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Fig. 1

Figure 1: Fig. 1

Abstract

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ON THE RESONANT CHARACTER OF THE EXCITATION OF MERCURY ATOMS IN COLLISIONS WITH SLOW ELECTRONS

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The experimental study of the excitation of atoms has hitherto been carried out with inhomogeneous electron beams. Only in some cases was the spread of electron energies narrowed to 0.6—0.5 eV (1—4). In the work of one of the authors (5) it was clearly shown how sharply the form of the excitation function of lines changes as the interval of electron inhomogeneity is narrowed from 3.5 to 0.5 eV. Therefore, the search for new possibilities for increasing the monochromatization of electron beams and the undertaking of more refined investigations of the processes of atomic excitation by monoenergetic electrons are highly timely.

At present, in our laboratory a device has been developed that makes it possible to form stable ribbon electron beams for which more than 90% of all electrons in vacuum ($\sim 10^{-6}$ mm Hg) have velocities lying in the interval 0.10—0.05 eV, while the electron energy is varied in the range from 0 to 40 eV*. In this case the intensity of the electrons in the beam is $i = 0.1$—$0.3\ \mu$A. Recently we have carried out a large series of refined experiments on the study of the excitation of spectral lines of mercury, sodium, and helium atoms by such monoenergetic beams.

Fig. 1

In the present note we set out the results of investigating the excitation functions of certain lines of mercury atoms. These measurements were performed using different versions of the device for obtaining a monoenergetic electron beam at current densities in the beam of $0.3 \cdot 10^{-5}$—$1 \cdot 10^{-5}$ A/cm^2 and vapor pressures of $6 \cdot 10^{-4}$—$1.5 \cdot 10^{-3}$ mm ($2 \cdot 10^{13}$—$5 \cdot 10^{13}$ atoms/cm^3). In all cases good reproducibility of the results was observed. The error in measuring the electron energy E_e in our experiments was ±0.05 eV, and in determining the photocurrent I, proportional to the intensity of the measured line, 2—3%.

The distribution of electrons in the beam by velocities in mercury vapor at a pressure of $1 \cdot 10^{-3}$ mm, obtained by the retarding-field method, is shown in Fig. 1. As can be seen, the half-width of the distribution function is 0.12 eV, and 90% of all electrons fall within an interval of only 0.14 eV.

The results obtained are presented in Figs. 2, 3, and 4. Table 1 gives the number and positions of the maxima of the observed fine structure, as well as the excitation potentials of certain levels of the mercury atom.

As can be seen from the graphs, a high resolution of the fine-structure maxima on the excitation functions of these lines has been achieved**. Characteristically there is the presence of very narrow maxima, for example the first maxima on the lines $\lambda\lambda$ 2537; 3650, 4916 Å, as well as the second and third on the line λ 5461 Å. Their half-width is close to the magnitude of the inhomogeneity interval of the electron beams used. Therefore one may suppose that, for ideal monochromaticity of the exciting electrons, these maxima should become extremely narrow. This directly indicates the resonant character of the excitation of certain energy levels of the mercury atom.

Table 1

λ, Å and transition	Number of max.	Position of maxima, eV	Excitation potentials of levels, V
25376^1S_0—6^3P_1	10	5.0	4.89 (6^3P_1)
25376^1S_0—6^3P_1	10	5.3	–
25376^1S_0—6^3P_1	10	5.6	5.46 (6^3P_2)
25376^1S_0—6^3P_1	10	8.5	–
25376^1S_0—6^3P_1	10	9.0	8.62—8.83 (7^3P_J); 8.85 (6^1D_2)
25376^1S_0—6^3P_1	10	9.7	9.45 (8^3P_J); 9.58 (5^3F_J)
25376^1S_0—6^3P_1	10	10.0	9.82 (9^3P_J), 9.86 (6^3F_J)
25376^1S_0—6^3P_1	10	10.4	–
25376^1S_0—6^3P_1	10	~ 11.2	–
25376^1S_0—6^3P_1	10	~ 12.5	–
36506^3P_2—6^3D_3	7	9.1 (?)	8.86 (6^3D_3)
36506^3P_2—6^3D_3	7	9.8	9.45 (8^3P_J); 9.58 (5^3F_J)
36506^3P_2—6^3D_3	7	10.2	9.82(9^3P_J); 9.86(6^3F_J); 10.03 (7^3F_J)
36506^3P_2—6^3D_3	7	11.1	–
36506^3P_2—6^3D_3	7	~ 11.7	–

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* Brief information on the apparatus and measurement procedure is given in ([6,7]).

** The observed shift of the maxima is, at least in part, due to the finite energy resolution of the instrument. The fact is that in the graphs the actual onset of excitation is compared with the excitation potential of the initial level.

λ, Å and transition	Number of max.	Position of maxima, eV	Excitation potentials of levels, V
36506$^3P_2$—6^3D_3	7	~ 12.2	–
36506$^3P_2$—6^3D_3	7	~ 12.6	–
54616$^3P_2$—7^3S_1	10	8.2	7.73 (7^3S_1)
54616$^3P_2$—7^3S_1	10	8.8	8.62—8.64 (7^3P_{01})
54616$^3P_2$—7^3S_1	10	9.0	8.83 (7^3P_2)
54616$^3P_2$—7^3S_1	10	9.6	9.45 (8^3P_J)
54616$^3P_2$—7^3S_1	10	10.2	9.82 (9^3P_J) and others
54616$^3P_2$—7^3S_1	10	10.4 (?)	9.82 (9^3P_J) and others
54616$^3P_2$—7^3S_1	10	11.1	–
54616$^3P_2$—7^3S_1	10	11.4 (?)	–
54616$^3P_2$—7^3S_1	10	11.9	–
54616$^3P_2$—7^3S_1	10	~ 12.5	–
49166$^1P_1$—8^1S_0	6	9.5	9.20 (8^1S_0)
49166$^1P_1$—8^1S_0	6	10.2	9.78 (8^1P_1); 9.89 (9^1P_1) and others
49166$^1P_1$—8^1S_0	6	~ 10.5 (?)	–
49166$^1P_1$—8^1S_0	6	11.4	–
49166$^1P_1$—8^1S_0	6	11.9	–
49166$^1P_1$—8^1S_0	6	~ 12.4	–

Another important feature of almost all the curves obtained is the presence of a distinct maximum lying just beyond the ionization potential of the mercury atom ($V_i = 10.44$ V).

Let us now examine the fine structure in more detail.

λ 2537 Å. The first high and narrow maximum on the excitation function of this line lies only 0.1 eV above the excitation potential of its upper level. This line was studied under the most favorable conditions, in which the electron-energy spread $\Delta\mathcal{E}$ was 0.08–0.1 eV for 75% of all electrons in the beam. Therefore it may be considered that, in reality, this maximum is still narrower and lies directly at the threshold for excitation of the line. Consequently, the first maximum reflects the resonant character of the excitation of the upper level of the 6^3P_1 line.

The main principal maximum of this line is located 0.6 eV farther than the first. Its half-width (~ 0.5 eV) is considerably larger than the interval of inhomogeneity of the electron beam. Therefore one may suppose that in form it is close to the true one, which should be observed for ideal homogeneity of the electron beam. The distance of 0.6 eV, within the experimental error, exactly corresponds to the difference in the energy levels of mercury 6^3P_1 and 6^3P_2.

Fig. 2. Excitation functions of the lines: 1—λ5461 Å, 2—λ2537 Å. Fig. 3. Excitation function of the line λ3650 Å.

Figure 2: Fig. 2. Excitation functions of the lines: 1—λ5461 Å, 2—λ2537 Å. Fig. 3. Excitation function of the line λ3650 Å.

Taking into account also the fundamental impossibility of cascade transitions to the 6^3P_1 level at electron energies up to 7.7 eV, the reason for the appearance of this maximum can be sought only in the existence of the metastable level 6^3P_2. Excited mercury atoms in this state begin to arise when the electron energy reaches 5.46 eV. As is known ([8]), in collisions of normal mercury atoms with metastable ones the level 6^3P_1 is excited with considerable probability, the transition to it from the 6^3P_2 level being accompanied by the release of 0.57 eV of energy. Thus, responsible for the main maximum is the excitation by electrons of metastable states of the mercury atom 6^3P_2, which,

therefore give the largest contribution to the excitation of the resonance line λ2537 Å.

There is no unambiguous explanation for the weakly expressed intermediate maximum at $E_\mathrm{e} = 5.3$ eV. It is possible that it arises, in accordance with the predictions of the authors of some theoretical works ([9]), at electron energies somewhat smaller than the excitation energy of the next level 6^3P_2.

Fig. 2. Excitation functions of the lines:
1—λ5461 Å, 2—λ2537 Å

Fig. 3. Excitation function of the line
λ3650 Å

A group of comparatively small and indistinctly expressed maxima in the region 8.5-12.5 eV is apparently due only in part to cascade transitions from the levels n^3S_1 and n^3D_J.*

λ5461 Å. The first maximum in the excitation function of this line is undoubtedly connected with direct excitation by electrons of its upper level 7^3S_1. However, since its peak is located only 0.5 eV beyond the excitation potential of the line (although, in measuring this line, $\Delta\mathcal{E} = 0.15$ eV), it cannot lie immediately at the threshold of the 7^3S_1 level.**

The second, third, and fourth maxima correspond, to an accuracy of 0.15-0.20 eV (see Table 1), to the excitation potentials of the levels n^3P_{012}. This gives us grounds to consider unequivocally that the appearance of these maxima is due to cascade transitions from 7^3P_{012}, 8^3P_J, and the group of unresolved levels n^3P_J $(n \geq 9)$.***

The incipient resolution of the second maximum into two (with a separation between the peaks of 0.2 eV) corresponds exactly to the difference between the almost merging levels 7^3P_{01} and the level 7^3P_2.

Fig. 4. Excitation function of the line $\lambda 4916$ Å

Figure 3: Fig. 4. Excitation function of the line $\lambda 4916$ Å

The last of the five well-resolved maxima lies entirely beyond the ionization potential and therefore cannot be associated with any cascade transitions.

$\lambda 3650$ Å. For this line no maximum near the excitation threshold is observed, possibly because here $\Delta\mathcal{E} = 0.15$ eV. The first very a significant and narrow maximum corresponds to the cascade transition from the 5^3F_J levels (and possibly also from the 8^3P_J levels). The second maximum also arises as a result of cascade transitions from the following n^3F_J levels ($n \geqslant 6$). This is supported by the fact that the distance between these maxima exactly corresponds to the difference in the excitation potentials of the indicated ^3F_J levels. The largest and broadest maximum of this line also lies beyond the ionization potential, $\lambda 4916$ Å. A very deep splitting of the maxima was also obtained in the excitation function of the singlet line $\lambda 4916$ Å, although the homogeneity of the electron beam in its measurements was somewhat worse ($\Delta\mathcal{E} = 0.25$ eV). The first maximum on the curve, within this spread, corresponds to excitation of the upper level of the 8^1S_0 line. The second large maximum is 0.7 eV farther from the first and, to an accuracy of 0.1 eV, corresponds to excitation of the line through a cascade transition from the group of levels n^1P_1 ($n \geqslant 8$). The third maximum is already located entirely beyond the ionization potential.

Fig. 4. Excitation function of the line $\lambda 4916$ Å

In the excitation functions of at least the last three lines, as already noted above, there are maxima located entirely (including their initial portions) outside the region up to the ionization potential. Therefore they cannot be associated with excitation of any discrete level or group of levels of the mercury atom.

A considerable contribution to the radiation of the lines under consideration, corresponding to these maxima, is most probably due to recombination radiation. It is clearly seen from the figures that the higher the initial level of the line, the greater the relative contribution of recombination transitions. For the resonance line, the contribution of these transitions does not make up a substantial fraction of its total radiation (see the footnote on p. 1055). All this

* The noticeable maximum in the excitation function of $\lambda 2537$ Å, lying at $E_e = 10.4$ eV, appears, apparently, because of the superposition of the nearby line $\lambda 2535$ Å (6^3P_0—7^3D_1).

** It is not excluded that in reality there may be one more very narrow maximum on the curve for this line immediately at its threshold.

*** This fully confirms the conclusion about the role of cascade transitions from the levels n^3P_j, made earlier in work (^{10}).

evidently indicates a high probability of recombination of Hg^+ mercury ions and very slow electrons arising in electron collisions.

In connection with this, it appears necessary to reconsider the established point of view on the excitation of spectral lines (^{11}), especially from highly excited levels, and to take into account, in addition to direct excitation by electrons and excitation through cascade transitions, also the population of levels due to electron-ion recombination.

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