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I. P. Zapesochnyi and V. S. Shevera

On the Fine Structure of the Excitation Functions of Certain Cadmium Lines

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K. Larche investigated the optical excitation functions of cadmium atoms by the photographic method (^1). The main results of his measurements amount to the fact that the excitation functions of all the lines he studied have one more or less sharply expressed maximum. He did not detect any secondary maxima in the optical excitation functions of cadmium. However, the establishment of a fine structure in the optical excitation functions of mercury (^2-4) gives grounds for assuming its existence also for the related elements cadmium and zinc. To clarify this question, new, more refined experiments were undertaken to study the excitation functions of these elements.

By the present time we have carried out measurements with cadmium lines in the visible and ultraviolet regions of the spectrum. The results obtained give grounds for asserting that the excitation functions of many cadmium lines do indeed have a fine structure.

In the present note the results are presented for the excitation functions of the resonance line λ3261 Å and of the lines of the visible triplet of cadmium $\lambda\lambda$4687, 4800, and 5086 Å, with which the most thorough investigations were carried out.

The measurements were performed on an apparatus consisting of an excitation tube with a window transmitting ultraviolet rays down to 2900 Å, a monochromator, and a device recording the radiation (a photomultiplier with an amplifier). The experimental setup is described in detail in our paper (^5). We add only that, unlike mercury, heating the tube with cadmium vapor to a temperature of 300° created additional difficulties in carrying out the experiments. The studies were further complicated by the fact that the energy levels of cadmium are more closely spaced than those of mercury.

Most of the measurements with the indicated lines were made on two excitation tubes with different geometries of the electrode systems and under conditions in which factors substantially distorting the true course of the excitation functions were completely eliminated. The investigations were carried out at cadmium-vapor pressures of $0.9 \cdot 10^{-3}$–$8 \cdot 10^{-3}$ mm Hg, electron-current densities of less than $1 \cdot 10^{-4}$ A/cm^2, and a width of the electron energy inhomogeneity of 1.0–0.6 eV. Within the limits of observational error, the measurements on both

Fig. 1

Figure 1: Fig. 1

tubes gave coincident curves.

Figure 1 shows the excitation function obtained by us for one of the lines of the visible triplet, λ5086 Å. The two other components of the triplet (as having the common upper level 6^3S_1) behave in a completely analogous manner. As can be seen from the figure, the experimental curve has 5 resolved maxima; their positions are given in Table 1.

The excitation function of the resonance intercombination line λ3261 Å is shown in Fig. 2. It has a more complex, although less clearly expressed, structure, consisting of 9 maxima; the corresponding electron energies are also given in Table 1.

Table 1

λ, Å	Transition	V_{exc}, V	Number of maxima	Electron energy corresponding to the observed maxima, eV
467848005086	5^3P_0—6^3S_1 5^3P_1—6^3S_1 5^3P_2—6^3S_1	7.35	5	7.3; 7.8; 8.5; 9.5; 12.2–12.4
3961	5^1S_0—5^3P_1	3.78	6	4.6; 5.7; 6.6; 7.2; 7.8; 8.6; 9.5; 10.4; 12.2–12.4

All these maxima in the excitation functions were detected only because it proved possible to obtain the necessary monoenergeticity of the exciting electrons at a considerable temperature in the tube. As the curves shown above in Fig. 1 indicate, more than 90% of the electrons in the beam had a velocity spread within 0.6 eV. Even a slight deterioration of the monoenergeticity of the beam in comparison with this value already leads to a blurring of weakly expressed maxima.*

Fig. 1 –excitation function of the line λ 5086 Å. The dashed lines show the excitation functions of the levels: 2 –6^3S_1, 3 –6^3P_{012}, 4 –7^3P_{012}, 5 –groups n^3P_{012} ($n \geq 8$); 6 –contribution of recombination radiation. At the top –

Fig. 2

Figure 2: Fig. 2

dependence of the current strength i in the beam on the retarding potential V_3 and its differential curve.

The occurrence of fine structure in the excitation functions of the indicated lines can be associated with cascade transitions. It was shown earlier ([2], [3]) that, when all secondary processes leading to excitation of a given atomic level are eliminated, the intensity of the line in the general case is not proportional to the effective cross section of the upper level and is related to it by the expression:

$$I_{ml}(V) = C\left[n_0 Q_{om}(V)N(V) + \sum_{i=m+1}^{\infty} A_{im}n_i\right],$$

where n_0 is the number of normal atoms; $N(V)$ is the number of electrons with the specified energy; $Q_{om}(V)$ is the excitation function of the m-level; n_i is the number of exc–

* On the role of monoenergeticity of the electron beam in studies of optical excitation functions, see ([3]).

excited atoms; A_{im} is the probability of a spontaneous transition; C is a proportionality coefficient. The first term in the square brackets gives the fraction of excited atoms arising as a result of direct collisions of electrons with normal atoms, and the second gives the fraction of excited atoms due to cascade transitions from higher i-levels to the upper m-level of the line. In the case when $A_{im}n_i \to 0$ for all i, we obtain $Q_{0m}(V) \sim I_{ml}(V)$, i.e., the excitation function of the level coincides with the excitation function of the line; otherwise there is no coincidence.

In accordance with what has been said, the fine structure of the excitation function of the line λ5086 Å can be unambiguously explained as follows. Only transitions from the n^3P_1-levels to the upper level of this line, 6^3S_1, will be significant; the remaining transitions (from singlet $^1P_1$-levels) are unlikely. Then, on the basis of Table 2, where the excitation potentials of the levels and the maxima on the experimental curve are compared, it becomes clear to which cascade transition a given maximum should be assigned.

Fig. 2. 1 –excitation function of the line λ3261 Å. 2 –excitation function of the line λ4800 Å, and 3 –its representation on a curvilinear abscissa axis

The first peak on the curve at $V = 7.3$ eV corresponds to the maximum of the effective excitation cross section of the upper level 6^3S_1. As the electron energy increases, the curve should have fallen sharply. However, the cascade transitions from the level 6^3P_{012}, beginning at $V = 7.3$ eV, noticeably increase the concentration of excited atoms at the level 6^3S_1, as a result of which the

line intensity again rises in a step-like manner, forming a second peak at 7.8 eV, which corresponds to the maximum effective cross section of the nearby levels 6^3P_{012}. The third maximum at 8.5 eV is due to transitions from the levels 7^3P_{012}, and the fourth at 9.5 eV is due to the remaining closely spaced n^3P_{012}-levels ($n \geq 8$), occupying an interval of 0.53 eV*. The last maximum at 12.2-12.4 eV is not connected with cascade transitions. It appears on all the cadmium lines we investigated, including the resonance line λ3261 Å, and is possibly due to ionization and subsequent recombination.

Table 2

Energy levels of cadmium	Excitation potential of level V_{exc}	Maximum of fine structure V_{max}	Difference $V_{max} - V_{exc}$
6^3S_1	6.4	7.3	0.9
6^3P_{012}	7.3	7.8	0.5
7^3P_{012}	8.1	8.5	0.4
$n^3P_{012}(n \geq 8)$	8.4	9.5	1.1

Proceeding from the above, the experimental curve can be decomposed into components whose onsets coincide with the excitation potentials of the levels (6^3S_1 and n^3P_1), and whose peaks coincide with the corresponding maxima of the fine–

* It may be assumed that, with a further improvement in monochromaticity, this fourth maximum will be resolved into finer ones.

structure*. Such a decomposition is shown in Fig. 1 (dashed line). Curve 2 represents the excitation function of the 6^3S_1 level, and curves 3, 4, and 5 the excitation functions of the n^3P_1 levels. Thus, from a single precision curve–the optical excitation function of a line–we obtain information on the form of the excitation functions for several energy levels at once.

The question of interpreting the fine structure of the excitation function of the line λ3261 Å, which cannot be explained solely on the basis of the role of cascade transitions, is more complicated. For the upper level of this line, 5^3P_1, the most important transitions are those from the triplet levels 6^3S_1 (λ4800 Å) and 5^3D_{12} (λ3468/3466 Å). In Fig. 2, for comparison with the resonance line, the excitation function of λ4800 Å is plotted (curve 2). Curve 3 represents this same excitation function, but its ordinates have been referred to a curvilinear abscissa axis, approximately reproducing the general course of the excitation function of the line λ3261 Å in the interval from 6 to 18 eV. The obvious similarity of curve 3 to the experimental curve for λ3261 Å, and the almost complete coincidence of all its maxima with the corresponding maxima of the principal curve 1 in Fig. 2, is striking. This indicates a definite, though not very large, contribution of cascade transitions from the 6^3S_1 level to the emission of the line λ3261 Å. Consequently, the maxima in the excitation function of the resonance

line at 7.2, 7.8, 8.6, and 9.5 eV are explained by precisely these transitions. The maximum at 10.4 eV is caused by cascade transitions from the 5^3D_{12} levels. This is confirmed by the fact that the maximum in the excitation function of λ3468/3466 Å, also investigated by us, falls in this region (two of its other maxima lie at 8.5 and 9.5 eV).

Thus, cascade transitions are responsible for 5 maxima out of 9. The nature of the maximum at 12.2–12.4 eV has already been discussed above. As for the first 3 maxima (at 4.6, 5.7, and 6.6 eV), none of them can be explained by cascade transitions. Apparently, they belong to the excitation function of the 5^3P_1 level itself. Theoretical work recently carried out by V. I. Ochkur and I. M. Matora on calculating effective cross sections for certain levels of hydrogen and helium ([6],[7]) allows for such a possibility.

In conclusion it should be emphasized that the excitation functions of the corresponding lines and levels of cadmium and mercury have a definite similarity. This similarity extends to a considerable degree also to the character of the fine structure, in particular for the lines of the visible triplets of cadmium and mercury. However, there are also substantial differences. First, the excitation functions of the levels of mercury (for example, $^3S_1$ and $^3P_1$) are sharper, i.e., their maxima lie considerably closer to the excitation potential (by $1^{1/2}$–2 times) than on the excitation functions of the corresponding levels of cadmium. Second, the role of cascade transitions in the optical excitation functions of mercury is more significant. For example, if the contribution of transitions only from the 7^3P_{012} levels leads to an increase in the intensity of the mercury line λ5461 Å (6^3P_2—7^3S_1) by more than a factor of 2 ([3]), then the contribution of the analogous cascade transition from the 6^3P_{012} level to the intensity of the corresponding cadmium line λ5086 Å (see Fig. 1) amounts to only about 50%.

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Uzhgorod State University

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* With such a decomposition there is some arbitrariness in drawing the (higher or lower) almost horizontal sections of the curves, but it does not affect the form or position of the maxima of these curves.

Note: Figure translations are in progress. See original paper for figures.