Excitation of metastable argon and helium atoms by electron impact*

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The excitation of argon and helium metastables by electron impact was studied in the energy range from threshold to about 50 eV with a time-of-flight method. The metastables were detected by Auger ejection of secondary electrons from a CuBeO surface. The argon cross section was obtained in two different ways yielding peak cross sections of 3.4×10^{-17} and 3.7×10^{-17} cm^2 at 22 eV, respectively. The estimated uncertainty for both values is a factor of 2. The helium cross section was measured with a trapped-electron method near threshold and found to have a peak value of $(6.2\pm2.0)\times10^{-18}$ cm^2 at the 25-eV maximum. The secondary-electron yields of the metastable detector used in this work are discussed in detail. The effect of metastable recoil is also discussed. Argon metastables suffer only negligible recoil because of their large atomic weight, but this is not the case for the lighter helium metastables.

I. INTRODUCTION

Most of the studies on the excitation of argon and helium metastables by electron impact have been confined to the threshold region and/or measurements of relative excitation functions.[1] It has been the purpose of this work to obtain excitation functions over an extended energy range and to estimate absolute cross sections for metastable production. The emphasis of the present work is on the excitation of argon metastables for which only few and conflicting measurements of excitation functions beyond the threshold region exist[2,3] and for which no absolute cross section is available. The work on helium is reported here to support the method used for argon and to compare with recent cross-section determinations at higher energy.[4] The argon cross section was obtained in two different ways. One method makes use of the absolute yield of the metastable detector.[5] The other method compares the argon and helium signals and employs the independently measured helium cross section together with the relative ratio of the detector yields for argon and helium metastables. The discussion of the present work concentrates on a comparison with other work where this is possible, secondary-electron yields of the metastable detector, and the effects of metastable recoil after excitation.

II. EXPERIMENTAL METHOD

A. Some experimental details

Metastables were excited by a pulsed electron beam and detected by the emission of secondary electrons from the first dymode of a nude CuBeO electron multiplier.[5,6] A time-of-flight (TOF) technique[6-8] was used to separate radiatively decaying from metastable atoms and measure velocity distributions of the metastables. An example of a TOF distribution for helium metastables is given in Fig. 1. The solid curve was calculated assuming a pure Maxwellian velocity distribution[6] containing the experimental parameters atomic mass, gas temperature, and length of the flight path between metastable source and detector. It is seen that the Maxwellian distribution fits the data points. Because of the long lifetimes of both the $2\,^1S_0$ (Ref. 9) and $2\,^3S_1$ (Ref. 10) metastable states of helium, the solid curve in Fig. 1 was calculated with no in-flight metastable decay. Such a decay would change the shape of the TOF curve.[6] The metastables were monitored at an angle of 90° with respect to the electron beam. A diffuse gas source was used in which ground-state atoms had an isotropic velocity distribution before electron impact. The electron beam was pulsed at time zero in Fig. 1 and was on for typically 2 μsec. Ultraviolet photons produced during the on-time of the beam disappeared very quickly after turning the beam off. It is seen in Fig. 1 that the uv signal decayed completely long before the arrival of the fastest metastables.

The TOF curves for argon metastables were similar to that shown in Fig. 1 and could again be fitted by Maxwellian distributions. Because of the long lifetimes of argon metastables,[11] no correction for in-flight metastable decay was necessary.

Excitation functions were obtained by summing all counts on the TOF curve over the significant

range of flight times and monitoring this total count rate as a function of electron energy. This was done by means of gating techniques.[6] An analog signal proportional to the total count rate was obtained from a ratemeter. This signal was displayed versus electron energy on an X-Y recorder. Excitation functions obtained in this way are shown in Fig. 2 and Fig. 3. The energy spread in the electron beam was about 0.3 eV full width at half-maximum (FWHM). Other experimental details have been previously described.[6,7]

B. Cross sections

The measured signal count rates [$\sec^{-1}$] are related to the cross section $\sigma(E)$ (cm^2) for excitation of metastables at an electron energy E according to the relation[8]

$$S(E) = (I/e)nl_{\text{eff}}(\Omega/4\pi)k\gamma_m\sigma(E), \quad (1)$$

where I is the electron beam current (in A), e the electronic charge (in C), n the gas density (in cm^{-3}), l_{eff} the effective scattering length in the collision chamber (in cm), Ω the solid angle subtended by the metastable detector at the center of the collision chamber, k the efficiency of the pulse counting system, and γ_m the yield for Auger emission of secondary electrons from the CuBeO detector surface by the metastables. It is assumed in Eq. (1) that the metastables move isotropically in all directions after the excitation. This assumption is a reasonable one for the heavy argon atoms, whereas metastable recoil in the case of helium can be a more serious problem (see below). If the yield γ_m is known, the cross section $\sigma(E)$ can be obtained from Eq. (1), and vice versa, because all the other quantities in Eq. (1) are experimentally known.

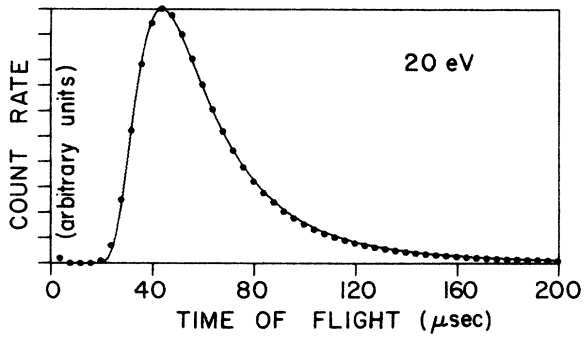

FIG. 1. Time-of-flight distribution of helium metastables excited by 20-eV electrons. The solid points are the measured counts accumulated in a multichannel analyzer. The solid curve was calculated from a pure Maxwellian velocity distribution and normalized in peak height to the data points.

C. Secondary electron yields

The secondary electron yields used in this work have been reported previously.[5] It seems appropriate to give a brief summary of these results, particularly in view of recent criticism by Rundel *et al.*[12] In the work reported,[5] yields for the emission of secondary electrons from contaminated CuBeO and tungsten surfaces by metastable atoms and molecules were plotted as a function of the metastable excitation energy. It was found that a smooth curve could be drawn through all data points, and that the contaminated CuBeO and polycrystalline tungsten surfaces studied had similar yields, in particular for helium. In the following, this curve shall be called the "yield curve" for the CuBeO detector surface. This yield curve has been used to estimate cross sections for metastable production in a variety of cases such as argon (present work), nitrogen,[8] and oxygen.[13] In the cases where a comparison with other cross-section determinations has been possible, agreement within the limits of error (~50%) was found to exist. This applies in particular to the cross section for the A state in N_2,[8,14] thus lending support to the secondary-electron yields that were used in estimating these cross sections. Further support for the correctness of the yields for argon and helium is obtained from the present work, in which two different methods (see below) yielded the same argon cross section. The case of helium is particularly straightforward, because of the availability of independent cross-section deter-

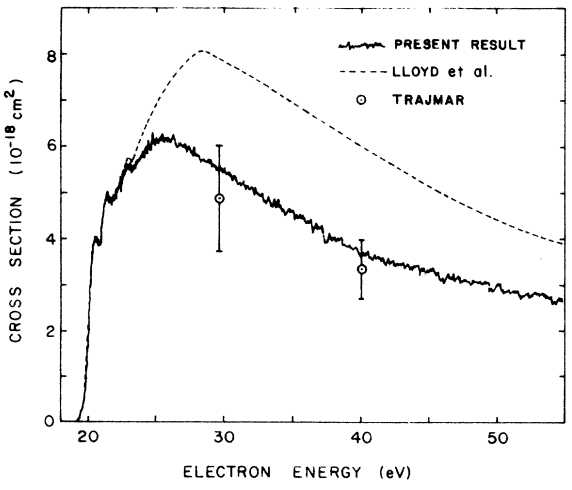

FIG. 2. Cross section for excitation of helium metastables vs electron energy. The curve of Lloyd *et al.* is relative and was normalized to the present curve at the first peak near 20.4 eV. The two data points of Trajmar near 30 and 40 eV represent absolute measurements.

minations as described below. From Eq. (1), the helium yield for contaminated CuBeO and tungsten surfaces was found to be $\gamma_m^{He} = 0.15$. This value agrees with other measurements of the yield for helium metastables[15] and ions[16,17] on contaminated tungsten surfaces.

The criticism concerning the present yields offered by Rundel *et al.*[12] centers around two issues. The first objection by these authors is that their measured yields for helium metastables lie in the range $0.4 < \gamma < 1.0$, which they claim to be typical of gas-contaminated surfaces. They proceed to state that this range in yields is well above the present yield for helium. It should be noted, however, that different detector surfaces were used. The present yield for helium holds for contaminated CuBeO and tungsten surfaces and not for the contaminated surfaces such as stainless steel used by Rundel *et al.* It has not been claimed that the present helium yield should be applicable to contaminated stainless steel, gold, and other surfaces studied by Dunning *et al.*[18,19] In fact, it is this author's own experience that contaminated stainless-steel surfaces show higher yields, and furthermore, that the yields, especially for low-lying metastable states, depend quite sensitively on the surface material used.[20]

The second objection by Rundel *et al.* consists in the statement that it is not possible to predict the value of the yield for *any* given metastable-surface combination from a "universal curve," thus implying that this was claimed to be possible. This objection represents a misinterpretation of the published work.[5] A "universal curve" of the yield as a function of metastable excitation energy for *any* given metastable-surface combination was never offered. It was made clear that the yield curve presented holds for CuBeO and tungsten surfaces. The claim of the existence of a "universal curve" would be invalidated by our own work,[20] in which a tantalum surface was used, that exhibited yields for lower-lying metastable states which were significantly different from those for CuBeO and which would not fit the yield curve for CuBeO. The general character of the yield curve referred to in the previous work[5] concerned the fact that all the known yields for metastables on CuBeO lie on a smooth curve. The accuracy of the cross-section estimates that were based on the yield curve seems to be of the order of 50%. Obviously, it is more desirable to measure the yield for a given metastable-surface combination *in situ*. However, this is possible only for high-lying metastable states, for which the process of Penning ionization can be utilized.[12,18,19] Unfortunately, this does not apply to most metastables, for instance those that are of aeronomic interest. For some of these metastables, the present method has yielded the only available cross-section estimates.

D. Metastable recoil

The present measurements were taken at a fixed angle of 90° with respect to the electron beam. A study of angular variations was not possible with the apparatus used. Since as a result of collisions, momentum is imparted to the metastables by the electrons, the metastables undergo recoil and the isotropic velocity distribution of the ground-state atoms before electron impact is distorted. This results in an additional forward component in the velocities of the metastables in the direction of the electron beam. A further complication arises

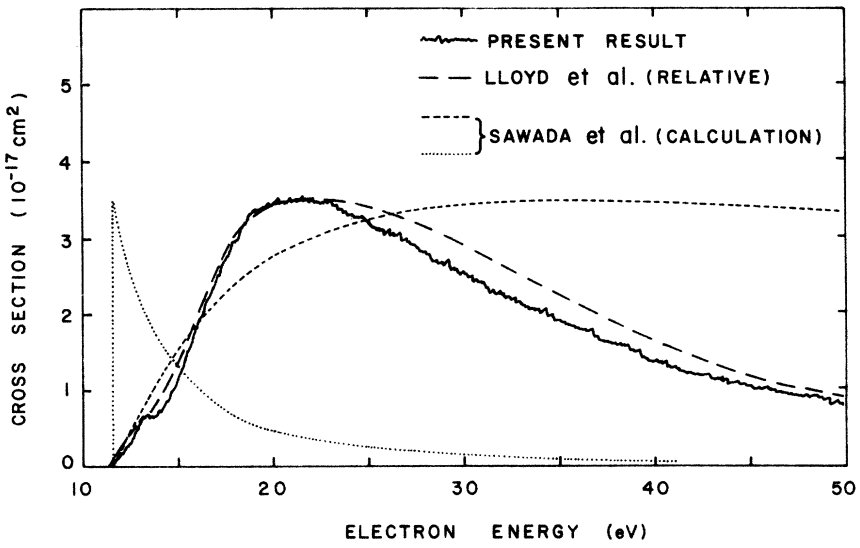

FIG. 3. Cross section for the excitation of argon metastables as a function of electron energy. The present measurement is absolute. The curve of Lloyd *et al.* is a relative measurement and was normalized to the same peak height. The dashed curve was calculated using the Born approximation for the transition $3p^6 \rightarrow 3p^5 4s$ in argon. The dotted curve represents the result of a distorted wave exchange calculation for the ^3P states of this configuration. The Sawada *et al.* curves were also normalized to the present peak height.

from the fact that this distortion in the velocity distribution generally depends on the electron energy. Thus excitation functions for metastables measured under a fixed angle may have a distorted shape. For a given electron energy, the metastable signal depends therefore on the angle of observation and increases with decreasing angle.

For heavy atoms such as argon, the recoil velocities are rather small and consequently the distortion in the velocity distribution is negligible.[6,21,22] In this case, the assumption of an isotropic Maxwellian velocity distribution for the metastables after excitation is valid and Eq. (1) holds. The problem of metastable recoil is more serious for light atoms such as helium. It has been found,[21] that the metastable signal for a fixed electron energy varies by about a factor of 3 in the angular range from 30° to 130° for electron energies near threshold. The question arises, what effects this may have on the present excitation function and absolute cross section for helium.

It seems that observation at an angle near 90° is particularly favorable. Data obtained as a function of angle[21,22] show that the increase in signal for small angles and the decrease in signal for large angles is approximately averaged out near 90°. It thus appears justified to apply Eq. (1) also in the case of helium at least at low energies, for which angular variations have been studied. For higher energies above 25 eV, the presently available information is insufficient for an accurate assessment of the recoil effects involved. The helium excitation functions in Fig. 2 are therefore subject to some uncertainty at these higher energies and have to be accepted with caution until further data become available.

There remains the question, whether recoil effects in the work of Lloyd *et al.* differed from those in the present work. Lloyd *et al.* do not present a TOF curve for helium, which could be compared with the present TOF distribution (Fig. 1). Their TOF curve for argon metastables, however, exhibits the expected Maxwellian shape. Although the experimental techniques used were similar, it is possible that part of the discrepancy in the helium excitation functions (Fig. 2) is due to the different geometries used for collecting the metastables. Lloyd *et al.*[2] used a small area channeltron multiplier at a distance of 5 cm from the source for detecting the metastables. In contrast to this, a large planar surface of a focussed mesh CuBeO multiplier with an effective diameter of about 2 cm was used at a distance of 6 cm in the present case.

The shape of the present excitation function for helium (Fig. 2) is in good agreement with a measurement in which metastables were collected over a large angular range (~2π solid angle) by a cylindrical tungsten surface that surrounded the collision region.[23] This measurement covered the threshold region within the first few eV and confirms the present result obtained at 90° at least at low energies.

III. RESULTS AND DISCUSSION

A. Cross sections

Two different methods were employed in determining the argon cross section. In the first method, a yield $\gamma_m = 0.035$ for argon metastables on a CuBeO surface was used[5] in Eq. (1), resulting in a cross section of

$$\sigma_A(22\ \text{eV}) = 3.4\times10^{-17}\ \text{cm}^2 \tag{2}$$

at the peak in the excitation function at 22 eV (Fig. 3). The uncertainty in this value is a factor of 2. The cross section in Fig. 3 contains both the $^3P_2$(11.5 eV) and the $^3P_0$(11.7 eV) metastable states of argon. The same yield was assumed for both states because of their closeness in energy.

In the second method, the signals from argon and helium metastables were compared. It follows from Eq. (1) that

$$\sigma_A = \frac{S_A}{S_{\text{He}}}\frac{\gamma_m^{\text{He}}}{\gamma_m^{\text{Ar}}}\sigma_{\text{He}}, \tag{3}$$

provided all the other quantities in Eq. (1) are the same. In this case, only the ratio of yields and not their absolute value enters. A yield ratio $\gamma_m^{\text{Ar}}/\gamma_m^{\text{He}} = 0.23$ was obtained from the yield data of the metastable detector.[5] According to Eq. (3), a knowledge of the helium cross section is necessary. This cross section was determined near threshold with a trapped-electron method[24] in a previous experiment in which trapped electrons and helium metastables could be monitored separately.[23] Values of 4.0×10^{-18} and 6.2×10^{-18} cm^2 were found for the 20.4-eV peak and the 25.5-eV maximum in the helium excitation function (Fig. 2), respectively, with a possible error of 30%. Comparing the argon signal at the 22-eV peak with that of helium at the 20.4-eV peak, and substituting the helium cross section into Eq. (3), the argon cross section was found to be

$$\sigma_{\text{Ar}}(22\ \text{eV}) = 3.7\times10^{-17}\ \text{cm}^2. \tag{4}$$

The uncertainty in this value is estimated to be again a factor of 2 and is comprised of the uncertainty in the helium cross section and in the yield ratio. However, from the agreement in the values in Eqs. (2) and (4), it seems that the actual error is much smaller.

B. Comparison with other work

1. Helium

The present cross section for helium agrees well with a recent determination by Trajmar[4] at energies of 29.6 and 40.1 eV (Fig. 2). Trajmar's separate cross sections for the $2\,^1S_0$ and $2\,^3S_1$ states of helium were added in order to compare with the present result, which contains both these states. Since the present curve in Fig. 2 also contains cascade contributions from higher states, it should lie above Trajmar's results, which did not contain such contributions.

For excitation of helium metastables near threshold, several other cross-section measurements exist. Schulz and Fox[25] and Maier-Leibnitz[26] obtained values of 4×10^{-18} and 5×10^{-18} cm^2 for the first peak in the excitation function, respectively. A value of 2.6×10^{-18} cm^2 obtained by Fleming and Higginson[27] is rather small but still within the limits of error associated with the various measurements.

The curve of Lloyd *et al.*[2] shown in Fig. 2 is a relative measurement. It agrees well with the present result in the detailed structure near threshold up to about 25 eV. The discrepancies above this energy are not understood. Possibly, the effects of metastable recoil may have been different in the two measurements (see above).

Several other measurements of excitation functions in the threshold region[28-32] show good agreement. Relative excitation functions for the $2\,^3S_1$ and $2\,^1S_0$ states have been reported by Čermák,[33] Holt and Krotkov,[34] and Hall *et al.*[35] in the energy region near threshold. There is some disagreement in these measurements as to the relative cross sections for the two states involved and the detailed structure. The shape of the relative excitation function determined by Kuprianov[3] is in serious disagreement with the present curve as it peaks near 60 eV and does not contain any structure in the threshold region.

A recent measurement of the cross section of the $2\,^3S_1$ state between 40 and 70 eV by Crooks *et al.*[36] contains a broad peak near 50 eV. This peak has a width of about 15 eV and results in a 25% increase in the cross section as compared to a smooth curve not containing the resonance. There is no strong evidence for this resonance in the two curves in Fig. 2. Since these curves contain both the $2\,^3S_1$ and $2\,^1S_0$ metastable states, this resonance should be less pronounced than in the cross section for the $2\,^3S_1$ state alone. Using Trajmar's[4] cross sections for the $2\,^1S_0$ and $2\,^3S_1$ states, it is estimated that the resonance should manifest itself as an 8% enhancement in the curves in Fig. 2 at an energy of 50 eV and should occur between about 45 and 55 eV. The estimated effect is rather small and may account for the lack of strong evidence for this resonance in the curves shown.

2. Argon

The present excitation function for argon agrees well in shape with the curve of Lloyd *et al.*[2] (Fig. 3). From the work published by these authors, it appears that their experimental technique used for monitoring relative excitation functions was similar to the present one. This is consistent with the agreement in the argon excitation functions. However, the problem with the discrepancy in the helium excitation functions remains.

Several relative excitation functions for argon metastables obtained near threshold[28-30] are in good agreement. The relative excitation function of Kuprianov,[3] which extends from threshold to about 150 eV, disagrees with the curves in Fig. 3 as it does not have structure near threshold and has its maximum near 30 eV.

No other absolute cross-section determination for argon metastables seems to exist. The present peak cross section for the two $^3P_0$ and $^3P_2$ metastable states is of the same magnitude as the combined peak cross section of about 4×10^{-17} cm^2 for the two radiatively decaying $^1P_1$ and $^3P_1$ states of argon.[37]

In Fig. 3, a comparison is also made between the present measurement and the calculations by Sawada *et al.*[38] In the LS coupling scheme used by these authors, the Born approximation (dashed curve) is only applicable to the excitation of the ^1P state in the $3p^5 4s$ configuration of argon, whereas the metastable states in question are ^3P states. Thus, a comparison with the present result is not possible at lower energies. However, Lloyd *et al.* have found a good fit of the Born cross section to their data at higher energies, indicating a substantial direct excitation contribution at these energies. The present maximum in the excitation function at the relatively low energy of 22 eV is indicative of an exchange process and can thus be compared with the distorted wave exchange calculation by Sawada *et al.* (dotted curve). The significant differences in the two curves seems to indicate the need for a different potential function than that used by these authors at low energies.

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