JOINT INSTITUTE FOR LABORATORY ASTROPHYSICS

REPORT

JILA REPORT #63

I.

INDIVIDUAL EFFICIENCY CURVES FOR THE EXCITATION OF 2^3S AND 2^1S STATES OF HELIUM BY ELECTRON IMPACT

II.

RETARDING POTENTIAL MEASUREMENT OF THE KINETIC ENERGY OF ELECTRONS RELEASED IN PENNING IONIZATION

by

V. Čermák

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University of Colorado
Boulder, Colorado
January 10, 1966
INDIVIDUAL EFFICIENCY CURVES FOR THE EXCITATION OF $2^3S$ AND $2^1S$ STATES OF HELIUM BY ELECTRON IMPACT

by

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INTRODUCTION

In the course of investigating Penning ionization of molecules (ionization by excited neutral particles), a Lozier stopping potential method has been applied for measuring the kinetic energy of released electrons. Once sufficient electron energy resolution has been achieved, the data obtained can be used in a straightforward way for the determination of the individual excitation functions for ionizing particles into different excited states. The merit of this procedure is that no separation or selective quenching of excited particles is necessary.

In particular, in the reaction

$$\text{He}^*(2^3S, 2^1S) + A = A^+ + \text{He} (1^1S) + e^-,$$  \hspace{1cm} (1)

the energy of released electrons differs by 0.8 eV, which is the difference in energy between the $2^1S$ and $2^3S$ states (20.61 and 19.81 eV).

* This work was supported in part by the Advanced Research Projects Agency (Project DEFENDER).

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Thus, the dependence of the abundance of electrons with the energies of 19.81 - 15.75 = 4.06 and 20.61 - 15.75 = 4.86 eV on the energy of exciting agents (electrons, photons) is related directly to the individual excitation functions for the $2^3S$ and $2^1S$ states.

EXPERIMENTAL

In this study helium atoms were excited by electron impact in the source presented in Fig. 1. Helium atoms entered the source through a multiple channel tube $^3T_1$ in the form of an atomic beam. The current of exciting electrons, emitted from a tungsten ribbon and collimated by a magnetic field of an intensity of about 100 G, was usually 100 µA. The pressure of helium in the excitation region was about $5 \times 10^{-4} - 10^{-3}$ mm Hg. Before entering the collision region B, the atomic beam of helium contained only atoms in the metastable $2^3S$ and $2^1S$ states and atoms in the ground state. Charged particles were removed from the beam by the electric field between the deflecting plates $P_1$ and $P_2$. The reaction (1) with argon atoms took place in the collision region B in which argon atoms were introduced through the multiple channel tube $T_2$. The pressure in the region B was about $5 \times 10^{-4}$ mm Hg.

The apparatus was pumped by the mercury diffusion pump (Edwards 6M3). The actual pumping speed at the entrance to the cold trap was about 120 l/sec. The total gas flow rate was 5 - 20 µl/sec.

Only electrons emitted perpendicular to the long axis of the collision chamber could escape the field-free region B through the channels in the cylinder C. These electrons were subjected to energy analysis by the variable stopping potential applied between the grid G and the cylinder C.
The grid used (80 lines per inch, line width 0.00096 in.) had a transparency of 85%. Those electrons which had enough energy penetrated to the collector, and their current was measured by a Cary vibrating reed amplifier (Model 31). A potential of 15 V, negative with respect to the grid, was applied between the grid and the collector to prevent positive ions from reaching it. The electron current to the collector was of the order of $10^{-13}$ up to $10^{-12}$ A. The whole electron detector region was shielded magnetically by a concentric shield made from Conetic metal.

The dependence of the collector electron current on the stopping potential for ionization of argon atoms by helium metastables is shown in Fig. 2. Curve 1 is the integral curve, and the measured energy distribution curve of the electrons reaching the collector is the first derivative of it. As no automatic derivating circuit was used, the difference curve, $\Delta i/\Delta E$, ($\Delta E = 0.1$ eV) was constructed (Fig. 2, curve 2). The two peaks on the electron energy distribution curve, belonging to two groups of electrons, are well separated; and the energy difference of the onsets of the steps on the integral curve or of the maxima on the derivative curve is 0.8 eV, as expected. In Fig. 3 are the integral and derivative curves for the ionization of xenon atoms. The curves reveal four steps or maxima, as the $\text{Xe}^+$ ions are doublets $\text{Xe}^+ (P_{3/2})$ and $\text{Xe}^+ (P_{1/2})$ (ionization potentials 12.16 and 13.44 V), and as two excited species of helium atoms, $2^3S$ and $2^1S$, are active in ionization.

*It was found that the energy resolution depended on the transparency, and increased when the transparency was lowered from 94 to 85% and when the field penetration decreased. This dependence, however, could not be studied in detail.
The energy resolution, $E/\Delta E$, calculated from the electron energy at the maxima of the peaks and from the width of the peaks at the half height (Fig. 3) is about $9.0/0.4 = 22$. It is much lower than the limiting resolving power derived from the dimensions of the channels in the cylinder. Their length is 5 mm and their width is 0.4 mm; therefore, the resolving power should be $E/\Delta E = v_x^2/v_y^2 = 5^2/0.4^2 = 156$ (Fig. 4). The low resolving power can be explained when considering that some electrons are elastically scattered in collisions with atoms of helium and argon in the channels and in the space between the grid and the cylinder (no differential pumping could be used) and when considering that some are reflected from the channel walls. In order to reduce the reflection of electrons, the channel walls were coated with Aquadag (colloidal graphite). But no substantial increase in resolving power was observed.*

In the optimal case the integral stopping potential curve should be a staircase function as presented in Fig. 5. Its actual form revealed that a continuous background is superposed on it (Figs. 2, 3, curve 1). This background was caused by the scattered electrons as well as by electrons with a spectrum of energies and was emitted by scattered excited helium atoms upon arrival at on cylinder walls.

The background presented a problem for the accurate measurement of the height of the steps on the integral curve. It was verified that the background is proportional to the number of electrons released and that it increases

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* According to Dr. McGowan, the very best coating is a deposit of black gold. This was tried also, but it was difficult for the evaporating gold to penetrate into the small channels.
with the decreasing stopping potential. Finally, the following procedure was adopted in determining the step height: The background curve was extrapolated to lower stopping potentials so that it had the same slope in the portions between the steps as the integral curve. The step height was then the difference between the two curves at the corresponding stopping potentials (Fig. 5). The assumed accuracy in determining the step height is approximately ± 5%.

RESULTS

The efficiency curves for the $2^3S$ and $2^1S$ states, i.e., the dependence of the step heights of the integral curve (Fig. 2) on the energy of exciting electrons, are shown in Fig. 6. They are not pure excitation functions for the upward transitions $1^1S \rightarrow 2^3S$ and $1^1S \rightarrow 2^1S$ as both states can be populated by cascading from higher triplet and singlet states. Figure 7 shows the ratio of the efficiency curves for the $2^1S$ and $2^3S$ states as a function of the energy of exciting electrons. It was found that this ratio does not depend on the pressure of helium in the excitation region A or on the current of exciting electrons (Fig. 8a, b). This ratio decreased when the pressure of argon in the collision region B increased (Fig. 8c).

DISCUSSION

The results obtained can be compared with three previous measurements. These were made by Schulz and Philbrick on resonance in the inelastic cross section of helium, by Chamberlain and Heideman on inelastic scattering of electrons by helium and by Holt and Krotkov on electron impact excitation of $2^1S$ and $2^3P$ states.
Schulz determined the excitation function for the sum of metastable atoms and for the $2^3S$ state only (for electron scattering at 72°) (Fig. 9). In Fig. 10 are the curves of Chamberlain and Heideman. In the present study no energy monochromatizing of exciting electrons was applied. Therefore, the peaks at 20.25 and 21.0 eV on the $2^3S$ curve (Fig. 9) (at 20.4 and 20.75 eV in Fig. 10) appear as a maximum at 20.8 eV on the curve presented in Fig. 6. Similarly, the peaks at 22.4 and 22.6 eV on the $2^3S$ curve (Fig. 9 and 10) and the peak at 22.6 eV on the $2^3P$ curve (Fig. 10) are smeared together in a hump at 22.5 eV in Fig. 6.

The main feature of the efficiency curve for the $2^3S$ in Fig. 6 is that it rises steadily at electron energies greater than 21.3 eV. This is partly due to cascading from higher triplet states which is absent in the measurements of both Schulz and Chamberlain. A large part is due, however, to the fact that the inelastic cross section for the electron scattering in helium is anisotropic.\textsuperscript{5,6} According to the curve in Fig. 10, the cross section for forward inelastic scattering is practically zero in the region 21.2 to 22.3 eV, and it is 3 times smaller at 22 eV than at 20.3 eV for scattering at 72° (Fig. 9). In the experiments presented here the anisotropy does not play any role, as the measurement of the density of the $2^3S$ state is based on the action of the atoms in this state, not on changes in the current of electrons exciting it.

The $2^1S$ state efficiency curve, obtained with energetically inhomogeneous electrons (Fig. 6), is quite smooth and has a broad maximum at $\sim 22$ eV. This is in good agreement with the data of Holt and Krotkov\textsuperscript{7} who used the deflection of the part of the $2^3S$ state in an inhomogeneous magnetic field and the quenching of the $2^1S$ state by an electric field.
for separating the $2^1S$ curve. They found that the cross section for $2^1S$ state rises from the threshold until a plateau is reached at about 212 eV and then the cross section remains constant up to 23 eV. Therefore, it must be concluded that the gross structure on the total efficiency curve for helium atoms in metastable states (Fig. 9) is due to the shape of the efficiency curve for the $2^3S$ state alone and cannot be attributed to the rise of the $2^1S$ excitation curve as was done in the past.\textsuperscript{8,9}

The data on the ratio of the $2^1S$ and $2^3S$ efficiency curves, shown in Fig. 7, differ from those reported by Dugan, et al.\textsuperscript{10}, (Fig. 7). According to them the ratio should be 0.5 at 30 eV, whereas the value presented here is 0.73 at 30 eV. They obtained the result by correcting for scattering of excited particles and imprisonment of resonance radiation by extrapolating to zero pressure. Secondary emission of electrons from metal surface was used for measuring the flux of metastable atoms. As no dependence on helium pressure was detected and the dependence on argon pressure has the opposite trend (Fig. 8a, c), one can conclude that selective scattering of excited atoms was insignificant in the experiments described here. Also the effect of photons, emitted isotropically in the excitation region A, was reduced in our measurements by collimating helium atoms which increased the number of events caused by excited helium atoms relative to those caused by photons. Even if electrons were released in photoionization, they could be responsible only for tailing of the peaks on the energy distribution curve at higher stopping potentials, as the photon energy should be greater than 19.8 or 20.6 eV. No substantial tailing was observed (Figs. 2, 3).
The difference could be explained if the cross sections for Penning ionization of atoms by the $2^1S$ helium atoms were greater than that by the $2^3S$ atoms. In particular, if secondary emission is used for detecting the metastable atoms, the ratio of the currents of electrons emitted by the impacting $2^1S$ and $2^3S$ atoms is given by

$$R_s = \frac{i_{-1s}}{i_{-3s}} = \frac{\sigma_1}{\sigma_3} \frac{\gamma_1}{\gamma_3} \quad . \quad \text{(a)}$$

where $\sigma_1$ and $\sigma_3$ are the excitation cross sections for the $2^1S$ and $2^3S$ states respectively and $\gamma_1$ and $\gamma_3$ are the corresponding secondary emission coefficients. Similarly, if ionizing action is used for detection, the measured ratio of the currents, $i_{-1c}$ and $i_{-3c}$, of electrons reaching the collector is

$$R_i = \frac{i_{-1c}}{i_{-3c}} = \frac{\sigma_{1i}}{\gamma_3} \frac{\sigma_{3i}}{\sigma_{3i}} \quad . \quad \text{(b)}$$

In equation (b) $\sigma_{1i}$ and $\sigma_{3i}$ are Penning ionization cross sections for the $2^1S$ and $2^3S$ states. As $\gamma_1/\gamma_3 = 1$ (see 10), it follows that

$$\frac{i_{-1c}}{i_{-3c}} > \frac{i_{-1s}}{i_{-3s}} \quad \text{when} \quad \frac{\sigma_{1i}}{\sigma_{3i}} > 1 \quad .$$
The experimental evidence on $\sigma_{1i}$ and $\sigma_{3i}$ is conflicting. Benton, et al.\(^{11}\), reported that the $2^1S$ Penning cross section for argon, $5.5 \times 10^{-16}$ cm\(^2\), appeared to be larger than the triplet cross section, $6.6 \times 10^{-16}$ cm\(^2\). They pointed out, however, that the singlet cross section may be too high by a factor of as much as two or three. On the other hand, Sholette and Muschitz\(^{12}\) found the helium singlet Penning cross section to be equal to the triplet cross section for argon, krypton, xenon, nitrogen, oxygen and carbon monoxide. The simple theoretical calculation of Fergusson\(^{13}\) predicts a ratio $\sigma_{1i}/\sigma_{3i}$ of about 1.1 to 1.2, which is due to the difference in Van der Waal's coefficients for the $2^1S$ and $2^3S$ states.

An estimate of the ratio of $\sigma_{1i}$ to $\sigma_{3i}$ can be obtained using Eqs. (a) and (b). If $\gamma_1/\gamma_3 = 1$ then

$$\frac{R_i}{R_s} = \frac{\sigma_{1i}}{\sigma_{3i}}.$$ 

Unfortunately, the results obtained from the curves on Fig. 7 and shown in Table I are not consistent enough. (The ratio $R_i/R_s$ in Table I should not depend on the electron energy, which is not the case.)

<table>
<thead>
<tr>
<th>Electron Energy, eV</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{R_i}{R_s}$</td>
<td>2.2</td>
<td>1.4</td>
<td>1.2</td>
<td>1.1</td>
<td>1.07</td>
<td>1.07</td>
<td>1.06</td>
</tr>
</tbody>
</table>
Another tentative explanation of the differences in the ratio of the efficiency curves might be that the conditions in excitation of helium atoms were different in the measurements presented here and those of Dugan, et al. It is known that the $^{1}S$ state is easily quenched in collisions with slow electrons.\textsuperscript{14} If this occurred in the experiments of Dugan, et al., because, for example, of a greater number of secondary electrons, the ratio would be lowered. Still another explanation might be that the three levels of the $^{3}S$ state were not equally populated due to cascading and that after passing the inhomogeneous magnetic field, more than two-thirds of the atoms in the $^{3}S$ state were deflected as probably supposed by Dugan, et al.

**SUMMARY**

It was shown that the direct measurement of the kinetic energy of the electrons released in Penning ionization is a useful method for obtaining separate efficiency curves for different ionizing excited particles. The particular merit of the method is that the total efficiency curves are determined and that the data obtained are not influenced by anistropies in the differential excitation cross section as is the case in energy-loss measurements.

The data obtained, even with unfavorable experimental conditions (lack of differential pumping and a big energy spread of exciting electrons), suggest that the total efficiency curve for the $^{1}S$ state is a smooth curve within the limits of the inhomogeneity of exciting electrons used. Therefore, the structure in the region 20 - 21 eV on
the total efficiency curve for metastable helium atoms should be ascribed to the shape of the efficiency curve for the $2^3S$ state.

The ratio of the cross sections for the $2^1S$ and $2^3S$ states as a function of the energy of exciting electrons has been measured without separating or quenching either of the two states. The dependence has the same general course as found by Dugan, et. al., but the ratio is larger. This seems to indicate that the ionization cross section for argon by the $2^1S$ state is larger than that by the $2^3S$ state.

The easy determination of the ratio for the two metastable states can be useful in finding the optimal conditions for producing atomic beams of excited helium atoms containing only one metastable state. This is important for future studies of the differences in ionization of diatomic and polyatomic molecules by excited atoms in the singlet and triplet states and for the comparative studies of Penning ionization and photo-ionization.
REFERENCES


2. (a) W. Lozier, Phys. Rev. 35, 1285 (1930).
   (b) J. Marriott and J. D. Craggs, EAR. Report L/T 308 (1954).
   (c) F. I. Vilesov, B. L. Kurbatov, and A. M. Terenin, Soviet Phys. 6, 490 (1961).


4. W. McGowan, [Private communication].


    (b) E. E. Muschlitiz, Jr., [Private communication to the author].


FIGURE CAPTIONS

1. Schematic Diagram of the Apparatus

A  excitation region
T₁, T₂  Multiple channel tubes
E  electron beam
P₁, P₂  charged particles deflecting field
Gₘ  grid for stopping electrons from entering the collision region
B  collision region
C  copper cylinder with channels
G  grid
Col  collector
S  secondary electrons suppressing grid

2. Ionization of Argon by Helium Metastables

Curve 1. Integral curve, i.e. the current of electrons reaching the collector as a function of the stopping potential. Stopping potential scale uncorrected.

Curve 2. Electron energy distribution curve. The Ar⁺ doublets, \(^2P_{3/2}\) and \(^2P_{1/2}\) (energy difference 0.17 eV) are not well resolved and the peaks are therefore broader.

3. Ionization of Xenon by Helium Metastables

Curve 1. Integral curve, 2. Derivative curve. The two Xe⁺ doublets (energy difference 1.29 eV) are well resolved in this case.

4. Limiting trajectory of an electron (e) through one channel, and the energy resolving power of the arrangement.
5. Curve 1. The shape of the integral curve for ionization of argon in the absence of the background.

Curve 2. The actual form of the integral curve and the procedure adopted for the measurement of the step height.

6. Efficiency curves for the helium metastables.
   Curve 1. $2^1S$ state; curve 2. $2^3S$ state. The estimated accuracy in current reading: $\pm 5\%$.

7. Ratio of the $2^1S$ to $2^3S$ states efficiency curves.
   Curve 1. Original data; curve 2. data of Dugan, et. al.

8a. Dependence of the ratio of the efficiency curves for $2^1S$ to $2^3S$ states on the pressure of helium in the excitation region. Electron energy: 23.5 eV. Instead of helium pressure the total pressure in the apparatus was measured but the linear relation between them was checked.

8b. Dependence of the ratio of the efficiency curves for $2^1S$ to $2^3S$ states on the exciting electrons current. Curve 0: Electron energy 24.0 eV. Curve X: Electron energy 23.2 eV.

8c. Dependence of the ratio of the efficiency curves for $2^1S$ to $2^3S$ states on the pressure of argon in the collision region. Electron energy: 23.6 eV. Electron current: 150 $\mu$A. Pressure measured is the total pressure in the apparatus.


10. Excitation functions determined by Chamberlain, et. al.
Figure 3

V_{stopping}
\[ \frac{E}{\Delta E} = \frac{V_y^2}{V_x^2} \]

Figure 4
Figure 8c
Figure 9

NORMALIZED CROSS SECTION

TOTAL METASTABLE PRODUCTION

$^2S (72^\circ \text{ SCATTERING})$

ELECTRON ENERGY, eV

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RETARDING POTENTIAL MEASUREMENT OF THE KINETIC ENERGY
OF ELECTRONS RELEASED IN PENNING IONIZATION*

by

V. Čermák †

INTRODUCTION

In studies of ionizing collisions, increasing attention has been
paid to ionizing collisions of excited neutral particles with atoms and
molecules (ionizing collisions of the second kind or Penning ionization).¹⁻⁴
These studies are important from several points of view:

1) Penning ionization differs from that caused by electron and
photon impact or charge transfer, as the collisions occur between uncharged
particles and the field of force is small unless the particles are very
close together.

2) The collision time is increased, and the collision may have an
adiabatic character. Collision complexes as intermediate steps may be
favored. If the complexes survive some vibrations, the Franck-Condon
principle may not be applicable in predicting the population of excited
levels in the ions formed.

*This work was supported in part by the Advanced Research Projects Agency
(Project DEFENDER).
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Czechoslovak Academy of Sciences, Prague, Czechoslovakia.
3) Because the population of various electronically and vibrationally excited states of polyatomic ions may differ from that attainable through ionization by charged particles or photons, the influence of the initial preparation of the ions on their subsequent dissociation may be investigated.

4) Only one electron is released in ionization. In measuring its kinetic energy, data related directly to the energy states of ions are accessible. Especially, data on the distribution of excitation energy in polyatomic ions are obtainable in a straightforward way. This is important for the theories of dissociative ionization of molecules.  

5) The determination of kinetic energy of electrons released in associative ionization (a special kind of Penning ionization) may be used, in some favorable cases, to estimate the binding energy of complex ions produced.

Studies have been undertaken already to determine the kinetic energy of electrons released in photoionization, but no work has dealt with such measurements in Penning ionization. It is quite clear that once the data about this process became available, comparative studies on all kinds of ionization of simple as well as polyatomic molecules would be of great importance.

This paper is closely related to a study published previously on Penning ionization of polyatomic molecules. This work presents an independent measurement of kinetic energy of electrons released for verifying the conclusions made in the earlier paper. The work reported here is preliminary in character and is limited to the ionization of \( \text{N}_2 \), \( \text{CO} \), \( \text{NO} \), \( \text{COS} \), \( \text{CO}_2 \), \( \text{C}_2\text{H}_2 \), and \( \text{CH}_4 \) by means of excited helium
atoms in the $^2S$ and $^3S$ metastable states.

EXPERIMENTAL

The apparatus used is the same as shown in Fig. 1, Part I, of this report. The molecular gases were admitted into the collision region through a variable leak. They were of the Matheson C.P. grade quality and were stored in the commercial lecture bottles. The pressure inside the collision region was of the order of $5 \times 10^{-4} - 10^{-3}$ mm Hg. The total gas flow rate was 5 - 25 µl/sec.

The data were obtained in the form of the integral stopping potential curves which show the dependence of the current of electrons reaching the collector on the potential difference applied between the grid G and the cylinder C (Fig. 2, Part I). A derivative of the stopping potential curve was then constructed as $\Delta i/\Delta V$, $\Delta V = 0.1$. Because of field penetration and contact potentials, the actual electron energy, and hence the data on the excitation energy of the ions, had to be obtained by calibration of the stopping potential scale. For this purpose argon was used. Electrons released in its ionization by helium atoms in the $^2S$ state have the energies of $20.61 - 15.76 = 4.85$ eV and $20.61 - 15.94 = 4.67$ eV, and those released in ionization by $^3S$ state have the energies $19.81 - 15.76 = 4.08$ and $19.81 - 15.94 = 3.87$ eV. In the arrangement used, the electron energy resolution is about 22 (see Part I) which is not high enough to separate the steps due to argon ion doublets, so that only two steps appear on the integral curve instead of four. The corrected stopping voltage scale was shifted to lower voltage, typically by about
0.7 eV. By means of calibration, steps on the integral curve were identified belonging to ionization with ground state ions formed. The onset of the first step (ionization by $2^1S$ helium atoms) was used as the zero for the excitation energy scale. The zero point on the excitation energy scale for ionization with the helium atoms in the $2^3S$ state is obtained by shifting the zero point to the left by 0.8 eV.

RESULTS

Nitrogen

The integral stopping potential curve and its derivative are shown in Fig. 1. In spite of considerable background the formation of $N_2^+$ in the ground state and in two excited states is clearly detected (peaks 1-3, curve 2). Peaks 1a, 2a, and 3a are due to the ionization by the $2^1S$ atoms and peaks 1b, 2b, and 3b by the $2^3S$ atoms. Their separation at the onset of the steps is 0.8 V which is the energy difference of the two states (20.61 - 19.81 eV). Peaks 1, 2, and 3 correspond to the following processes:

$$\text{He}^* (2^1S, 2^3S) + N_2 \rightarrow \begin{cases} N_2^+ (x^2\Sigma_g^+) \\ N_2^+ (A^2\Pi_u) \\ N_2^+ (B^2\Sigma_g^+) \end{cases} + \text{He} (1^1S) + e \quad (1)$$

The onsets of the peaks 2b and 3b are separated from the onset of peak 1b by 1.1 and 3.3 V respectively. These energies are close to the $A^2\Pi_u - x^2\Sigma_g^+$ and $B^2\Sigma_g^+ - x^2\Sigma_g^+$ separations, the spectroscopi:
values of which are $^{16,17}$ respectively 1.1 eV and 3.15 eV.

The peaks of the ground state and of the $B^2\Sigma_+^*$ state are narrower than the peak of the $A^2\Pi_u$ state as if only a few vibrational levels were excited in the ground and $B^2\Sigma_+^*$ states. This is in complete agreement with the shape of the potential energy curves for the three states in question. The internuclear separation in the $N_2^+ A^2\Pi_u$ state, 1.190 Å, is larger than in neutral $X^1\Sigma_g^+$ ground state, 1.094 Å, whereas the $N_2^+ X^2\Sigma_g^+$ state or the $B^2\Sigma_g^+$ state has equilibrium separations close to the neutral ground state (1.116 and 1.075 Å respectively).$^{16,17}$ Higher vibrational levels are, therefore, excited in the $A^2\Pi_u$ state; and the peaks 2a and 2b spread to lower electron energies.

**Carbon Monoxide**

The integral and derivative curves are shown in Fig. 2. The peaks 1a and 1b correspond to CO$^+$ formed in the ground state. Peak 3 is due to the process

$$\text{He}^* (2^1S) + \text{CO} \rightarrow \text{CO}^+ (B^2\Sigma^+) + e + \text{He} (1^1S) \quad (2)$$

The spectroscopically determined energy of the $B^2\Sigma^+$ state is 5.68 eV above the CO$^+$ ground state, and the measured difference of the stopping potentials at the onsets of peaks 1a and 3a is 5.6 eV. The very small and broad peak 2 in the region of uncorrected stopping potential $\sim 3.3$ V is due to the ionization to the first excited state of CO$^+$, $A^2\Pi$, by helium atoms in the $2^3S$ state. The peak belonging to the ionization by the $2^1S$ atoms is too small to be seen.
Nitric Oxide

There are no pronounced steps or breaks on the integral curve at stopping potentials larger than 5 V which would belong to the first or second ionization potential of NO (9.24 and 14.2 V). Therefore, instead of using the calibrated excitation energy scale, the energy is given in ionization potentials corresponding to the onsets of the steps on the integral curve caused by the $2^1S$ atoms.

The ionization by both $2^1S$ and $2^3S$ atoms is clearly detectable at 16.3 and 17.1 V. The value of 16.3 V is very close to the ionization potential of the $3^3\Delta$ state at 16.55 V. The broad peak with the maximum at ~ 19.2 V belongs probably to ionizations to the $1^1\Pi$, $3^3\Sigma^-$ and $1^1\Sigma^-$ states lying at potentials 18.3 and 18.7 V.

The absence of the steps for NO$^+$ in the $1^1\Sigma^+$ ground state and in a $3^3\Sigma^+$ first excited state is striking in comparison with the results in N$_2$ and CO, where the Franck-Condon transitions seem to occur. It is probable that a collision complex HeNO$^*$ is formed and that preionization of the complex determines the population of various excited states of NO$^+$. If this occurs, the energy of electrons released will be indicative of the energy states of NO$^+$ ions only when no transformation of internal energy of the complex HeNO$^*$ into kinetic energy of He and NO$^+$ takes place. Such transformation could account for the broad peak on the derivative curve at about 10.5 – 12 V. This peak would then correspond

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*The tendency of the NO molecule to form complexes is well known, and its odd electron is responsible for it.*
to the ionization of NO and to the formation of NO\(^+\) ions in the ground state in a process in which He and NO\(^+\) ions acquire together a kinetic energy of about 1.2 eV.

**Carbonyl Sulphide**

The integral and derivative curves, shown in Fig. 4, reveal quite clearly the ionization by both \(2^1\text{S}\) and \(2^3\text{S}\) atoms into the COS\(^+\) ion ground state (peaks 1a, 1b) and into the first and second excited states (peaks 2 and 3). The excitation energy of the first excited state is 4.8 eV and that of the second excited state is 6.8 eV. These values compare well with the spectroscopic values of 4.74 and 6.64 eV\(^1\text{8}\).

**Carbon Dioxide**

According to the integral and derivative curves shown in Fig. 5, the CO\(_2\)\(^+\) ions are formed not only in the ground state (peaks 1a, 1b) but also in three excited states lying 3.6, 4.2, and 5.6 eV above the ground state of CO\(_2\)\(^+\) (peaks 2, 3, and 4). Accidentally, peak 2b, due to the ionization by \(2^3\text{S}\) atoms and to the formation of the CO\(_2\)\(^+\) ions in the first excited state, coincides with peak 3a due to its ionization by \(2^1\text{S}\) atoms into the CO\(_2\)\(^+\) second excited ionic state. The spectroscopically determined excited states of CO\(_2\)\(^+\) ions have the energies of 3.53, 4.24, and 5.51 eV above the CO\(_2\)\(^+\) ion ground state (I.P. 13.78 V)\(^1\text{2}\). The agreement between the energy separations observed here and the spectroscopic energies is quite good.
Acetylene

The integral stopping potential curve, shown in Fig. 6, curve 1, differs from those for \( \text{N}_2 \), \( \text{CO} \), \( \text{NO} \), \( \text{COS} \), and \( \text{CO}_2 \) in two respects: the steps on the curve become unsymmetrical, and the first step is relatively smaller. The tailing, well marked on the derivative curve (Fig. 6, curve 2), is due to vibrational excitation of the \( \text{C}_2\text{H}_2^+ \) ion and to the decreasing transition probability of excitation of higher vibrational levels. The width at the bottom of the larger peak 1b is about 2.5 V. Correcting for the width of the peak due to incomplete energy resolution by subtracting 0.7 V (peak width for argon, see Fig. 2, Part I), a value of 1.8 eV is obtained for the vibrational energy which can be stored in the \( \text{C}_2\text{H}_2^+ \) ion. More vibrational excitation is still possible, but the transition factors beyond this are very small.

The relatively small cross section for ionization by the \( 2^1\text{S} \) atoms is surprising. It was checked by changing the current of exciting electrons so that it is not due to an unexpected quenching of the \( 2^1\text{S} \) state in the source by secondary electrons. A tentative explanation might be that an important part of the ionization of \( \text{C}_2\text{H}_2 \) occurs in two steps, the first being the formation of a superexcited molecule in a triplet state

\[
\text{He}^* (2^3\text{S}) + \text{C}_2\text{H}_2 (^1\text{g}) \rightarrow \text{C}_2\text{H}_2^{**} (^3) + \text{He} (1^1\text{S}) , \tag{3}
\]

and the second step being the preionization of the excited molecule

\[
\text{C}_2\text{H}_2^{**} \rightarrow \text{C}_2\text{H}_2^+ + e . \tag{4}
\]
Total electron spin is conserved in reaction (3), but it would be changed if the atoms in the $^{2}_{1}S$ state reacted. The $^{2}_{1}S$ state can, of course, react according to

$$\text{He}^* (^{2}_{1}S, ^{2}_{3}S) + C_2H_2 \rightarrow C_2H_2^{+ (2)} + e + \text{He} (^{1}_{1}S).$$  \hspace{1cm} (5)$$

The reaction (5) with the $^{2}_{1}S$ atoms then accounts for the first step on the curve.

The break on curve 1 or the broad peak at $3 - 4.5$ V on curve 2 in Fig. 6 could be explained assuming that it manifests a second ionization potential of $C_2H_2$ with the $C_2H_2^{+}$ ions formed with $5.1$ eV excitation energy. The ionization potential of $C_2H_2$ corresponding to this value was reported by Al-Joboury and Turner$^{12}$ but not by Dibeler, et. al.$^{19}$ The value, I.P. $= 15.5$ V, for the first excited state of $C_2H_2^{+}$ ions, obtained by Lindholm$^{20}$ in charge transfer experiments, is lower, but the correct value is probably about $16.5$ V.$^*$

Similarly, the rise on the derivative curve at stopping potential $\sim 2.6$ V might be connected with an excited state of $C_2H_2^{+}$ ions having an energy higher than $\sim 7.0$ eV. An excited state found earlier$^{12}$ lies $7.15$ V above the ground state.

It is important to note that valuable conclusions on the mechanism of dissociative ionization of $C_2H_2$ can be made from the shape of the

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* E. Lindholm, (Private communication).
electron energy distribution curve. In ionization of C\textsubscript{2}H\textsubscript{2}, electrons with kinetic energy of 20.6 - 17.8 = 2.8 eV and 19.8 - 17.8 = 2.0 eV (17.8 V is the appearance potential of C\textsubscript{2}H\textsuperscript{+} ions from C\textsubscript{2}H\textsubscript{2}\textsuperscript{2+}) corresponding to the dissociative ionization, well known from electron-impact studies

\[ C\textsubscript{2}H\textsubscript{2}^+ \rightarrow C\textsubscript{2}H^+ + H \] (6)

could appear as a separate peak on the energy distribution curve. This would be the case if the dissociation occurred from a repulsive state. There is no indication of a peak in the region mentioned. Thus, it can be concluded that either the C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} ions dissociate from sufficiently high vibrational levels of the first electronically excited state or that the repulsive curve has a shape leading to a big energy spread of electrons released. It is also possible that the ionization and dissociation proceeds via a preionizing superexcited state which can be formed in electron impact but which is not accessible in collisions with excited neutral atoms. These questions could be answered using an apparatus with sufficiently high energy resolution.

Methane

The integral curve (Fig. 7) is S-shaped with long tailing and without prominent separation into two steps. The two groups of electrons with energies 20.61 - 12.98 = 7.63 eV and 19.81 - 12.98 = 6.83 eV are poorly discernible even on the derivative curve. The electron energy distribution peaks are broader here due to more vibrational degrees of
freedom in the $\text{CH}_4^+$ ion with corresponding states which can be excited in ionization. The total width of the peaks on curve 2 in Fig. 7 is 4.4 eV. Subtracting 0.8 eV (the energy difference of the $2^1\text{S}$ and $2^3\text{S}$ states) and 0.7 eV (peak broadening at the bottom due to imperfect energy resolution) a value of 2.9 eV is obtained for the vibrational energy which can be accommodated in the $\text{CH}_4^+$ ion. Higher vibrational excitation is still possible, but the transition probabilities already became very small.

The maximum on the derivative curve (Fig. 7) is not located close to the zero excitation energy but is shifted to lower electron energies. These results and the tailing at the bottom of the peaks seem to indicate that the differences in the geometry and frequencies of the $\text{CH}_4^+$ ion and $\text{CH}_4$ molecule are reflected in the transition probabilities in Penning ionization as in photoionization.¹¹

There is no indication, within the limits of the sensitivity of the apparatus, of a second ionization potential in the energy range 13 - 19 V. The dissociative ionization of $\text{CH}_4$ to $\text{CH}_3^+$ and to $\text{CH}_2^+$ ions at the potentials of 14.25 and 15.16 V respectively remains undetected in Penning ionization. This means that it occurs from the vibrationally excited $\text{CH}_4^+$ ions in the ground state. Preionizing states lying at the appearance potentials of $\text{CH}_3^+$ and $\text{CH}_2^+$ ions (14.25 and 15.16 V) can be excluded in impact with helium metastables, as is the case in photoionization by resonance photons studied by Al-Jobouy and Turner.¹²
CONCLUSIONS

The data obtained in measuring the kinetic energy of electrons released in Penning ionization and pertaining to the location of electronically excited ionic states point out some similarities and differences with respect to photoionization.

The ionization by helium metastables of \( \text{N}_2 \), \( \text{CO} \), \( \text{COS} \), and \( \text{CO}_2 \) occurs probably in a Franck-Condon transition with the populating of all energetically accessible, spectroscopically known excited ionic states.

The ionization of \( \text{NO} \) seems to proceed through preionization of a \( \text{HeNO}^* \) complex, as some electronically excited states of \( \text{NO}^+ \) are not populated. When the \( \text{HeNO}^* \) complex preionizes and decomposes, a part of its inner energy is probably converted into kinetic energy of both \( \text{He} \) and \( \text{NO}^+ \).

The shape of the electron energy distribution curve in ionization of acetylene and methane indicates that the transition factors for conferring more excitation energy than about 1.8 eV to the \( \text{C}_2\text{H}_2^+ \) ion and about 2.9 eV to the \( \text{CH}_4^+ \) ion become very small.

The type of apparatus used did not allow either for the determination of the population of vibrational levels of various electronically excited states or for the precise measurement of the ionization potentials. In future studies planned, use will be made of the electrostatic electron energy analyzer and of ionization with the beam of helium atoms containing metastable atoms of one kind only. Promising data could then be obtained on the mechanism of dissociative ionization as well.
REFERENCES

3. E. E. Muschlitz, Jr. and M. J. Weiss, Atomic Collision Processes
   (M. R. C. McDowell, Ed., North-Holland Publishing Co., Amsterdam,
5. H. M. Rosenstock and M. Kraus, Mass Spectrometry of Organic Ions
7. B. L. Kurbatov, F. I. Vilesov, and A. N. Terenin, Soviet Phys. - Doklady
   6, 490 (1961); 6, 883 (1962).
   1088 (1963).
    International Conference on the Physics of Electronic and Atomic
    Collisions, Quebec, 1965.
    the IVth International Conference on the Physics of Electronic and
    Atomic Collisions, Quebec, 1965.


FIGURE CAPTIONS

Fig. 1. Integral and Derivative Stopping Potential Curves for \( \text{N}_2 \).

Fig. 2. Integral and Derivative Stopping Potential Curves for \( \text{CO} \).

Fig. 3. Integral and Derivative Stopping Potential Curves for \( \text{NO} \).

Fig. 4. Integral and Derivative Stopping Potential Curves for \( \text{COS} \).

Fig. 5. Integral and Derivative Stopping Potential Curves for \( \text{CO}_2 \).

Fig. 6. Integral and Derivative Stopping Potential Curves for \( \text{C}_2\text{H}_2 \).

Fig. 7. Integral and Derivative Stopping Potential Curves for \( \text{CH}_4 \).
Figure 1: Graph showing the relationship between current density ($i = f(V)$) and excitation energy ($\Delta i / \Delta V = f(V)$). The graph includes peaks labeled 1, 2, 3a, 3b, 2a, 2b, 1b, and 1a. The ionization potential of $N_2$ is indicated as $15.6 \text{ V}$. The x-axis represents excitation energy (eV) and the y-axis shows stopping energy (2's).
Figure 7

eV 5 4 3 2 1 0 EXCITATION ENERGY (2'S)