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Radiationless deexcitation of excited helium atoms at surfaces*

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Impact of 20–30-keV He^+ ions on polycrystalline niobium and copper surfaces causes some projectiles to be backscattered in a neutral excited state. These projectiles subsequently decay, radiatively emitting Doppler-broadened spectral lines; the broadening is characteristic of the distribution in speeds and direction of the scattered excited projectiles. Analysis of the line shape shows that slow reflected particles have a high probability of losing the excited electron by a radiationless transition while they are close to the surface. The spectral line shape has been predicted using the backscattering theory of McCracken and Freeman with the inclusion of a radiationless deexcitation term. By suitable choice of the radiationless deexcitation coefficients the theory and experiment may be brought into acceptable agreement. The coefficients so derived are in surprising agreement with calculated values of Cobas and Lamb for an Auger deexcitation mechanism.

I. INTRODUCTION

Kerkdijk and Thomas[1] have shown that when an He^+ ion is incident on a metal surface, some of the projectiles are scattered as neutral excited atoms. These atoms subsequently decay by photon emission. The resulting spectral line is Doppler broadened and the line shape is directly related to the distributions of speeds and distributions in angle of the scattered projectiles. Kerkdijk and Thomas[1] developed a theoretical model for predicting these line shapes based on a number of simplifying assumptions. It was basically assumed that excited atoms were formed only from projectiles that were scattered by a single encounter with an atom in the surface of the target; this may be termed a "surface-scattering model." On this basis the speed of a backscattered particle is dependent only on the angle through which it is scattered and the masses of the projectile and target atoms; hence the Doppler shift associated with a particular backscattered trajectory may be calculated. The angular distribution of the scattered atoms was assumed to be proportional to the Rutherford cross section appropriate to the two isolated nuclei; hence relative probabilities of particular trajectories are known and the contribution to light intensity at the relevant Doppler shift may be evaluated. The line shapes calculated on this basis were in general qualitative agreement with the experimental data but there were substantial quantitative discrepancies.

The objective of the present work was to test further the model of Kerkdijk and Thomas[1] with the hope of resolving the discrepancies between predicted and measured line shapes. We have performed additional measurements of line shapes for visible He I emissions induced by He^+ impact on polycrystalline surfaces of niobium and copper. As we shall show later, substantial discrepancies are found between the measured line shapes and the predicted shape using the surface-scattering model.

A serious fault in the surface-scattering theory is the neglect of projectile penetration into the target. McCracken and Freeman[2] have shown, both theoretically and experimentally, that most projectiles penetrate some distance before undergoing the large-angle scattering event that returns them to the surface. As the projectile proceeds to and returns from the scattering site it suffers energy loss by collisions with electrons (electronic stopping) but no appreciable deviation. As a result, the backscattered flux exhibits a distribution of energies with a peak flux at low energies. The work of Kerkdijk and Thomas[1] shows quite definitely that the backscattered excited-atom flux includes only small amounts of slow particles so that one may conclude that slow excited atoms are deexcited while still close to the surface. Two such deexcitation mechanisms have been discussed by Hagstrum.[3] The first is "resonance ionization" where the excited electron tunnels through the potential barrier at the metal surface to enter a vacant state above the conduction band of the metal; the second mechanism is "Auger deexcitation" where a conduction-band electron from the metal falls to the ground state of the helium atom and the excited electron is ejected to a continuum state. For either mechanism, the probability of radiationless decay when the atom is a distance s from the surface is given by[3]

$$P(s)=Ae^{-as}, \qquad (1)$$

where A and a are constants related to the wave functions of the electrons and the form of the potential barrier, respectively. Furthermore, the probability that a particle having a velocity component $V_\perp$ perpendicular to the surface will escape without radiationless decay is[4]

$$R(V_\perp) = \exp(-A/aV_\perp). \quad (2)$$

Clearly, the effect of radiationless decay is to remove the slow excited atoms. We shall show that the Doppler-broadened line shape can be predicted by combining the scattered-particle velocity distribution of McCracken and Freeman[2] with the radiationless decay factor described above; by suitable fitting of theory to experiment the ratio of parameters A/a in Eq. (2) may be derived. We shall henceforth refer to the ratio A/a as the "survival coefficient."

There are already two previous determinations of the survival coefficient based on the measurement of optical emissions induced by ion impact on solids. Van der Weg and Bierman[4] studied the line shape of the Cu I 3247-Å emission emanating from copper atoms sputtered from a copper target by 80-keV Ar^+ impact. They derived a survival coefficient of 2×10^6 cm/sec. White and Tolk[5] have considered the same process and show that the dependence of line intensity on projectile energy can be analyzed to give a measure of the survival coefficient; they also determine a coefficient of 2×10^6 cm/sec. These two previous experiments are concerned with relatively slow-moving heavy atoms sputtered out of the target. The present experiments are for high-velocity light projectiles scattered from a target; one might anticipate that the survival coefficient for the present case would be greatly different from the previous work of White and Tolk[5] and that of Van der Weg and Bierman.[4]

II. EXPERIMENTAL ARRANGEMENT

The experimental arrangement is shown schematically in Fig. 1. The He^+ ions obtained from an rf discharge source are mass analyzed, collimated, and directed onto the target surface at some incidence angle φ with respect to the target-surface normal. A grating monochromator views the surface through a sapphire window; the monochromator axis is perpendicular to the projectile beam direction and lies in the same plane as the projectile beam and the target-surface normal. The monochromator is fitted with a photomultiplier detector operated in the counting mode; the spectral line shape is recorded by scanning the monochromator.

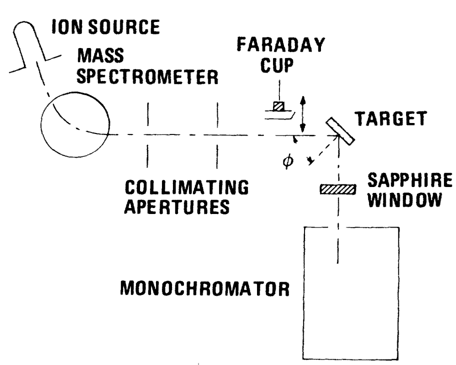

FIG. 1. Schematic diagram of the apparatus.

The targets were polycrystalline metals of very high purity (99.999%). Before use, the samples were mechanically polished, electropolished, cleaned with solvents, and rinsed with distilled water. The samples were mounted in the vacuum system on a standard Varian manipulator. It was possible to rotate the sample to change the angle of beam incidence φ, and also translate the sample to ensure that the axis of rotation intersected the optical and projectile beam axes. The vacuum environment of the target was maintained by ion pumping at a base pressure of 10^{-9} Torr or better. The target chamber was isolated from the relatively poor vacuum of the accelerator region by two stages of differential pumping.

Projectile beam currents were monitored on a Faraday cup that could be inserted to the beam line periodically. The current measured on the target itself was used to monitor beam stability during optical measurements; this target current was not considered to be a reliable measure of the projectile flux because it was impossible to guarantee complete suppression of all secondary ejected particles. Currents were typically 1–10 μA in a beam of about 1-mm^2 cross-sectional area.

The projectile beam flux was sufficient to sputter off a few monolayers of target material every minute. It is felt that a preliminary bombardment of the surface with the ion beam itself is sufficient to guarantee target cleanliness. It was found that the optical signals showed some variation with time for a few minutes after the beam was directed at a new target; beyond that point the signals remained stable for many hours. Data taken during the first few minutes of bombardment were discarded.

III. GENERAL SPECTRAL CHARACTERISTICS

The observed spectra have essentially the same general characteristics as reported by Kerkdijk and Thomas.[1] For He^+ on copper and niobium there were strong emissions of the following He I lines: 5876 Å ($3\,^3D \rightarrow 2\,^3P$), 4472 Å ($4\,^3D \rightarrow 2\,^3P$), and 3889 Å ($3\,^3P \rightarrow 2\,^3S$). There were also weak emissions of He I lines at 6678 Å ($3\,^1D \rightarrow 2\,^1P$) and

7065 Å ($3\,^3S \to 2\,^3P$). We also observe a broad band emission centered at 3500 Å which is similar to that reported by Kerkdijk and Thomas[1]; the origin of this band remains unclear and we will not consider it further.

Detailed study of the He I lines indicates that they are of the order of 20–30 Å in breadth with a sharp peak on the blue side. In Fig. 2 we show a number of measurements on the 5876-Å ($3\,^3D \to 2\,^3P$) line. It is observed that, as incidence angle increases, the line width broadens and total intensity increases. There is an obvious sharp peak on the low-wavelength (blue-shifted) side of the line.

IV. ANALYSIS OF THE LINE SHAPE

The objective of this work was to further test and refine the predictions of line shape initiated by Kerkdijk and Thomas[1] (see the Introduction). In Fig. 3 we show the shape of the 5876-Å line induced by 30-keV He^+ on niobium at an incidence angle φ of 45°; this is compared with the predicted line shape using the surface-scattering model. Clearly there is a substantial discrepancy between prediction and experiment; the discrepancy is qualitatively similar to that exhibited in some of the original work by Kerkdijk and Thomas.[1]

As discussed in the Introduction one of the most serious inadequacies of the surface-scattering model is its neglect of projectile penetration into the target. The work of McCracken and Freeman[2] predicts the energy distribution of backscattered projectiles. Figure 4 shows a two-dimensional diagram of the problem which includes the beam

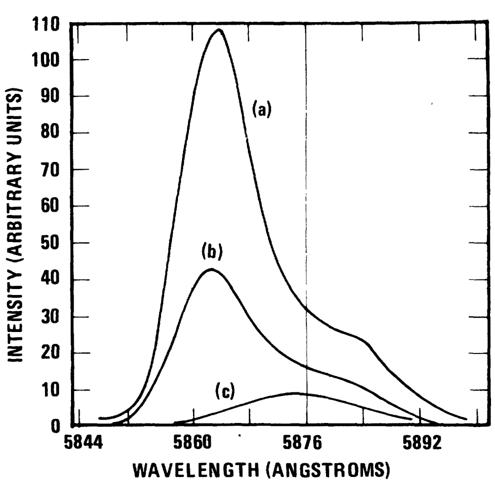

FIG. 2. Line shape of the 5876-Å ($3\,^3D \to 2\,^3P$) He I emission induced by 30-keV He^+ impact on niobium at an incidence angle φ of (a) 60°, (b) 45°, and (c) 0°. Only a smoothed curve is shown; for a representation involving actual data points see Fig. 3.

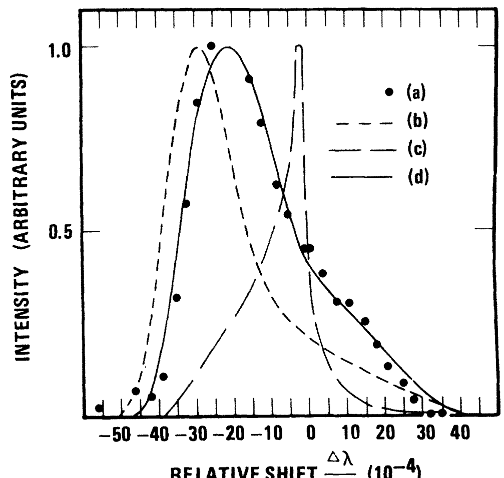

FIG. 3. Measured and predicted line shape of the 5876-Å ($3\,^3D \to 2\,^3P$) He I emission induced by 30-keV He^+ impact on niobium at an incidence angle φ of 45°. Intensity is shown as a function of relative wavelength shift, defined as the shift ($\Delta\lambda$) from the 5876-Å line divided by the wavelength of that line, 5876 Å (λ). (a) Individual experimental data points; (b) prediction by surface scattering model; (c) prediction by present model with survival coefficient (A/a) of zero; (d) prediction by present model with survival coefficient chosen for best fit to data points ($A/a = 1.2\times10^8$ cm/sec).

axis and optical axis. The approach of McCracken and Freeman is to consider the projectile as incident at point A with some angle φ, with respect to the surface normal, and penetrating to the point P where it undergoes a close encounter with an atom of the target lattice and scattering through an angle θ to return eventually to the surface at B. Along the paths AP and PB it is assumed that the projectile undergoes only collisions with free electrons causing loss of energy but no appreciable

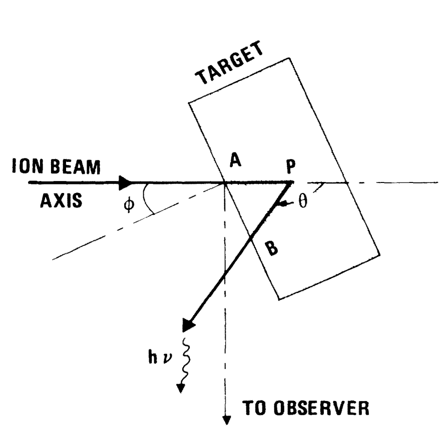

FIG. 4. Geometry of the scattering problem shown in two dimensions only.

deviation; the rate of energy loss is taken to be proportional to the square root of energy. At the point P we assume that the collision cross section is appropriate to the interaction of the two nuclei, i.e., a Rutherford cross section is used. Based on this picture one may formulate an expression for the probability that a projectile will emerge at B with an energy between E_s and E_s+dE_s and moving into some element of solid angle $d\omega$. We will denote this probability as

$$P(E_s)=N(E_s)\,dE_s\,d\omega. \tag{3}$$

McCracken and Freeman state the expression for $P(E_s)$ for the two-dimensional problem shown in Fig. 4 [Eq. (6) of Ref. 2]. For the present problem, however, we have modified this somewhat to represent the three-dimensional problem which includes scattering at the point P out of the plane of Fig. 4; thus the azimuthal angle has been included. The predictions of McCracken and Freeman have been tested experimentally[2] and do seem to represent the total scattered flux of projectiles.

There is, unfortunately, no information on the proportion of the scattered projectiles which might be neutralized into a specific excited state. We shall therefore assume that this proportion, F, is independent of the emergent particle's energy and direction.

The final factor we must account for is the probability that an excited particle will escape from the influence of the surface without undergoing radiationless decay. This is given by Eq. (2).

These excited particles will eventually decay radiatively and a certain fraction, dependent on apparatus geometry, will be detected. Let us denote by the factor F', the fraction of excited atoms that will give a photon that is detected by the observer. For a given transition, this fraction F' is independent of the speed and direction of the projectiles.

Thus, combining these various terms we have the probability $P(E_s)$ of detecting a photon from an emergent particle of energy E_s, scattered into a solid angle $d\omega$, which is

$$P(E_s)=F'F\exp(-A/aV_\perp)\,N(E_s)\,dE_s\,d\omega. \tag{4}$$

The wavelength of the photon can be simply calculated by the Doppler-shift formula: The nonrelativistic form is adequate at the energies used here.

With this information one can use Eq. (4) to calculate the spectral line shape in relative terms; since we do not attempt to estimate the factors F or F' we do not get an absolute figure for intensity. The calculation has been performed by numerical integration. The range of scattered-particle energies, E_s, is divided into segments ΔE_s; the range of scattered-particle angles is divided into elements of solid angle $\Delta\omega$. The probability of scattered particles being in $\Delta E_s\Delta\omega$ is evaluated from Eq. (4); this provides the contribution to intensity at the Doppler-shifted wavelength λ. This procedure is repeated for all energies and angles to build up the final intensity distribution.

In practice, we have no accurate prior knowledge as to magnitude of the survival coefficient A/a in Eq. (2). So the calculation is performed for a range of values and the value chosen which provides the best fit to the data. In practice we find the coefficient to be determined principally by the position of the maximum intensity in the line.

The ranges used in the integration are as follows. The maximum value of E_s, the emergent-particle energy, is given by an elastic encounter between the projectile and a target atom in the surface. We somewhat arbitrarily assume that the minimum value of E_s is 20 eV; the rationale is that any projectile that has been reduced to this energy will probably be captured by the lattice. In practice we find that the survival coefficient is such that very slow projectiles do not survive radiationless decay; in fact the minimum value of E_s could be raised to 1 or 2 keV with absolutely no change to the derived value of the survival coefficient. The minimum value of scattering angle θ is taken to be that angle for which the particle is scattered parallel to the surface; this minimum θ obviously depends on azimuth.

As a further complication, it is quite possible for an excited atom to emit a photon towards the target which then reflects to the observer. This is also taken into account in the calculation in a similar manner to that described by Kerkdijk and Thomas.[1] There is difficulty in that the reflectance of the surface is unknown. One is tempted to use a value of reflectance for a polished surface as given in standard tables. Visual observation, however, shows that the metal surface becomes pitted by the ion bombardment and the reflectance is thereby reduced. To accommodate this we regard the reflectance as unknown and alter this also to give a best fit to the experimental data. In practice the reflected component contributes significantly only to the red-shifted component of the line; the derived value of the survival coefficient is related to the position of the intensity maximum in the blue shift and is completely insensitive to the reflectance that is adopted. Figure 5 shows a calculated line shape with an indication of the reflected component; the calculated line is the same as the best-fit line shown in Fig. 3.

We also take into account the influence of monochromator resolution; generally this was kept at 8 Å but on occasion it was reduced to 4 Å for spe-

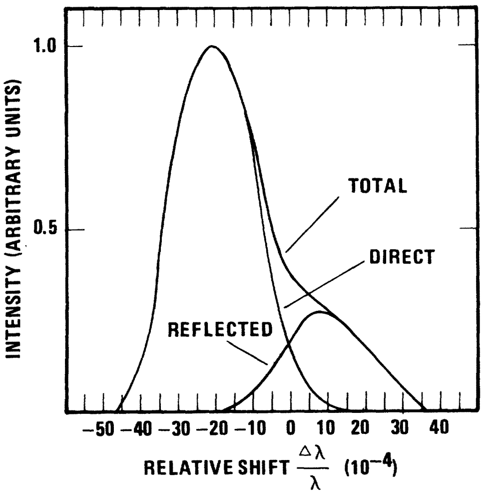

FIG. 5. Predicted shape of the 5876-Å line induced by 30-keV He^+ ions on niobium at an incidence angle of 45°, calculated with $A/a = 1.2\times10^8$ cm/sec and a surface reflectance of 0.28, and showing the component of emission received directly by the observer, component of emission received via reflection from the surface, and total emission intensity (this is in fact line d of Fig. 3).

cific tests. This resolution is comparable to the width of the spectral line. To accommodate this, our predicted line shapes have been convoluted with the triangular bandpass characteristic of the monochromator so that this is taken into account in fitting the calculated curve to the experimental data.

The result of this calculation is that a line shape is predicted which is the same form as that observed experimentally. Moreover, with suitable choice of the survival coefficient A/a and surface reflectance R one can get a very good agreement with the measured line shape. A particular example is shown in Fig. 3. We find that for large angles of incidence the fit to the line shape is quite sensitive to the choice of survival coefficient. For large angles ($\varphi \geq 45°$) we believe that the survival coefficient can be determined to an accuracy of ±50%; varying the survival coefficient by this amount from the "best-fit" interaction can shift the wavelength at which maximum intensity occurs by 4 Å or more and so distorts the curve that it bears little resemblance to the measured line shape. For small incidence angles ($\varphi < 45°$) the fitting of calculated and measured line shapes becomes progressively less sensitive to the choice of survival coefficient.

We show in Fig. 3 an extreme case of how the survival coefficient changes line shape by calculating the case of $A/a = 0$. This represents the situation where radiationless decay does not occur and all excited atoms escape and subsequently radiate. Clearly the predicted shape for this situation bears little resemblance to observation.

V. RESULTS

The consequence of this analysis is that we may determine, from the line shape, a measure of the survival coefficient A/a defined in Eq. (2). We consider that the accuracy with which A/a may be established is poor for incidence angles below 45° due to the low signal strengths and the insensitivity of line shape to the value of A/a adopted; thus the results quoted here are derived for incidence angles of $\varphi \geq 45°$. It has been shown that the derived values are consistent with the experimental data for lower angles of incidence.

The survival coefficient for the $3\,^3D$ state of helium as determined from the 5876-Å emission induced by He^+ on niobium is found to be 1.0×10^8 cm/sec; this is the mean of several determinations at different energies (20–30 keV) and angles (45°–70°). The individual observed values range from 0.8 to 1.2×10^8 cm/sec with no apparent systematic variation with impact energy or incidence angle; we therefore assign a reliability of ±0.2 $\times10^8$ cm/sec to this determination. For the $4\,^3D$ state of He, measurements on the 4472-Å line induced by He^+ on niobium give a survival coefficient of 0.7×10^8 cm/sec; again the same limits of accuracy apply.

For similar measurements on a copper target

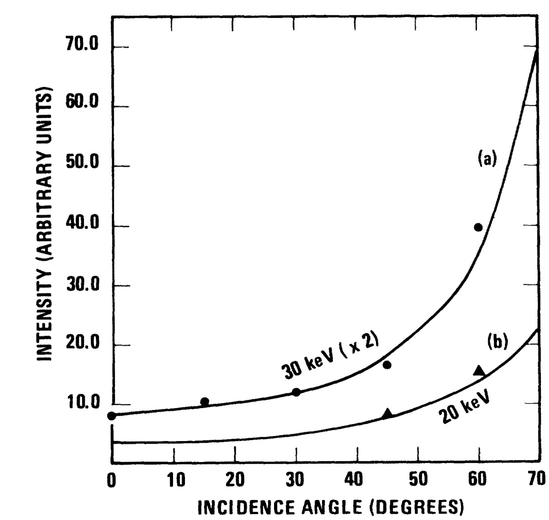

FIG. 6. Total intensity of the 5876-Å He I ($3\,^3D \rightarrow 2\,^3P$) line shown as a function of angle of incidence for incident projectiles of energy (a) 30 keV and (b) 20 keV. Circles, experimental data points; lines, predicted variations with $A/a = 1.0\times10^8$ cm/sec and $R = 0.21$. The experimental and theoretical values at 30 keV have been multiplied by 2 for clarity. Theory and experiment are normalized together at 30-keV energy and 30° incidence angle.

the survival coefficient for the $3\,^3D$ state is found to be 1.0×10^8 cm/sec and for the $4\,^3D$ state 0.7×10^8 cm/sec; again both with an accuracy of $\pm0.2\times10^8$ cm/sec.

With these coefficients it is now possible to calculate how the total intensity of a line should vary with impact energy and with angle of incidence. One simply uses the derived coefficient in the calculation scheme outlined in Sec. IV above and integrates the predicted intensity distribution over all wavelengths within the line; this is repeated for various angles of impact and energies of impact. One may also provide an experimental quantity by integrating the measured line over all wavelengths. In Fig. 6 we show the predicted angular distribution at two energies compared with experimental data. Since both the experiment and theory are designed to give only relative values we have normalized them together at one point. The observed agreement between prediction and experiment is very satisfactory.

VI. DISCUSSION

The primary conclusion from this study is that excited atoms recoiling from a target have a high probability of radiationless decay. For example, using our measured value of A/a (1.0×10^8 cm/sec) in Eq. (2) to calculate the probability, $R(V_\perp)$, that a 30-keV ($V=1.2\times10^8$ cm/sec) helium atom recoiling normal to surface will not undergo radiationless decay we get $R(V_\perp)=\exp(1.0/1.2)=0.43$. Thus only 43% of these rather fast recoils escape without radiationless decay. For slower recoils, which are in the majority, the survival probability is correspondingly less.

We are now in a position to understand why the "surface-scattering" model of Kerkdijk and Thomas[1] gave an apparently adequate prediction of line shape. That early work assumed, arbitrarily, that only fast atoms, scattered elastically from the surface, emerge in an excited state. We have shown here that particles scattered at all depths in the solid may in fact emerge in the excited state but only those of highest velocity have any substantial probability of surviving radiationless decay; these faster atoms arise from scattering close to the surface. Thus the principal contribution to line shape does in fact arise from the scattered flux component considered by Kerkdijk and Thomas.[1]

There have been only two previous attempts to measure the probability of radiationless deexcitation by optical means; these were both[4,5] concerned with copper atoms sputtered from solid copper by argon impact. In that case the value determined for A/a is 2×10^6 cm/sec. The interaction of a copper atom with a surface is likely to be greatly different from that for a helium atom and so the difference from the coefficient determined here is not surprising.

There have been some limited attempts to calculate the probabilities for radiationless transitions at surfaces; those relevant to the present work are summarized in convenient form by Hagstrum.[3] In particular, Cobas and Lamb[6] have made a prediction of the radiationless decay for metastable helium close to a tungsten surface; calculations were performed for both the process of resonance ionization and the process of Auger deexcitation discussed in the Introduction. These predictions are relatively unsophisticated and utilize hydrogenic wave functions; they are not expected to be accurate to more than an order of magnitude. The calculations of Cobas and Lamb,[6] as interpreted by Hagstrum[3] provide separate values for the coefficients A and a of Eq. (1). In the case of Auger deexcitation the predicted ratio A/a is 1.3×10^8 cm/sec; this is remarkably close to our present measured value of 1.0×10^8 cm/sec. By contrast, for the resonance ionization process the predicted ratio by Cobas and Lamb is 4.8×10^{10} cm/sec and that by Shekhter[7] is 1.8×10^{11} cm/sec; these are in gross disagreement with the present measured value. Our present experiments cannot determine which of these two processes are occurring; we can only say the measured ratio of coefficients is consistent with the prediction of Cobas and Lamb[6] for Auger deexcitation.

An inadequacy of our present line-shape analysis that is also to be found in earlier work,[1,4,5] is that we have no information on the process whereby the excited atom is created. Yavlinskii *et al.*,[8] suggest that the ion is neutralized as it finally emerges from the target; the neutralization is supposed to take place by a process of three-body recombination in the surface layer of electrons. We would note that, on theoretical grounds, recombination in a plasma should be primarily to d states[9]; moreover, the afterglows of high-density helium plasmas show[10] atomic lines that are principally from $3\,^3D$, $4\,^3D$, and $3\,^3P$ states. Thus the spectra observed in the present work are qualitatively similar to those observed in the decaying-plasma situation where a three-body recombination process is expected to be a primary source of excited atoms.

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