nitrogen. The gas pressure within the cell is measured with a Baratron capacitance manometer. Pressures between 5 and 50 mTorr are used and background pressures never exceed 2×10^{-5} Torr.

At right angles to the beam, a quartz lens with a 75-mm focal length is used to focus a 2-mm section of the beam onto the entrance slit of an $f/6.8$ monochromator. The resolution of the monochromator is set at 40 Å. The photons transmitted through the monochromator are detected by an RCA 8850 photomultiplier.

The usual technique of delayed coincidence is used. The nitrogen in the gas cell is excited each time the gun is pulsed on. The pulser which supplies the voltage for gun modulation also supplies a trigger pulse coincident with the start of each gun pulse. The trigger pulse establishes the time base such that the probability for getting a photon count at any time with respect to the start of the gun pulse is directly proportional to the number of excited molecules at that particular time in the cycle. The probability for getting a photon count during each cycle of the gun is typically 10^{-3}.

The photon pulse from the photomultiplier is amplified, shaped, and sent into the start channel of a time-to-amplitude converter (TAC). The next trigger pulse stops the TAC, thus establishing the position of the photon count within the pulsing cycle of the gun. The TAC signals are pulse-height analyzed and stored in a segment of a 4096-channel analyzer.

After an accumulation period, the photon intensity as a function of time is displayed on the readout of the multichannel analyzer. Figure 2 shows the results of such a display schematically. The gun is turned on at *a* and the number density of the *C*-state molecules, which is proportional to the photon intensity, increases to an equilibrium value at *b*. The gun is then turned off at *c* and the emission from the *C*-state molecules falls exponentially back to its original equilibrium value at *d*. The lower equilibrium level is established by processed photomultiplier pulses which arrive at the TAC at random times during the beam pulsing cycle. One source of these random pulses is the photomultiplier dark current. A second source is population of the *C* state from long-lived states which have lifetimes much longer than the period of one pulsing cycle. In the present experiment the *C*-state lifetime, which was measured to be 37.4 ± 0.6 nsec, is short compared to the 1-μsec period of the gun. Therefore the directly excited *C*-state molecules decay completely within each cycle. The delayed radiation has a pressure-dependent apparent lifetime of the order of 10 μsec in the pressure range used. These photons contribute only to the lower equilibrium level, since they arrive at random times within any given cycle.

The intensity of the photomultiplier dark current is established by running the experiment with the gas removed from the cell.

III. EXPERIMENTAL PROCEDURE

The electron beam is focused at each energy so that a maximum current is collected by the Faraday cup. The total charge collected in the cell and the Faraday cup is measured by a current integrator. Photon counts are accumulated for times between 20 and 200 min depending on the count rates.

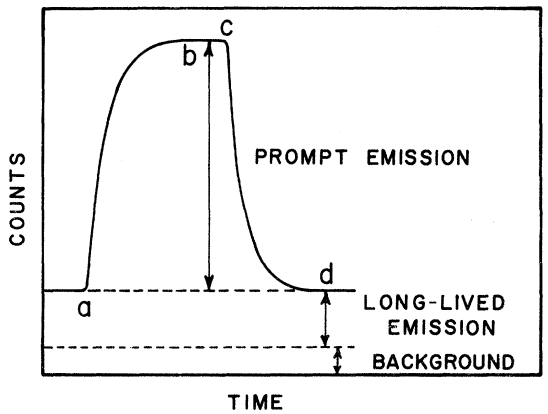

FIG. 2. Schematic representation of count rate as a function of time.

At the end of each run the intensities of the upper and lower equilibrium levels are recorded. A relative emission value for prompt C-state emissions is determined by subtracting the lower-level intensity from the upper-level intensity and dividing the result by the total charge collected and the gas-cell pressure. To get the relative emission function for the delayed photons, the photomultiplier background intensity is subtracted from the lower-level intensity and the result is divided by the total accumulated charge and the gas-cell pressure.

A third relative intensity of interest is the total emission intensity from a gas excited by an electron beam. This is given by the total number of counts taken during the run minus the dark-current pulses expected during that time; the result is then divided by pressure and total accumulated charge.

The electron energy scale was calibrated by observing the 11.48-eV transmission resonance using electron transmission spectroscopy on the nitrogen-gas target while simultaneously observing the C-state emission.

IV. RESULTS AND DISCUSSIONS

A. Electron-Beam Energy Calibration

The method of retarded energy modulation as described by Golden *et al.*[9] is used to measure the transmitted current through the nitrogen-filled cell as a function of energy. The electron transmission spectra shown in Fig. 3 is found using a 100-meV modulation energy. The electron energy calibration is accomplished by recognition of the 11.48-eV transmission resonance, which was first reported by Heideman *et al.*,[10] as the positive bump in the decreasing transmission current at an energy just above the onset of C-state emission. Since the retarded energy-modulation technique results in the differential of any structure which varies slowly compared to the effective beam spread,[9] the transmission spectrum was numerically integrated to yield the dotted line shown in Fig. 3. With the 11.48-eV energy position established, decreases in the transmitted current due to inelastic scattering at the threshold energies of the $C\,^3\Pi_u^+$ state at 11.02 eV, the $E\,^3\Sigma_g^+$ state at 11.87 eV, and the $D\,^3\Sigma_u^+$ state at 12.84 eV may be recognized on this integrated curve. The energy calibration is believed to be correct to better than ± 0.1 eV.

The electron energy calibration is carried over to the photon channel by simultaneous measurement of the delayed-emission function and the transmitted electron spectra. Figure 3 shows a sharp peak at 12.0 eV in the delayed-emission function which appears at the same energy as a sharp valley in the transmitted electron current. These simultaneous effects are attributed to the excitation of the $E\,^3\Sigma_u^+$ state. The sharp peak in the delayed-emission function at 12 eV establishes the energy scale for photon emission.

As a check on the differential nature of the electron transmission spectra, a method analogous to retarded energy modulation was carried out on the delayed-photon emission. The photon count rates were compared as a function of the phase of the energy modulation much as the electron currents were compared by phase-sensitive detection. The differential photon emission as a function of electron energy is shown in Fig. 3. It may be seen that, in the region of E-state excitation, the shape of the differential of the delayed-photon emission is very nearly the negative of the simultaneously observed electron transmission spectra. This is a strong indication that the structure in the delayed-photon emission and the transmitted current is due to the excitation of the same state. A complete description of this electron energy calibration will be given elsewhere.

B. Prompt and Delayed C-State Emission Functions

The total relative intensity of the $C\,^3\Pi_u \rightarrow B\,^3\Pi_g$ (0, 0) transition at 3371 Å caused by electron impact on a 20-mTorr nitrogen-gas target is given in Fig. 4(a). When corrected for difference in electron energy spreads, this emission function is in

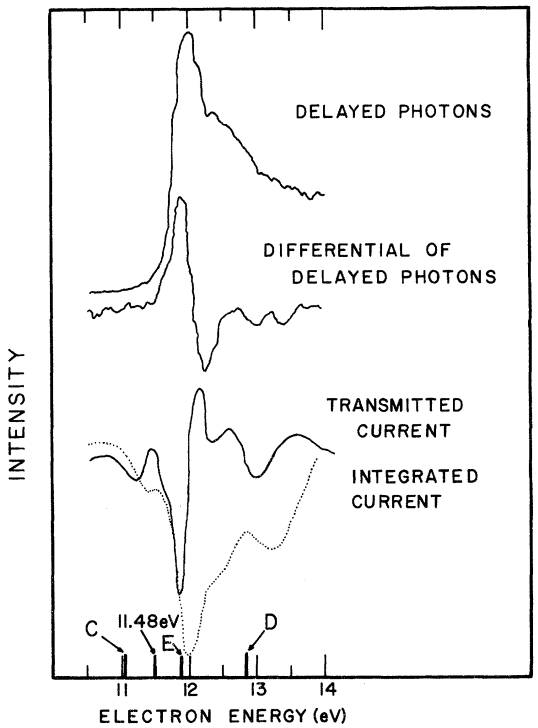

FIG. 3. Electron transmission spectra compared to the emission function of the delayed radiation from the C state. Energy levels of the C, D, and E states and the 11.48-eV resonance are shown.

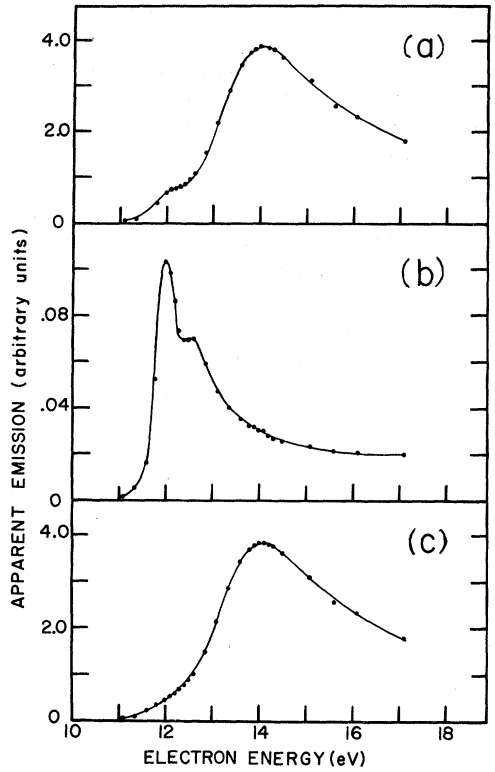

FIG. 4. Electron-impact 3371-Å emission functions for (a) total emission, (b) delayed emission only, and (c) prompt emission only.

good agreement with the results of Finn *et al.*[8] for threshold emission of the C state.

Using the time-resolving techniques described, the threshold structure of the C-state emission is separated into that due to C-state population through a metastable intermediary, as shown in Fig. 4(b), and that due to C-state population by direct excitation, as shown in Fig. 4(c). The delayed contribution to the emission appears to consist of two closely spaced peaks, while the prompt emission displays a smooth threshold behavior.

The first of these delayed-emission peaks has a maximum at 12.0 eV and is due to the excitation of the $E\ ^3\Sigma_u^+$ state. When the results of Heideman *et al.*[10] for the E-state electron-impact excitation function, as measured in inelastic electron scattering, are folded with the present energy spread, the resultant curve (labeled 1 in Fig. 5) agrees very well in both shape and position on the energy scale with the first peak in the present delayed-emission function. The position of this long-lived emission peak also agrees very well with the E-state excitation peak as measured by Lawton and Pichanick[5] on metastable nitrogen. The position of this E-state excitation peak is in disagreement, however, with the results of Borst *et al.*,[4] who made their measurements on metastable beams, and Ehrhardt and Willmann,[11] who used electron scattering at 20° from nitrogen. In both of these experiments, the E-state peak was found to be at 12.2 eV.

When the short-dashed line 1 in Fig. 5, which represents the E-state resonant excitation, is subtracted from the total delayed-photon emission, a second peak with a maximum at 12.7 eV results. This curve is drawn with long dashes in Fig. 5. In the energy range of this second peak, between 12.5 and 13.6 eV, Lawton and Pichanick[5] find a series of metastably excited vibrational states of molecular nitrogen. These excited states have also been seen by Ehrhardt and Willmann[11] as resonances in electrons scattered at 20° with 12.23-eV energy loss. These resonances have been associated with the excitation of the $a'^1\Sigma_g^+$ state which is the singlet analog to the E state.

Since these resonances are separated by energies smaller than the energy spread of the present electron beam, they appear as a single peak in the present experiment. When the data for the 12.23-eV energy-loss excitation function as measured by Ehrhardt and Willmann are folded with our energy spread, the short-dashed curve labeled 2 in Fig. 5 results. Fairly good agreement between this curve and the second peak can be seen.

To determine whether the two closely spaced peaks in the delayed-emission function from the C state may have different origins, the delayed-emission function was studied as a function of gas pressure, upper vibrational state of the second positive system, and time after excitation. The delayed-emission intensity was found to be pressure dependent in agreement with Finn *et al.*, and it was found

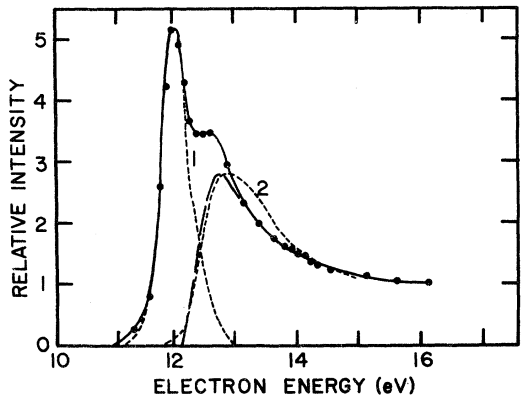

FIG. 5. The solid line shows the measured delayed-emission function. The short-dashed line (1) represents the data of Heideman *et al.* (Ref. 10) for the excitation function of the E state folded with the present energy spread of the electron beam. The long-dashed line represents the difference between the solid line and the short-dashed line (1). The short-dashed line (2) represents the data of Ehrhardt and Willmann (Ref. 11) folded with the present energy spread.

that the ratio of the first-peak to the second-peak intensity remained constant to better than 5% over the pressure range 20–50 mTorr. The relative intensities of the two peaks were also found to be independent of the upper vibrational state of the C-to-B transition observed. The peaks in the delayed-emission functions for the bands (0, 0), (1, 3), and (2, 4) of the second positive system all had the same position in energy, the same shape, and the same ratio of peak intensities to within 3%. Measurements of the apparent lifetimes of the two peaks were also found to be the same to better than 5% at a pressure of 20 mTorr.

These experimental results strongly indicate that the two peaks are due to molecules in the same metastable state and that the molecules arrive in that state in times less than the lifetime of the C state. Molecules in the metastable state then collisionally deactivate and populate the C state. Since the first of the peaks corresponds to the direct resonant excitation of the E state, the metastable state in question is most likely that state.

The method by which the 12.23-eV energy-loss resonances, which are presumably associated with excitation of the $a''\,^1\Sigma_g^+$ state, wind up in an 11.87-eV $E\,^3\Sigma_u^+$ state is unknown. Electron scattering experiments[11,12] indicate that there are no exit channels for excitation of the E state in the energy region of the presently observed second peak.

The results of Finn *et al.* pose a similar dilemma. In their experiment it was found that there was a pressure-independent contribution to the (0, 0) band of the second positive system at the position of the 11.48-eV resonance. Indications of this same effect are also found in the prompt-emission functions of the present experiment. The experiments of Swanson *et al.*,[12] however, show no indications of the C state or any other molecular-nitrogen state forming an exit channel for the decay of the 11.48-eV resonance. The method by which the C state is populated by the 11.48-eV resonance may be the same as the method by which the E state is populated by the resonances associated with the a'' state. Since the present results for excitation of the E state via the a''-state resonances and those of Finn *et al.* for excitation of the C state via the 11.48-eV resonance show no pressure dependence, collisional effects appear to play no role. A two-step decay of these resonances may be a possible explanation.

When data are taken out to electron energies of 40 eV, yet another maximum in the emission function of the delayed photons from C-state emission is observed. This maximum appears as a broad peak at 22 eV. These results and the results of Cermak,[6] for production of metastable nitrogen which causes molecules with ionization potentials between 11.4 and 11.6 eV to become Penning ionized, are shown in Fig. 6. Cermak's results, shown by the dashed curve, are placed on the energy scale so that the sharp peak has a maximum at 12.0 eV. The agreement of the two results indicates that, to a great extent, the same metastable states are involved. When this broad peak is observed as a function of pressure, $C\,^3\Pi_u$ vibrational state, and time, it is found that the ratio of the broad peak and the previous peaks remains constant to within experimental error. It is concluded that this broad peak also results in a population of the E state. The excitation functions for inelastic electron scattering as measured by Brinkmann and Trajmar[13] display a change in slope for the E-state excitation function at about 22 eV and a maximum at about 22 eV for the a''-state excitation function. This again suggests that electrons with energy losses equivalent to excitation of the a'' state cause excitation of the E state by some indirect process.

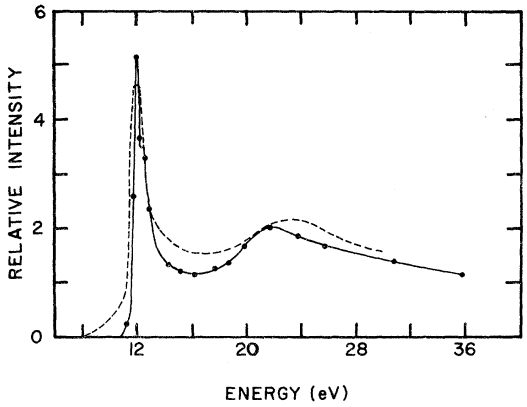

FIG. 6. The solid line is the emission function for the delayed 3371-Å photons under 8–40-eV electron impact. The dashed line is the data of Cermak (Ref. 6) with its energy scale normalized so that the maximum is at the position of the E-state peak at 12.0 eV.

V. CONCLUSIONS

The method of delayed coincidence is shown to be an effective tool for studying metastable excitation and may be applied to the study of various decay processes.

The pressure-dependent structure in the threshold region of the C-state emission function is found to be due to the excitation of the metastable E state which collisionally deactivates into the C state.

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Perturbed-Stationary-State Theory of Atomic Inner-Shell Ionization by Heavy Charged Particles*

George Basbas,† Werner Brandt, and R. H. Ritchie‡
Department of Physics, New York University, New York, New York 10003
(Received 26 December 1972)

Cross sections for inner-shell ionization by slow heavy charged particles, if compared to predictions given in the plane-wave Born approximation, are reduced strongly by the Coulomb deflection of the particle in the field of the target nucleus, and by the increase in binding energy of the target electrons induced by the presence of the particle. We use the framework of the perturbed-stationary-state approximation to incorporate these effects *ab initio* into the theory of inner-shell ionization and derive the binding effect given by Brandt, Laubert, and Sellin. Our result formally unifies the Coulomb deflection of the particle trajectory with the perturbation of the atomic states in their effect on the ionization cross section and suggests systematic ways for further improvements.

I. INTRODUCTION

When an energetic charged point particle passes through matter it may eject inner-shell electrons of the target atom into excited or ionized states by direct Coulomb encounters. The resulting vacancies may be detected by observing characteristic x-radiation or Auger-electron spectra. Theoretical ionization cross sections for production of these vacancies have been studied in the plane-wave Born approximation (PWBA), usually employing hydrogenic wave functions for the atomic system,[1-3] and in a classical binary-encounter approximation.[4]

Consider the regime where the incident velocity v_1 of the particle is so low that $(v_1/Z_2^* v_0) \ll 1$, where Z_2^* is the effective atomic number of the target for the shell in question and $v_0 = e^2/\hbar$. In this regime two substantial v_1-dependent effects appear which are not included in these approximations: (i) Coulomb deflection of the particle by the target nucleus, and (ii) increased binding of the target electrons owing to the presence of the slowly moving particle. The theory of the first of these effects has been studied thoroughly by Bang and Hansteen,[5] who obtain cross sections in a semiclassical approximation in the sense that they incorporate the hyperbolic trajectory of the (heavy) particle in the Coulomb field of the bare target nucleus.

Brandt, Laubert, and Sellin,[6] hereafter referred to as BLS, discovered that the binding effect may give rise to K-shell ionization cross sections considerably smaller than those calculated from these theories. They arrive at a successful description of their experimental results by employing the deflection-corrected PWBA formula for the cross section, but, in addition, they replace the binding energy of the K electron for the isolated atom as it occurs in this formula by an augmented energy which allows for the binding effect of the finite positive charge of the particle. The incremental binding energy is evaluated by bound-state perturbation theory at a given impact parameter and averaged over impact parameters according to the excitation probability, before integrating the cross section over all final electron states. This approach was reviewed recently[2] and has been studied