

ATOMIC EXCITATION BY MONOENERGETIC ELECTRON BEAMS

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Excitation of Zn, Cd, Hg, N, K, and He atoms by slow electrons was studied using an optical method. The monoenergetic electron beam of 0.05-0.1 eV energy half-width was generated by a 127° cylindrical electrostatic selector. A number of pronounced maxima are observed on the energy dependence curves of the excitation cross sections for the investigated lines. The resonance nature of the excitation of some energy levels is established. An explanation is proposed for the origin of the maxima appearing above the ionization threshold.

INTRODUCTION

DURING the past decade laboratories in different countries have reported many studies of the excitation of atoms and diatomic molecules by electron impact. Nevertheless, we are still far from understanding the excitation mechanism of the atomic and molecular energy levels, especially when the electron energies are not two to three times greater than the threshold values. This situation has resulted from the utilization of insufficiently monoenergetic electron beams. The prominent part played by the degree of electron homogeneity in atomic excitation became evident in earlier work by one of the present authors.^[1]

The great difficulties that were previously encountered had prevented the attainment of electron beams with an actual spread of less than 0.5 eV for use in atomic and molecular excitation. Spreads smaller by a factor of two to four in beams used for the same purpose have been reported only in recent years. This development has led to the detection of new qualitative excitation properties near threshold, such as resonance maxima.^[2,3]

In the present work it was our aim to construct apparatus for producing very homogeneous electron beams and to investigate atomic excitation cross sections near threshold.

APPARATUS

Our measuring apparatus consisted of an excitation tube, optical system, and photoelectric unit. The most important part of the apparatus was the electron monochromator, which utilized the principle of electron deflection in the field of a Hughes-Rojansky cylindrical condenser.^[4]

We used two types of selectors, the first of

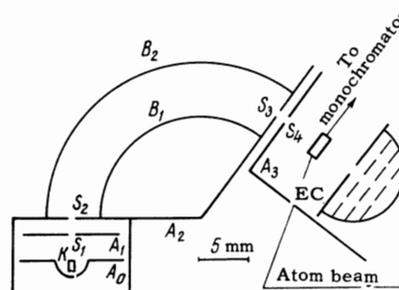


FIG. 1. Scheme of the electron monochromator.

which was essentially similar to that used by Marmet and Kerwin^[5] and was described earlier in^[6]. The scheme of the second selector, shown in Fig. 1, consisted of an electron gun $K_0 - A_0 - A_1$ that formed a parallel electron beam with a 0.5 eV spread, plane electrodes A_2 and A_3 , cylindrical electrodes B_1 and B_2 , and an electron collector EC. The electron emitter was an indirectly heated oxide ribbon cathode. The technology involved in constructing this apparatus was fairly complex, and included the careful grinding and polishing of parts as well as their high-temperature outgassing in a good vacuum. The parts of the selector were assembled and adjusted precisely under a microscope.

The assembled electron monochromators were mounted on the metal inlets of a glass tube (when the measurements required filling of the entire tube volume with the atoms to be investigated), or on the corresponding flange of a metal tube (when intersecting atom and electron beams were employed). In both instances, radiation resulting from electron-atom collisions passed out of the collision chamber through sapphire windows that were transparent to a broad optical range of frequencies. The greatest vacuum in the tube was

10^{-6} mm Hg. The electron energy in the collision region was measured within 0.025 eV. The monochromators furnished electron beams with 0.05–0.1 eV energy half-width, with 0.1–0.3 μ A collector current in a broad energy range (0–50 eV).

Both spectral monochromators and light filters were employed in the optical system. The detectors were FÉU-18A, FÉU-64, FÉU-38, and FÉU-39 photomultipliers, and photon counters.

A series of control measurements showed that our electron monochromators possess better focusing properties than the earlier instruments^[5, 6] and permit doubling of the current strength with the same energy spread. The accelerating potential has practically no influence on the collector current strength or on the beam energy homogeneity within quite broad limits (with deflections not exceeding $\pm 7\%$). This means that no effects will be present as a result of changes in the electron density and energy spread.

It is interesting that the experimental electron energy spread at the monochromator outlet in a vacuum agrees well with a theoretical prediction.^[7] However, in the presence of a working gas or vapor the monokinetic quality is slightly impaired. For example, in mercury vapor at 10^{-3} mm the energy spread is 0.14 eV for 90% of

all electrons, while the half-width is about 0.12 eV.^[3]

EXPERIMENTAL RESULTS AND DISCUSSION

Using the described apparatus under very clean conditions we measured carefully the excitation functions of resonance and other spectral lines emitted by He, Zn, Cd, Hg, Na, and K. In all cases very small electron and atom concentrations were used in order to ensure single collisions.

The principal results are represented in the table and in Figs. 2–5, which show the dependences of the excitation cross sections Q for the lines (and for atomic ionization) on the electron beam energy. Because of the very low intensities of some lines or insufficient detector sensitivity the electron beam current was augmented, leading to a corresponding impairment of electron energy homogeneity. Therefore for each case the table indicates the electron inhomogeneity ΔE (for 90% of all electrons in the beam).

The most important result of our work was the detection of many well resolved excitation maxima near threshold. A comparison between the positions of these maxima and the excitation potentials of the energy levels shows that many of the maxi-

Atom level	λ , Å	E_{exc} , eV	ΔE , eV	Number of maxima	Positions of maxima, eV	E_{ion} , eV
Helium						24.59
3^3S_1	7065	22.72	0.5	3	23.4; 23.9; 26–28	
4^3S_1	4713	23.58	0.3	4	23.9; 24.2; 24.7; \sim 27	
3^3P_{012}	3889	23.00	0.3	4	23.4; 23.6; 23.9; 28–30	
3^3D_{123}	5876	23.07	0.3	3	23.4; 24.0; 26–29	
3^1D_2	6678	23.07	0.5	2	23.6; \sim 30	
Zinc						9.39
4^3P_1	3076	4.03	0.3	5	4.4; 6.9; 7.9; 8.5; \sim 11.5	
5^3S_1	4811	6.65	0.4	5	7.1; 7.8; 8.4; 9.5; \sim 12.5	
Cadmium						8.99
5^3P_1	3261	3.80	0.2	5	4.1; 6.3; 7.3; 8.1; \sim 12.3	
6^3S_1	5086	6.38	0.4	7	6.9; 7.5; 8.0; 8.6; 9.0; 9.3; \sim 12.3	
Mercury						10.44
6^3P_1	2537	4.89	0.10	10	5.0; 5.3; 5.6; 8.5; 9.0; 9.7; 10.0; 10.4; 11.2; 12.5	
7^3S_1	5461	7.73	0.15	8	8.2; 8.8; 9.0; 9.6; 10.2; 11.1; 11.9; \sim 12.5	
6^3D_3	3650	8.9	0.15	7	9.1; 9.8; 10.2; 11.1; 11.7; \sim 12.2; 12.6	
8^1S_0	4916	9.2	0.25	5	9.5; 10.2; 11.4; 11.9; 12.4	
Sodium						5.14
$3^2P_{1/2,3/2}$	5890/96	2.10	0.25	4	2.4; 2.8; 3.5; 6–7	
Potassium						4.34
$4^2P_{1/2,3/2}$	7665/98	1.61–1.62	0.4	3	2.1; 4.0; 10–12	
$5^2P_{1/2,3/2}$	4044/47	3.06	0.4	4	3.7; 4.2; 4.8; \sim 5.5	

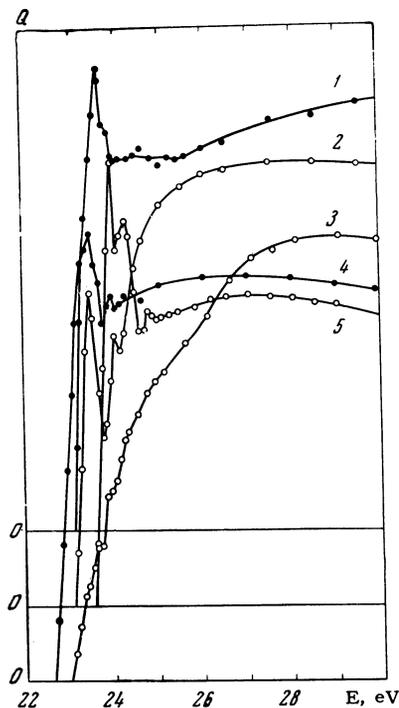


FIG. 2. Excitation cross sections of helium lines vs. electron energy. 1— $\lambda = 6678 \text{ \AA}$, 2— 5876 \AA , 3— 3889 \AA , 4— 7065 \AA , 5— 4713 \AA .

ma result from electronic excitation out of the normal state to higher-lying levels than the initial levels for any given lines. On the other hand, some maxima are definitely associated with direct excitation of the upper levels associated with observed lines (see the table).

Another important result, which is of special interest for the theory of electron-atom collisions, is the observance of very narrow "resonance" maxima. These characterize specifically the excitation of the 4^3S_1 and 3^3D_{123} helium levels, the 6^3P_1 , 7^3P_{012} , and 5^3F_{234} mercury levels, and the $5^2P_{1/2}$ $3/2$ potassium levels. The narrowest maximum was observed at the excitation threshold of the mercury resonance line.¹⁾ Here the instrumental half-width $\Delta \mathcal{E}_{1/2}$ of about 0.1 eV coincides with the energy spread ΔE of the electron beam. The figures show that this agreement between $\Delta \mathcal{E}_2$ and ΔE also occurs for the other aforementioned maxima. It follows that these maxima would be even narrower if very highly monochromatic electron beams were used. It can therefore be affirmed that the excitation of some levels, at least, by electron impact is actually of resonance character.

It must be emphasized that our observed "resonances" near the excitation thresholds of the

¹⁾It should be noted that similar "resonances" are observed in the total cross section for electron scattering from Hg atoms.^[6]

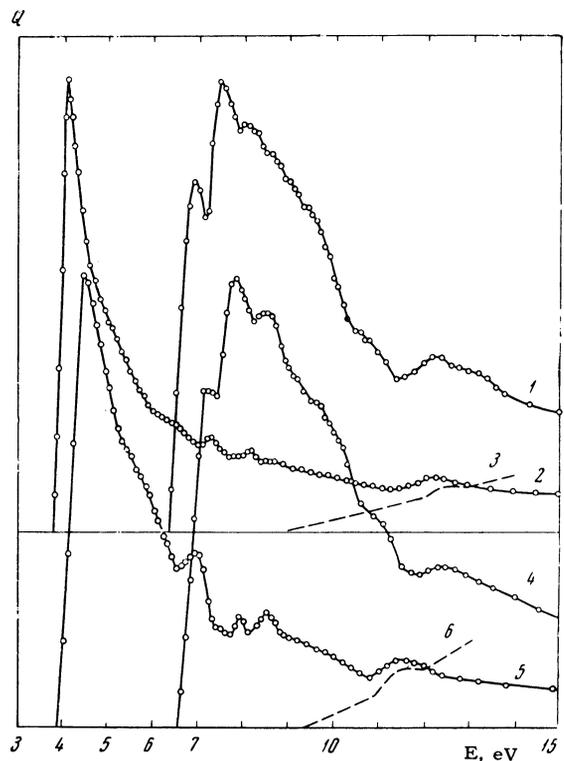


FIG. 3. Excitation cross sections vs. electron energy. Cadmium lines: 1— $\lambda = 5086 \text{ \AA}$, 2— 3261 \AA ; zinc lines: 4— 4811 \AA , 5— 3076 \AA . Curves 3 and 6 represent the ionization cross sections of cadmium and zinc, respectively.

4^3S_1 and 3^3S_1 helium levels are well consistent with a similar maximum for the lowest metastable 2^3S_1 level, which was observed by Schulz and Philbrick,^[2] who investigated helium excitation electrically (using a double analyzer). We suggest that the narrow excitation maxima, especially in the

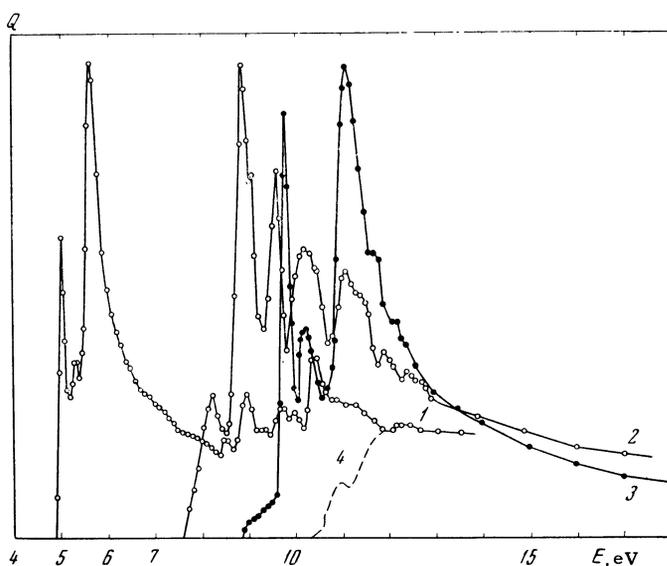


FIG. 4. Excitation cross sections of mercury vs. electron energy. 1— $\lambda = 2537 \text{ \AA}$, 2— 5461 \AA , 3— 3650 \AA ; 4—ionization cross section of mercury.

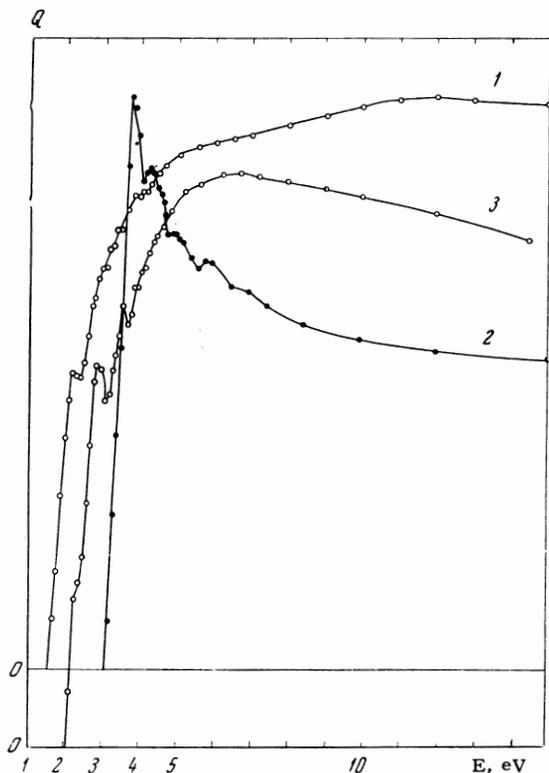


FIG. 5. Excitation cross sections vs. electron energy. Potassium lines: 1— $\lambda = 7665\text{-}7698 \text{ \AA}$, 2— $4044\text{-}4047 \text{ \AA}$; sodium lines: 3— $5890\text{-}5896 \text{ \AA}$.

cases of such levels as mercury 6^3P_1 and helium 3^3D_{123} , can serve as an objective criterion of the experimental electron-beam energy homogeneity and can be used as reference points for calibrating the energy scale.

We shall now examine the results for mercury, cadmium, and zinc more thoroughly. The first three maxima on the excitation curve of the 2537 \AA mercury resonance line (Fig. 4) undoubtedly reflect the complex excitation character of the upper 6^3P_1 level. While the first of these maxima, as already stated, represents resonant excitation of this level at threshold, the third maximum results possibly from a quantum-mechanical interaction between the resonant level and the metastable 6^3P_2 level. Some confirmation of this hypothesis may lie in the fact that the separation of the first and third maxima agrees exactly with the difference between the excitation potentials of the 6^3P_1 and 6^3P_2 levels. The remaining maxima on this curve up to the ionization energy E_{ion} represent cascades from the 3^3S_1 and 3^3D_{123} levels.

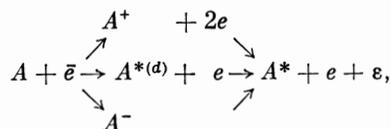
The maxima of the 5461 \AA excitation curve can be interpreted uniquely through a comparison with suitable mercury levels. The first maximum corresponds to the direct excitation of 7^3S_1 , and the second, third, and fourth maxima to the excitation of 7^3P_{012} , 8^3P_{012} , and a group of unresolved n^3P_{012}

($n \geq 9$) levels, respectively. A similar treatment of the 3650 \AA line shows that the weak threshold maximum corresponds to excitation of its upper level; the second, sharp, maximum corresponds to excitation of 8^3P_{012} and 5^3F_{234} ; the third maximum corresponds to excitation of unresolved levels n^3P_{012} ($n \geq 9$) and n^3F_{234} ($n \geq 6$).

The origins of the curve maxima from the levels 4^3P_1 and 5^3S_1 of zinc, and from 5^3P_1 and 6^3S_1 of cadmium (up to E_{ion}) are analogous to those from 6^3P_1 and 7^3S_1 of mercury. The finding that the principal maxima on the resonance-line excitation curves of these atoms are not split is attributed to the fact that the difference between the resonant and metastable levels is considerably smaller than the energy spread of the utilized electron beams.

We shall now discuss briefly the maxima lying above the ionization threshold. Figures 3 and 4 as well as the table show that different lines of a single given element exhibit maxima at approximately the same electron energy, and that these also coincide (taking ΔE into account) with the maxima of the ionization functions^[9] (the dashed curves in Figs. 3 and 4). This indicates, in any event, that the corresponding maxima in the two inelastic types of events may have a common basis.

We propose the following reaction scheme for electron-atom collisions resulting in the excitation of an atomic state A^* when $E \geq E_{ion}$:



where ϵ represents energy.

All three intermediate states with the participation of a positive ion,^[10] an atom excited through a d-electron transition (Beutler levels),^[11] and a negative ion^[8] are actually observed. Since the probabilities of these processes are unknown, it is difficult to determine which of the three competing processes is dominant in populating a given excited atomic state.

It must be noted, in conclusion, that the optical method of investigating atomic excitation by monoenergetic electrons yields a considerably larger amount of information than the electrical method. This information pertains to both the initial levels for emitted lines and a large number of higher-lying levels in a given atom.

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112