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Emission cross sections for spectral lines transiting from the Cd II $4d^95s5p$ states and high-lying $4d^{10}nl$ states excited by single-electron impact on Cd atoms

T. Goto, K. Hane, and S. Hattori
Department of Electronics, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan
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Emission cross sections have been measured for about 60 lines from the $4d^95s\,5p$ inner-shell electron excited states and high-lying $4d^{10}nl$ excited states formed by single-electron impact in the electron-energy region of 10—200 eV using a photon-counting technique. Those for the lines from the $4d^95s\,5p$ states all show their maxima around 50 eV. Those for the lines from the $4d^{10}nl$ states reach their maxima between 40 and 70 eV, and the shapes of the optical excitation functions are somewhat different for various nl. The measured emission cross sections are of order of 10^{-19}—10^{-21} cm^2 in magnitude at 50 eV.

I. INTRODUCTION

Lines from low-lying excited states $4d^95s^2$ and $4d^{10}(5p,6s,5d)$ of Cd II are very strong, some of which are used as practical laser lines. Emission cross sections for those lines and direct excitation cross sections for those states excited by single-electron impact have been measured in our previous work.[1] In this paper, emission cross sections for many but weak lines from the $4d^95s5p$ and high-lying $4d^{10}nl$ states excited by single-electron impact are investigated.

For the lines from the $4d^95s5p$ and high-lying $4d^{10}nl$ states excited by single-electron impact, there are very few measurements of the emission cross sections[2–4]: for only two lines from the former and only nine lines from the latter. Moreover, the optical excitation functions for the corresponding lines in Refs. 2—4 are not in good agreement. This might have been caused by the following: Additional collision processes other than the single-collision process existed because those measurements were made at rather high Cd vapor pressures of 10^{-4}—10^{-2} Torr and it was difficult to know the zero level of each excitation function accurately when the detection system was not sensitive enough. The absolute values of the emission cross sections in Refs. 2—4 are also different from one another.

In this experiment, the emission cross sections for about 60 lines from the Cd II $4d^95s5p$ and high-lying $4d^{10}nl$ states formed by single-electron impact have been measured in the electron energy region of 10—200 eV under low Cd vapor pressures using a photon-counting system of high sensitivity.

II. EXPERIMENTAL METHODS

The experimental apparatus used here is almost the same as that in our previous work.[1] The details were described there. A Cd atom beam and an electron beam with an energy spread of about 1 eV were crossed in an excitation part which was placed in a vacuum chamber of 45 cm diameter evacuated up to 10^{-8} Torr. Cd atoms were excited to various Cd II states by single-electron impact and then emitted photons. Photons emitted from the collision volume were measured with the photon-counting technique. The control of the system and the data analysis were made by a minicomputer.

The emission cross section Q_{ij} for one Cd II line transiting from the state i to the state j was determined by measuring the ratio of the calibrated photon count rate of the line to that of the Cd II 274.9-nm line, the absolute emission cross section of which was determined to be 2.5×10^{-18} cm^2 with an uncertainty of $\pm24\%$ at the electron energy of 50 eV in our previous work.[1] The measurements were made for the lines between 190 and 800 nm in the electron energy region of 10—200 eV. They were made with and without a lens in the vacuum chamber between 200 and 800 nm and without the lens between 190 and 200 nm. Two kinds of photomultiplier tubes of low noises manufactured for the photon-counting technique were used for the measurements of the (190—550)-nm lines and the (550—800)-nm lines, respectively. The relative sensitivity of the optical detection system was calibrated with a tungsten and deuterium lamp. The uncertainty of this relative calibration was estimated to be $\pm3.5\%$ at 210—700 nm and $\pm5\%$ at 190—210 nm and 700—800 nm.

The above measurements were all carried out at the Cd vapor pressures of the order of 10^{-5} Torr. Under these conditions, it was confirmed that the signal count was proportional to the Cd vapor pressure and electron current, implying that only the single-collision process occurred dominantly.

III. RESULTS AND DISCUSSIONS

Tables I and II show the emission cross sections Q_{ij} for 22 lines from the $4d^95s5p$ inner-shell electron excited states and for 38 lines from the high-lying $4d^{10}nl$ states, respectively, measured at an electron energy of 50 eV. The ratios of these cross sections were independent of the Cd vapor pressure under our experimental conditions. The $\epsilon_{\rm rel}$ is the uncertainty of the relative value of Q_{ij} which was obtained by combining in quadrature those of the calibrated relative sensitivity of the detection system

TABLE I. Emission cross sections Q_{ij} for the lines from the $4d^9 5s5p$ states at the electron energy of 50 eV.

Transition	Wavelength (nm)	Q_{ij} (10^{-20}cm^2)	ϵ_{rel} (%)
$5s5p\ ^2D_{3/2}-5s^2\ ^2D_{3/2}$	220.9	2.3	8.5
$5s5p\ ^2D_{5/2}-5s^2\ ^2D_{3/2}$	215.5	9.0	7.2
$5s5p\ ^2D_{5/2}-5s^2\ ^2D_{5/2}$	192.2	21	10.0
$5s5p\ ^2D_{5/2}-5d\ ^2D_{5/2}$	318.0	0.3	10.0
$5s5p\ ^2F_{5/2}-5s^2\ ^2D_{3/2}$	237.7	6.8	5.3
$5s5p\ ^2F_{5/2}-5s^2\ ^2D_{5/2}$	209.6	23	5.5
$5s5p\ ^2F_{5/2}-5d\ ^2D_{3/2}$	366.7	1.5	5.4
$5s5p\ ^2F_{7/2}-5s^2\ ^2D_{5/2}$	199.5	35	4.2
$5s5p\ ^2F_{7/2}-5d\ ^2D_{5/2}$	338.6	8.5	5.8
$5s5p\ ^4P_{3/2}-5s^2\ ^2D_{3/2}$	289.4	0.4	9.5
$5s5p\ ^4P_{3/2}-5s^2\ ^2D_{5/2}$	248.8	1.6	17.0
$5s5p\ ^4P_{5/2}-5s^2\ ^2D_{5/2}$	270.7	35	4.0
$5s5p\ ^4D_{5/2}-5s^2\ ^2D_{3/2}$	249.6	5.3	10.0
$5s5p\ ^4D_{5/2}-5s^2\ ^2D_{5/2}$	218.8	35	4.0
$5s5p\ ^4D_{5/2}-5d\ ^2D_{3/2}$	395.7	0.6	10.0
$5s5p\ ^4D_{7/2}-5d\ ^2D_{5/2}$	400.7	6.3	4.7
$5s5p\ ^4F_{3/2}-6s\ ^2S_{1/2}$	335.5	1.2	6.5
$5s5p\ ^4F_{5/2}-5s^2\ ^2D_{3/2}$	283.4	5.8	5.5
$5s5p\ ^4F_{5/2}-5d\ ^2D_{3/2}$	488.2[a]	27	4.0
$5s5p\ ^4F_{5/2}-5d\ ^2D_{5/2}$	491.9	2.3	8.3
$5s5p\ ^4F_{7/2}-5s^2\ ^2D_{5/2}$	247.0	34	4.6
$5s5p\ ^4F_{7/2}-5d\ ^2D_{5/2}$	502.6[a]	9.0	5.0

[a]Laser oscillation was reported for these lines.

TABLE II. Emission cross sections Q_{ij} for the lines from the high-lying $4d^{10}nl$ states at the electron energy of 50 eV.

Transition	Wavelength (nm)	Q_{ij} (10^{-20} cm^2)	ϵ_{rel} (%)
$8s\ ^2S_{1/2}-6p\ ^2P_{1/2}$	428.5	1.5	6.0
$9s\ ^2S_{1/2}-6p\ ^2P_{1/2}$	344.2	0.6	6.3
$9s\ ^2S_{1/2}-6p\ ^2P_{3/2}$	352.4	2.1	10.0
$10s\ ^2S_{1/2}-6p\ ^2P_{3/2}$	314.7	1.0	6.9
$6p\ ^2P_{3/2}-6s\ ^2S_{1/2}$	806.7	75	9.5
$7p\ ^2P_{3/2}-6s\ ^2S_{1/2}$	338.9	1.1	10.0
$7p\ ^2P_{3/2}-5d\ ^2D_{3/2}$	438.5	1.0	6.1
$8p\ ^2P_{1/2}-5s^2\ ^2D_{3/2}$	218.6	3.8	9.6
$8p\ ^2P_{1/2}-5d\ ^2D_{3/2}$	323.2	0.6	7.8
$8p\ ^2P_{3/2}-5s^2\ ^2D_{3/2}$	218.2	1.3	20.0
$8p\ ^2P_{3/2}-5s^2\ ^2D_{5/2}$	194.3	12	9.4
$8p\ ^2P_{3/2}-5d\ ^2D_{3/2}$	322.3	0.6	7.8
$8p\ ^2P_{3/2}-5d\ ^2D_{5/2}$	323.9	1.1	6.5
$6d\ ^2D_{3/2}-6p\ ^2P_{1/2}$	646.5	11	6.8
$6p\ ^2D_{3/2}-6p\ ^2P_{3/2}$	675.9	1.6	40.0
$6d\ ^2D_{5/2}-6p\ ^2P_{3/2}$	672.6	18	6.0
$7d\ ^2D_{3/2}-6p\ ^2P_{1/2}$	402.9	3.8	5.5
$7d\ ^2D_{5/2}-6p\ ^2P_{3/2}$	413.5	6.5	5.8
$8d\ ^2D_{3/2}-6p\ ^2P_{1/2}$	334.3	1.8	5.5
$8d\ ^2D-6p\ ^2P_{3/2}$	341.8	4.0	6.7
$9d\ ^2D_{3/2}-6p\ ^2P_{1/2}$	303.1	0.9	6.7
$9d\ ^2D-6p\ ^2P_{3/2}$	309.3	2.5	6.2
$11d\ ^2D-6p\ ^2P_{3/2}$	279.9	0.9	9.2
$4f\ ^2F_{5/2}-5d\ ^2D_{3/2}$	533.7[a]	38	4.0
$4f\ ^2F_{5/2}-5d\ ^2D_{5/2}$	538.2	3.0	20.0
$4f\ ^2F_{7/2}-5d\ ^2D_{5/2}$	537.8[a]	55	4.0
$5f\ ^2F_{5/2}-5d\ ^2D_{5/2}$	348.3	0.8	8.5
$5f\ ^2F_{7/2}-5d\ ^2D_{5/2}$	349.5	13	4.5
$6f\ ^2F_{5/2}-5d\ ^2D_{3/2}$	291.5	3.8	5.8
$6f\ ^2F_{5/2}-6d\ ^2D_{3/2}$	723.7[a]	1.8	50.0
$6f\ ^2F_{7/2}-5d\ ^2D_{5/2}$	292.9	3.8	5.8
$6f\ ^2F_{7/2}-6d\ ^2D_{5/2}$	728.4[a]	3.9	20.0
$7f\ ^2F_{7/2}-5d\ ^2D_{5/2}$	267.3	1.0	6.7
$8f\ ^2F_{5/2}-5d\ ^2D_{3/2}$	251.6	0.3	24.0
$6g\ ^2G-4f\ ^2F_{5/2}$	635.5[a]	2.3	28.0
$6g\ ^2G-4f\ ^2F_{7/2}$	636.0[a]	3.8	18.0
$7g\ ^2G-4f\ ^2F$	527.0	3.8	6.7
$8g\ ^2G-4f\ ^2F$	474.3	3.0	12.0

[a]Laser oscillation was reported for these lines.

and the signal count S. In this paper, the uncertainty of S is defined as $2(N+S)^{1/2}/S$, where N is the noise count and $(N+S)^{1/2}$ is the standard deviation of the Poisson statistics of the total count $N+S$. The uncertainty of the absolute value of Q_{ij} is obtained by combining in quadrature ϵ_{rel} and the uncertainty ($\pm 24\%$) of the absolute emission cross section of the 274.9-nm line used as a reference. The ϵ_{rel} are somewhat large for the weak lines because it took a long time to reduce $(N+S)^{1/2}/S$, for the (190—200)-nm lines because the absorption by air weakened the signals and those lines were influenced by the contamination considerably more than longer lines were, and for the lines with closely adjacent lines because the narrow slit width of the monochromator had to be used. The values of Q_{ij} may include systematic uncertainties for the lines below 200 nm because of the difficulty of the calibration. The Cd II lines which the Cd I lines or unidentified lines appeared to overlap were not included in the tables even though they were relatively strong. On the other hand, in case the Cd III lines overlap the Cd II lines, their influence is negligible at the electron energy of 50 eV because the thresholds for excitation of most of the strong Cd III lines by single-electron impact are above 45 eV.

It is seen from Table I that Q_{ij} are relatively large for many lines from the $4d^9 5s5p$ states to the $4d^9 5s$ states and three lines from the $4d^9 5s5p\ ^{2,4}F$ states to the $4d^{10} 5d\ ^2D$ states. The absolute values of them are of the order of 10^{-19} cm^2. The lines from the $5s5p\ ^2P$ states were measured but not included in the table because they could not be separated from others completely.

It is seen from Table II that Q_{ij} for the lines from the $4d^{10}nl$ states are different by nl and generally decrease with the principal quantum number n as expected. Although it is difficult to find some definite formula on the n dependence of Q_{ij} from only the present results, Q_{ij} appear to decrease roughly with n^{-5} and $n^{-7.5}$ for the lines from the nd and nf states, respectively. The absolute values of Q_{ij} are of order 10^{-19}—10^{-21} cm^2.

The emission cross sections as a function of electron energy have been measured for most lines listed in Tables I and II. The results obtained with the low uncertainties among them are summarized in Figs. 1—6.

Figures 1 and 2 show the results on the $4d^9 5s5p$ doublet and quartet states, respectively. The uncertainty of the shape of each optical excitation function is less than $\pm 4\%$ in the region of 30—200 eV. All Q_{ij} have maxima around 50 eV and then decrease. The optical excitation functions

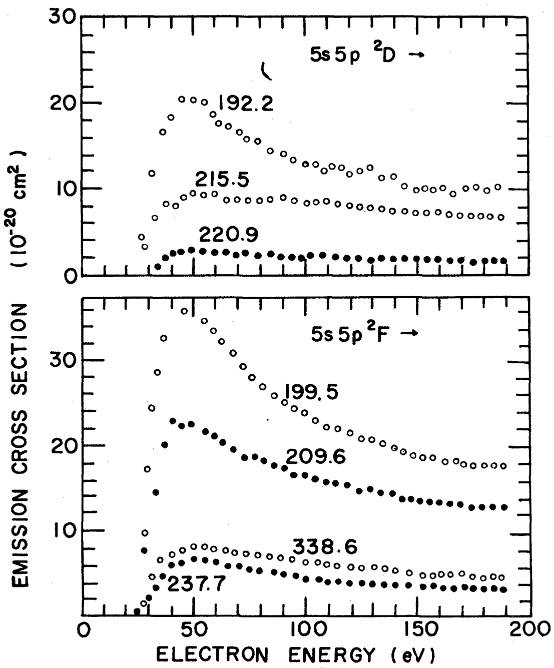

FIG. 1. Emission cross sections for the lines from the $4d^9 5s5p$ doublet states as a function of electron energy: 220.9 ($^2D_{3/2}$—$5s^2\,^2D_{3/2}$), 215.5 ($^2D_{5/2}$—$5s^2\,^2D_{3/2}$), 192.2 ($^2D_{5/2}$—$5s^2\,^2D_{5/2}$), 237.7 ($^2F_{5/2}$—$5s^2\,^2D_{3/2}$), 209.6 ($^2F_{5/2}$—$5s^2\,^2D_{5/2}$), 199.5 ($^2F_{7/2}$—$5s^2\,^2D_{5/2}$), and 338.6 ($^2F_{7/2}$—$5d^2\,^2D_{5/2}$).

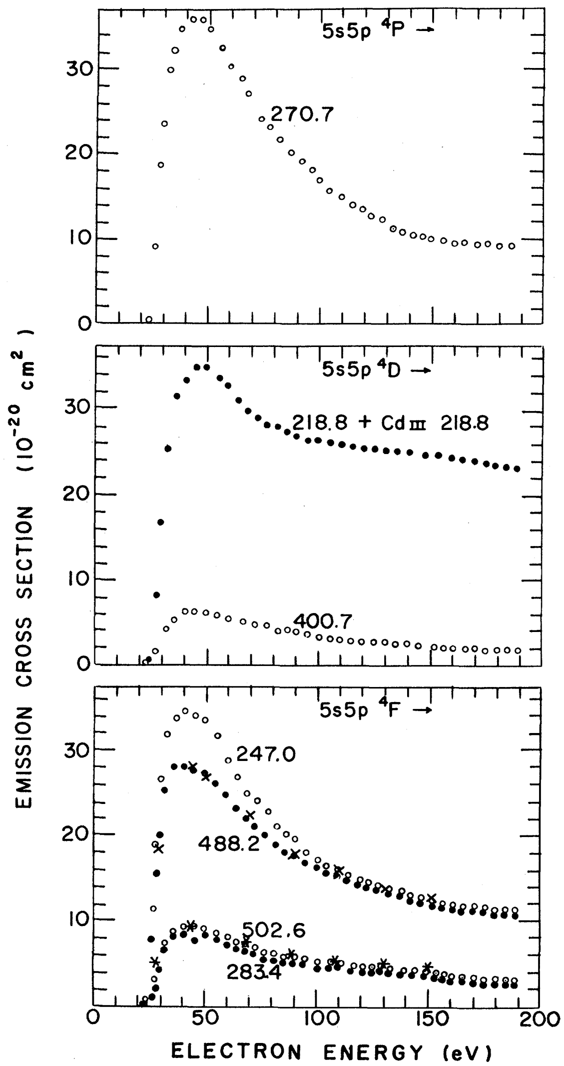

FIG. 2. Emission cross sections for the lines from the $4d^9 5s5p$ quartet states as a function of electron energy : 270.7 ($^4P_{5/2}$—$5s^2\,^2D_{5/2}$), 218.8 ($^4D_{5/2}$—$5s^2\,^2D_{5/2}$), 400.7 ($^4D_{7/2}$—$5d\,^2D_{5/2}$), 283.4 ($^4F_{5/2}$—$5s^2\,^2D_{3/2}$), 488.2 ($^4F_{5/2}$—$5d\,^2D_{3/2}$), 247.0 ($^4F_{7/2}$—$5s^2\,^2D_{5/2}$), and 502.6 ($^4F_{7/2}$—$5d\,^2D_{5/2}$). ○ and ●, present measurement; × and ∗, Q_{ij} obtained by multiplying the emission cross sections for the 488.2 and 502.6-nm lines in Ref. 4 by a factor of 1.6, respectively.

for the measured doublet lines are similar and decrease to about 60% of the peak values at 190 eV. Those for the measured quartet lines except for the 218.8-nm line are similar and decrease to about 35% of the peak values at 190 eV. For the 218.8-nm line, since the nonseparable Cd III 218.8-nm line becomes appreciable above 90 eV, the optical excitation function possibly does not decrease in that region. If the Cd III line is separated, it is expected that the optical excitation function for the 218.8-nm line is similar to that for other quartet lines. It is to be noted that the shapes of these optical excitation functions are very different from those for the 441.6-, 325.0-, and 353.5-nm lines from the $4d^9 5s^2$ inner-shell electron excited states which reach maxima around 90 eV and then are almost constant.[1,3–5] It would be expected that the $4d^9 5s5p$ states are formed by ionization of one electron and excitation of another electron while the $4d^9 5s^2$ states are formed almost exclusively by the removal of a single inner-shell electron (one of the $4d^{10}$ electrons). Then the cross sections for the $4d^9 5s^2$ states should be those normally ascribed to ionization and are rather larger in magnitude than those for the $4d^9 5s5p$ states and different in shape from those for the $4d^9 5s5p$ states.

Figures 3—6 show the results on the $4d^{10}nl$ states. The uncertainty of the shape of each optical excitation function is less than ±6% for most lines and less than ±8% for several weak lines in the region of 30—200 eV. They reach maxima at 40—70 eV. The position of the maximum tends to shift to the higher electron energy for the line from the higher state. The optical excitation functions are similar for the lines of the identical nl but different for those of the different nl. After passing the maxima, they tend to decrease more slowly for the lines of the larger n at the same l and for the lines of the smaller l at the same n. For example, the values of Q_{ij} at 190 eV decrease to about 25% of the peak values for the lines from the $4f$ states while the value of Q_{ij} is almost constant above 70 eV for the line from the $10s$ state.

Among the autoionization states, probably the $4d^9 5s^2 nl$ series are excited relatively easily since they are formed by one electron excitation from the Cd I ground state ($4d^{10}5s^2$). The ionization limits ($4d^9 5s^2$) of the $4d^9 5s^2 nl$

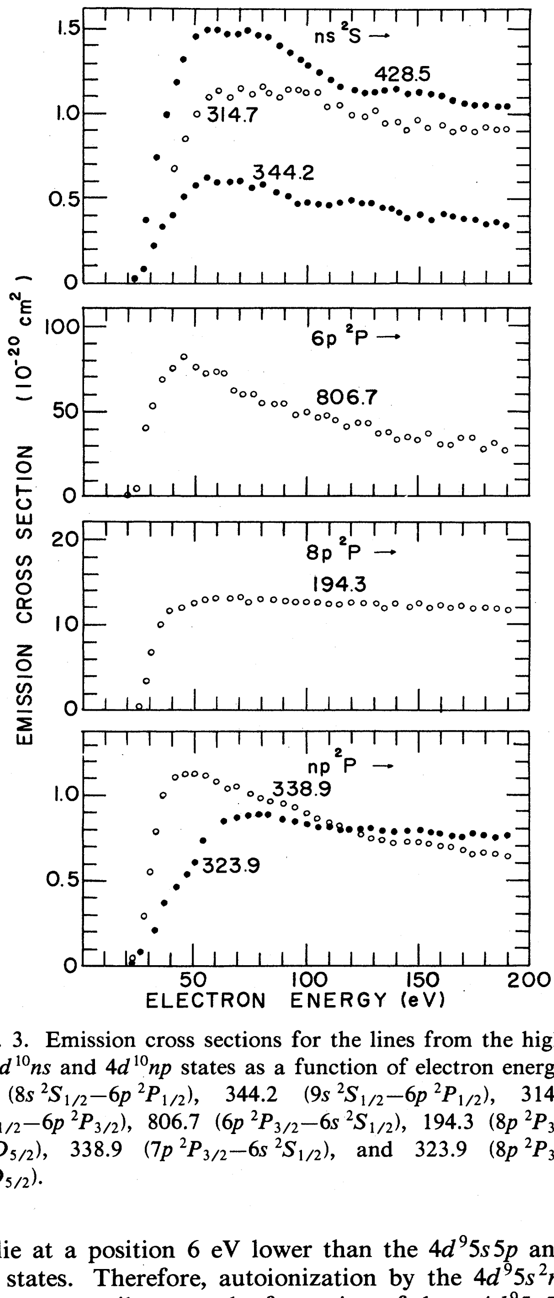

FIG. 3. Emission cross sections for the lines from the high-lying $4d^{10}ns$ and $4d^{10}np$ states as a function of electron energy: 428.5 ($8s\,^2S_{1/2}$–$6p\,^2P_{1/2}$), 344.2 ($9s\,^2S_{1/2}$–$6p\,^2P_{1/2}$), 314.7 ($10s\,^2S_{1/2}$–$6p\,^2P_{3/2}$), 806.7 ($6p\,^2P_{3/2}$–$6s\,^2S_{1/2}$), 194.3 ($8p\,^2P_{3/2}$–$5s^2\,^2D_{5/2}$), 338.9 ($7p\,^2P_{3/2}$–$6s\,^2S_{1/2}$), and 323.9 ($8p\,^2P_{3/2}$–$5d\,^2D_{5/2}$).

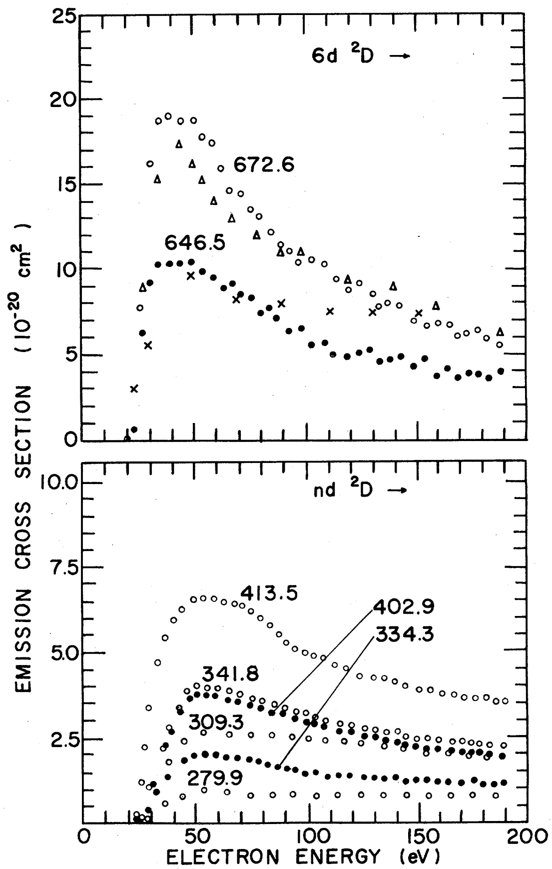

FIG. 4. Emission cross sections for the lines from the high-lying $4d^{10}nd$ states as a function of electron energy: 646.5 ($6d\,^2D_{3/2}$–$6p\,^2P_{1/2}$), 402.9 ($7d\,^2D_{3/2}$–$6p\,^2P_{1/2}$), 334.3 ($8d\,^2D_{3/2}$–$6p\,^2P_{1/2}$), 672.6 ($6d\,^2D_{5/2}$–$6p\,^2P_{3/2}$), 413.5 ($7d\,^2D_{5/2}$–$6p\,^2P_{3/2}$), 341.8 ($8d\,^2D$–$6p\,^2P_{3/2}$), 309.3 ($9d\,^2D$–$6p\,^2P_{3/2}$), and 279.9 ($11d\,^2D$–$6p\,^2P_{3/2}$). ○ and ●, present measurement; △, Q_{ij} obtained by multiplying the emission cross section for the 672.6-nm line in Ref. 2 by a factor of 1.6; and ×, Q_{ij} for the 646.5-nm line in Ref. 4.

series lie at a position 6 eV lower than the $4d^95s5p$ and $4d^{10}nl$ states. Therefore, autoionization by the $4d^95s^2nl$ series never contributes to the formation of those $4d^95s5p$ and $4d^{10}nl$ states. Moreover, since the accidental degeneracies do not happen in the Cd II states examined here, the nonradiative transitions do not occur. On the other hand, the mechanisms of the formation of some Cd II states[2] and the He II states[6] of electron configurations similar to Cd II states have been explained by direct two-electron transitions (ionization of one electron and excitation of another electron). From the above, we believe that the Cd II $4d^{10}nl$ and $4d^95s5p$ states are formed by the direct two-electron transitions and cascade from higher states.

It is for only the 488.2- and 502.6-nm lines on the $4d^95s5p$ states[4] and only nine lines in total on the high-lying $4d^{10}nl$ states[2–4] that Q_{ij} have been measured. Some of the cross sections reported by other investigators previously are shown in Figs. 2, 4, and 5 for comparison. The optical excitation functions obtained in Ref. 2 and at a Cd vapor pressure of 0.1 mTorr in Ref. 4 agree with the present ones qualitatively. Namely, they reach maxima around 50 eV and then decrease. However, in Ref. 3, the optical excitation functions for the 533.7- and 537.8-nm lines have maxima around 150 eV; this is possibly because the measurements were made at high Cd vapor pressures. Some additional processes become more important at higher metal vapor pressures, as demonstrated in Ref. 4. The ratios of Q_{ij} for the few lines obtained in Refs. 2 and 4 seem to be in relatively good agreement with the present ones. On the absolute values of Q_{ij}, the present result and those in Ref. 4 are close. In Ref. 4, the Q_{ij} for the 441.6-nm line from Ref. 5 was used as reference, and in the present experiment, the Q_{ij} for the 274.9-nm line from Ref. 1 was used as reference. In Refs. 1 and 5, the Cd atom densities were measured with the absorption method directly. On the other hand, Q_{ij} for some of the strongest lines in Ref. 2 are smaller by a factor of 3 or more and Q_{ij} in Ref. 3 are larger by 1 order of magnitude, compared

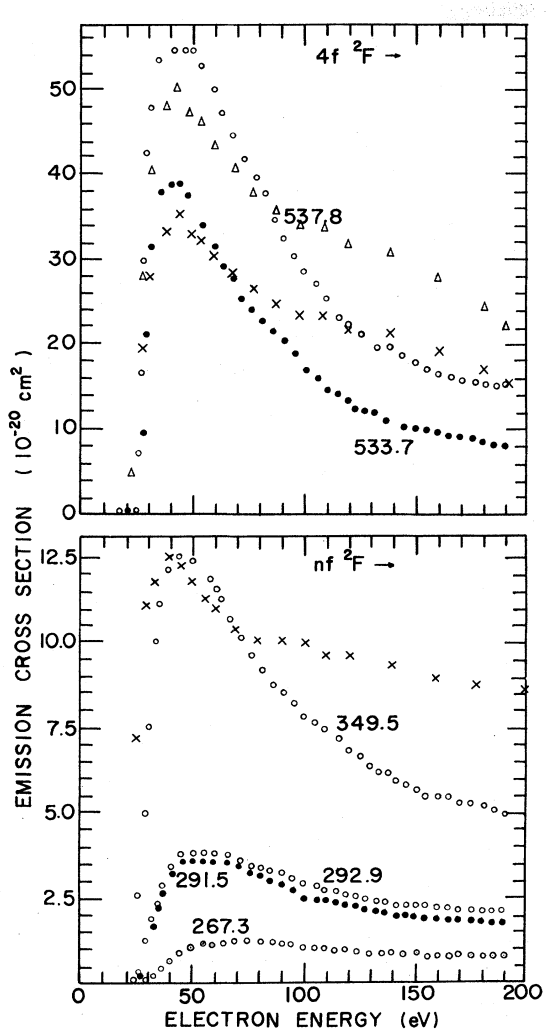

FIG. 5. Emission cross sections for lines from the high-lying $4d^{10}nf$ states as a function of electron energy: 533.7 ($4f\,^2F_{5/2}$–$5d\,^2D_{3/2}$), 291.5 ($6f\,^2F_{5/2}$–$5d\,^2D_{3/2}$), 537.8 ($4f\,^2F_{7/2}$–$5d\,^2D_{5/2}$), 349.5 ($5f\,^2F_{7/2}$–$5d\,^2D_{5/2}$), 292.9 ($6f\,^2F_{7/2}$–$5d\,^2D_{5/2}$), and 267.3 ($7f\,^2F_{7/2}$–$5d\,^2D_{5/2}$). ○ and ●, present measurement; △ and ×, Q_{ij} obtained by multiplying the emission cross sections for the 537.8- and 533.7-nm lines in Ref. 2 by a factor of 1.7, respectively; ×, Q_{ij} obtained by multiplying the emission cross section for the 349.5-nm line in Ref. 2 by a factor of 2.0.

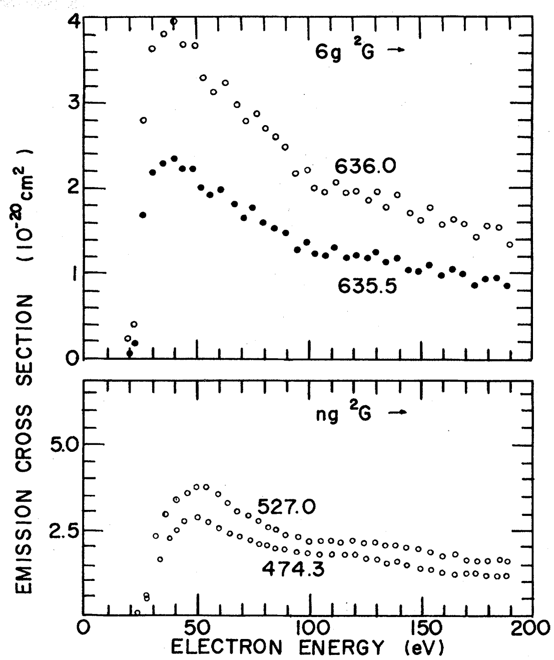

FIG. 6. Emission cross sections for the lines from the high-lying $4d^{10}ng$ states as a function of electron energy: 635.5 ($6g\,^2G$–$4f\,^2F_{5/2}$), 636.0 ($6g\,^2G$–$4f\,^2F_{7/2}$), 527.0 ($7g\,^2G$–$4f\,^2F$), and 474.3 ($8g\,^2G$–$4f\,^2F$).

with the present ones. In Refs. 2 and 3, the Cd atom densities were deduced from the temperatures of the metal containers, which may have resulted in unreliable density estimates.

It is difficult to obtain the direct excitation cross sections for the Cd II excited states using the present results because all appreciable cascade lines to them were not measured. However, the result of the emission cross sections for the eight laser lines (see the footnotes to I and II) could be sufficiently useful in estimating the contribution of the direct excitation process for the formation of the laser upper states in the hollow-cathode or positive-column He-Cd discharge roughly.

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