

Efficiency of associative ionization in cesium vapor as a function of the quantum state and thermal energy of the interacting atoms

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The rate constants $\langle \sigma_{ik} v_0 \rangle$ for associative ionization during the interaction between excited cesium atoms in nP and nD states, and atoms in the ground state, have been measured. It is shown that a reduction in the potential energy of the interacting atoms from 3.6 to 2.7 eV is accompanied by a reduction in $\langle \sigma_{ik} v_0 \rangle$ by four orders of magnitude (from 4×10^{-10} to 1.6×10^{-14} cm³·sec⁻¹). Measurements of $\langle \sigma_i k v_0 \rangle$ as a function of the energy of the interacting atoms have shown that, with the exception of Cs(7P) + Cs(6S), the associative reactions that were investigated do not exhibit a threshold-type behavior, so that the reduction in $\langle \sigma_i k v_0 \rangle$ is due to a reduction in the cross sections σ_{ik} . The measured energy threshold for the Cs(7P) + Cs(6S) reaction has been used to determine the dissociation energy of the Cs₂⁺ ion. The result is $D_m^+ = 1.10 \pm 0.05$ eV. Compensation of the electron space charge by positive ions was used as a means of amplifying the ion current. The validity of this method in absolute measurements is substantiated experimentally.

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1. INTRODUCTION

It has been suggested¹ that associative ionization may play an important role in the production of charged particles in the plasma of gas discharges, flames, shock tubes, and so on. However, the current state of experimental and theoretical studies of this problem is such that even very approximate estimates of the efficiency of this process cannot be made for most interacting atoms. The only experimental estimates of the cross sections for the process are those reported for a few excited states of helium,² argon,^{3,4} and cesium.⁵⁻⁸ The associative ionization cross section has been calculated theoretically only in the case of the hydrogen atom.⁹ The cross section turns out to be much smaller than the cross section determined experimentally for the above three atoms. This discrepancy may be due to the different behavior of the terms of quasimolecules consisting of atoms of different elements under excitation by electron impact, or by the inadequacy of the model used in the calculation.

Mohler and Boeckner¹⁰ were the first to observe associative ionization. They recorded the ion current produced when cesium vapor was exposed to light with wavelengths corresponding to lines in the principal series of cesium atoms, and assumed that the ionization process was accompanied by the formation of the molecular ion Cs₂⁺. Much later, Ono *et al.*¹¹ used mass-spectrometric identification of ions and confirmed the validity of this assumption. Molnar and Hornbeck¹² found associative ionization in inert gases during the population of the excited states of the atoms by electron impact.

The work of Mohler and Boeckner¹⁰ was followed by a large number of publications on associative ionization in cesium vapor. References to all this work can be found in the papers by Marr and Wherrett¹³ and Klyucharev.¹⁴ The aim was to identify the atomic states participating in the production of Cs₂⁺, so that, in this

sense, these researches did not extend the information reported by Mohler and Boeckner.¹⁰ The first estimates of the cross sections for a few associative-ionization channels were reported by Dobrolezh,⁵ Antonov *et al.*,⁶ and Korchevoĭ *et al.*^{7,8} There are considerable discrepancies between some of these cross sections, and further measurements are clearly necessary.

Important information on the efficiency of associative ionization with the participation of different excited states can be obtained by studying the dependence of this efficiency on the thermal energy of the interacting atoms. This was obtained theoretically by Nielsen and Berry⁹ in the case of hydrogen atoms. However, hardly any attention had been paid to the experimental study of this question. We know of only two such attempts, namely, the early work of Freudenberg,¹⁵ who investigated cesium atoms but, as will be shown below, this work is subject to methodologic errors, and the work of Klyucharev *et al.*¹⁰ who studied Na, K, Rb, and Cs atoms, but in a very small temperature interval. Both these attempts were directed toward a determination of the appearance energy threshold E_m and the dissociation energy D_m^* of the molecular ion. The results were found to differ by 0.3–0.4 eV.

Marr and Wherrett¹³ attempted to reconcile the contradictions in the literature between the values of E_m , D_m^* , and the ionization energy $E_{i,m}$ of the Cs₂ molecule, but their interpretation of the experimental data reported by Ono *et al.*¹¹ and Freudenberg¹⁵ was erroneous in that they overestimated the influence of the heating of the cesium vapor on the efficiency of associative ionization between the atoms in the 7P and 8P states. In fact, ionization involving the 7P state was seen in the Freudenberg experiment¹⁵ because of the strong increase in the photon flux populating this state (through the replacement of the monochromator with a light filter which defined the required radiation from the source). The heating of cesium from 270 °C to 440 °C led to an increase in the signal by a factor of only two.

In the experiments by Ono *et al.*,¹¹ ionization involving the $8P$ state was produced by using a helium-discharge source emitting the strong 3888 \AA line which coincided with the $8P_{1/2} - 6S_{1/2}$ cesium line within the limits of the Doppler half-width, whereas the heating of the cesium vapor was not examined at all.

Although the cross sections corresponding to the different associative ionization channels were not determined in the two experiments just mentioned, their results nevertheless clearly show a sharp reduction in the ionization efficiency between the $10P$, $9P$ and $8P$, $7P$ atomic levels. This reduction in the ionization yield may have been connected both with a reduction in the cross section for the process and with the appearance of an energy threshold for the reaction. The relative contribution of these two effects can be established by simultaneous measurements of the rate constants as functions of the quantum state and the thermal energy of the interacting atoms. This program was, in fact, carried out in the research reported here.

2. EXPERIMENTAL METHOD AND RESULTS OF MEASUREMENTS

A. Apparatus and optical and electrical measurement systems

The measurements were performed in two modifications of the reaction chamber (I and II), shown schematically in Figs. 1a and b. They were made of molybdenum glass with sealed sapphire windows whose transparency remained constant as the temperature T and pressure p of the cesium vapor was increased. Each chamber was provided with a long stub containing a drop of cesium. The glass chambers were subjected to standard vacuum-technology procedures prior to the introduction of cesium.

During the measurements, the working chamber was placed in a thermostat with two compartments whose temperatures could be varied independently. One compartment contained the chamber itself, and its temperature T determined the temperature of the cesium vapor, whereas the other compartment contained the side tube with the cesium drop, and its temperature t governed the saturated vapor pressure p ($t < T$). The two temperatures T and t were maintained constant to within 0.5 and 0.2°C , respectively. The thermostat was pro-

vided with quartz windows that were coaxial with the sapphire windows of the working chamber.

The cesium vapor was excited in the space between windows 1, separated by $l=0.4$ cm (in chamber I) and $l=1$ cm (in chamber II). The window diameters were 1.5 cm. The ion current produced in the system was amplified by the well-known method of compensating the electron space charge by positive ions.¹⁰ This was done with the aid of thermionic diodes (detectors) sealed into the chamber. The anodes 3 of these diodes were in the form of a nickel grids (transmission approximately 95%), and the thermionic cathodes 4 were tungsten wires, 50μ in diameter. In chamber I, the detector was mounted directly between windows 1 and, in chamber II, it was located outside the region of photoexcitation. In the latter case, the ions were drawn into the space between the electrodes by a small ($1-2\text{V}$) extracting voltage between electrodes 5 and anode 3. In the case of chamber I, another pair of sapphire windows 2 was used for spectroscopic measurements of the concentration of excited cesium atoms (it is shown in Fig. 1c, which illustrates another section through the chamber).

The optical arrangement used in these experiments is shown in Fig. 1c (the system of focusing lenses is omitted for simplicity). The flux of radiation PF populating the excited states of the atoms in the chamber was produced by a cesium discharge lamp. Absorbing glass filters LF_1 were placed between the pump and the chamber in order to define the individual segments of the spectrum. The quality of these filters was checked with the aid of a spectrograph. The use of these filters instead of a monochromator enabled us to obtain considerable concentrations of excited nP states and to populate the nD states in two steps. The flux density Φ of the populating radiation was measured with the aid of neutral attenuators NA.

The concentration N_i of excited cesium atoms was measured with the aid of the MDR-3 diffraction spectrometer by two optical methods for the different energy levels, namely, by measuring the absolute intensities and by examining the inversion and absorption of spectral lines. The absolute intensities I_{ik} of the lines re-emitted by the cesium atoms were measured relative to the emission of a standard ribbon lamp. This lamp was also used to determine the inversion temperature in the second method. The strip lamp was replaced by a cesium discharge source in the case of measurements on the absorption of spectral lines. To increase the sensitivity with which the intensity of the spectral lines was measured, we used the well-known method whereby the beam intensity was modulated and the photomultiplier signal was selectively amplified.

The experimental conditions were such that we were able to determine only the average values of N_i for the chamber. It is therefore important for the subsequent quantitative determinations of the rates of associative ionization to ensure that the detector gain is independent of the position of the point at which the ions are created in the space between the electrodes.

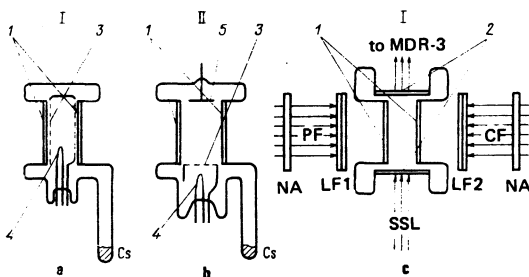


FIG. 1. Experimental setup and method used in optical measurements: 1, 2—sapphire windows, 3—anode grids, 4—cathodes, 5—electrode, PF—populating flux, CF—calibrating flux from mercury source, SSL—flux from standard strip lamp, LF_1 and LF_2 —light filters, NA—neutral attenuators.

The gain k_d of the detector (for chamber I) was determined as follows. The cesium vapor was exposed to the calibrating flux CF with wavelengths of 3126 and 3132 Å (defined with the aid of the light filters LF₂ from the spectrum emitted by a mercury discharge lamp). The energy of photons corresponding to these wavelengths is sufficient for the direct ionization of the cesium atoms, and the current of atomic ions generated in the chamber in this way can be calculated from the formula $J_a = e\sigma N_{6S} \Phi_{H\kappa} I$, where e is the electron charge, $\sigma = 2.2 \times 10^{-19}$ cm² is the photoionization cross section of the cesium atom,¹⁷ N_{6S} is the concentration of atoms in the ground state, and $\Phi_{H\kappa}$ is the absolute intensity of the flux entering the chamber with wavelengths of 3126 and 3132 Å. This flux produces an increase ΔJ_{ea} in the electron current through the detector, and the gain is defined by $k_{da} = \Delta J_{ea} / J_a$.

It was then assumed that the space-charge compensation effect was the same for the Cs⁺ and Cs₂⁺ ions, i.e., $k_{da} = k_{dm} = k_d$, and that the current of molecular ions was $J_m = \Delta J_{em} / k_{da}$, where ΔJ_{em} is the increase in the electron current through the detector due to associative ionization. The validity of this was confirmed by Marr and Wherrett,¹³ who used a thermionic detector to determine the ratio of J_a to J_m , produced by direct photoionization of the cesium atoms and molecules. This ratio was found to be in satisfactory agreement with the values calculated from the known cross sections for the two processes.

Most of our measurements were performed for $\Phi_{H\kappa} = 1.6 \times 10^{12}$ kV/sec and $N_{6S} = 6.1 \times 10^{13}$ cm⁻³. This corresponds to a calculated current $J_a = 1.7 \times 10^{-12}$ A, which produced an increase in the electron current in the detector $\Delta J_{ea} = 3 \times 10^{-6}$ A. Consequently, under these conditions, $k_d = 1.8 \times 10^6$. This gain was very dependent on the experimental conditions (p , T , and the cathode temperature). It was therefore determined for each particular experimental situation separately. To determine the function $J_m(\Phi)$ from $\Delta J_{em}(\Phi)$, we also determined the relative variation in k_d with the ion current (i.e., with the increase in $\Phi_{H\kappa}$). In our examination of the temperature dependence of the associative ionization rate constants, we determined only the relative variation in k_d with J_m and T .

Experiment has shown that the above method of detecting the ion current was characterized by the following features:

1) The gain was practically independent of the position of the point at which the ions were created in the space between the electrodes in the detector (this was verified by scanning a very narrow beam of light of constant intensity over the surface of the sapphire window of chamber I; the detector signal ΔJ_{em} was found to remain constant to within 5–10%).

2) The photoelectron current from the electrodes in the detector was negligible in comparison with the useful signal ΔJ_{em} .

3) The ion current produced by thermal ionization of the excited atoms on the heated cathode surface provided no contribution to the useful ion-current signal (this

was established by photoexcitation of cesium vapor¹⁰ at different distances from the cathode surface).

4) It was possible to eliminate the shunting effect of leakage between the electrodes (this was achieved by the above calibration method for which the resistance between the cathode and anode on the detector was unimportant).

5) The heating of the cesium vapor by the hot cathode could be neglected because of the low temperature and small surface area of the latter (this was confirmed by the fact that the rates of associative ionization as functions of temperature for chambers I and II were the same, where, in chamber I, the cathode was in the region of photoexcitation and, in chamber II, it was located outside this region; additional confirmation of this is also provided by the fact that the ionization rates obtained with chamber I at cathode temperatures differing by about 100 °K were found to be the same).

All these detector properties suggest that it can be used for both qualitative (as was done before) and quantitative studies of associative ionization. The ion currents J_m , determined with the aid of this detector, can be used to calculate the rate constant $\langle \sigma_{ik} v_0 \rangle$ for different channels of associative ionization from the formula

$$J_m = a e \langle \sigma_{ik} v_0 \rangle N_i N_k V, \quad (1)$$

where $a = 1$ for different and $a = 0.5$ for identical reagents, σ_{ik} is the cross section for associative ionization during the interaction between atoms in the i -th and k -th states, v_0 is the relative thermal velocity of the atoms, N_i and N_k are the concentrations of atoms in the i -th and k -th states, and $V = 0.5$ cm³ is the volume of the photoexcitation region in chamber I. It is clear from (1) that the relative values of J_m and T are in complete agreement with the character of the function $\langle \sigma_{ik} v_0 \rangle = f(T)$.

B. Temperature dependence of the rates of associative ionization¹

The relative rates $\langle \sigma_{ik} v_0 \rangle$ were determined as functions of T in the temperature range 475 °K to 713 °K for the following reactions:



Most of the measurements were performed on chamber II. To ensure that the ions were extracted from the region of photoexcitation in the same way for different temperatures T of the cesium vapor, steps were taken to ensure that the concentration of atoms in the ground state was held constant ($N_{6S} = 5.4 \times 10^{14}$ cm⁻³). This was achieved by the necessary change in the temperature t of the compartment containing cesium.

The population of the excited states in reactions (2), (3), and (4) was produced by the flux Φ_{nP} of radiation corresponding to the 9P, 8P, and 7P → 6S transitions, defined in turn by the light filters out of the spectrum emitted by the cesium lamp. The flux Φ_{nP} was measured

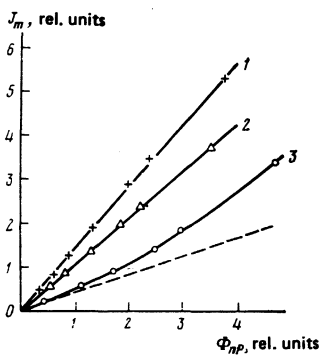
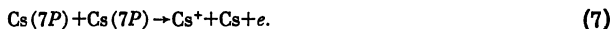


FIG. 2. Ion current J_m as a function of the exciting flux Φ_{nP} : 1—Cs(9P)+Cs(6S) reaction, 2—Cs(8P)+Cs(6S), 3—Cs(7P)+Cs(6S); broken line represents the function $J_m(\Phi_{1P})$.

relative to the standard source and was varied by the neutral attenuators.

Figure 2 shows an example of the dependence of J_m on Φ_{nP} for reactions (2)–(4) at $T=563^\circ\text{K}$. In accordance with (1), the currents J_m in reactions (2) and (3) are proportional to the corresponding fluxes Φ_{nP} . This indicates the absence of parasitic processes such as ionization by relectrons due to the excited atoms and ionization as a result of collisions between two excited atoms. The first of these two processes is unimportant in the subsequent measurements as well because the maximum increase in the electron current through the detector was achieved in the case of reaction (2). For reactions (2) and (3), the variation in the relative values of $\langle\sigma_{ik}\nu_0\rangle$ with temperature T can be determined from the slope of the function $J_m(\Phi_{nP})$ for different T .

It is clear from Fig. 2 that, in the case of reaction (4), the ion current varies more rapidly than Φ_{7P} . The departure of the function $J_m(\Phi_{7P})$ from linearity may be due to the production of atomic ions in the process



The resultant ion current recorded by the detector, due to processes (4) and (7), can then be written in the form

$$J_m' = J_m + J_a = \text{const}_1 \cdot \langle\sigma_{ik}\nu_0\rangle \Phi_{7P} + \text{const}_2 \cdot \Phi_{7P}^2,$$

where the two constants are independent of T . If one then plots J_m'/Φ_{7P} as a function of Φ_{7P} , the result should be a straight line intercepting the ordinate axis. This is shown in Fig. 3 for different values of T . The results are in good agreement with the foregoing discussion, and the variation in the intercept for different T gives the variation in the relative value of $\langle\sigma_{ik}\nu_0\rangle$ with temperature T .

In the case of reactions (5) and (6), the 6P and 6D states were populated simultaneously by the resultant

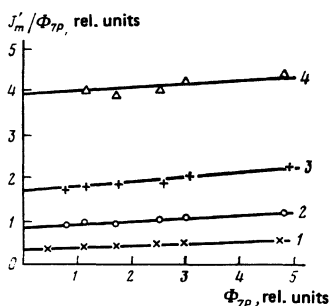


FIG. 3. Ratio J'_m/Φ_{7P} plotted as a function of Φ_{7P} : curve 1— $T=563^\circ\text{K}$, 2— 633°K , 3— 673°K , 4— 713°K .

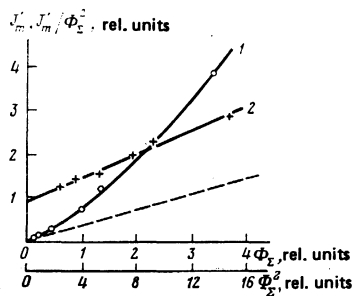


FIG. 4. Current J'_m plotted as a function of Φ_L (curve 1) and J'_m/Φ_L^2 as a function of Φ_L (curve 2). Broken straight line shows the function $J_m(\Phi_L^2)$.

flux $\Phi_L = \Phi_{6P} + \Phi_{6D}$ due to the 6P → 6S and 6D → 6P transitions. The ion current J_m should then be proportional to Φ_L^2 . However, it is clear from curve 1 in Fig. 4 that, in fact, it increases more rapidly than Φ_L^2 . As in the previous case, the departure from the quadratic dependence may be due to the production of atomic ions in the process



The resultant ion current due to (5), (6), and (8) can be written in the form

$$J_m' = J_m + J_a = \text{const}_1 \cdot \langle\sigma_{ik}\nu_0\rangle \Phi_L^2 + \text{const}_2 \cdot \Phi_L^3.$$

If one then plots J_m'/Φ_L^2 as a function Φ_L , the result should be a straight line intercepting the ordinate axis (curve 2, Fig. 4). The variation in the size of the intercept with T gives the variation in the relative value of $\langle\sigma_{ik}\nu_0\rangle$ with T for the unseparated reactions (5) and (6).

The dependence of $\langle\sigma_{ik}\nu_0\rangle$ on T for reactions (2)–(6) is shown in Fig. 5. The uncertainties in these measurements are not more than $\pm 10\%$, since the fluctuations in the intensities of the photoexciting and calibrating fluxes did not exceed $\pm 3\%$.

C. Rates of associative ionization

The constants $\langle\sigma_{ik}\nu_0\rangle$ were determined for reactions (2)–(6) with the aid of chamber I at $T=500^\circ\text{K}$. The sen-

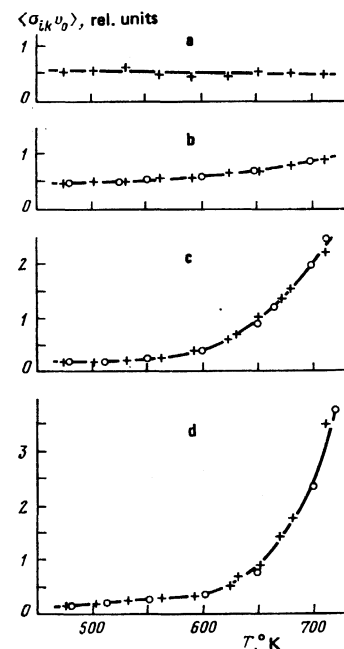


FIG. 5. Dependence of $\langle\sigma_{ik}\nu_0\rangle$ on T : a—Cs(9P) + Cs(6S), b—Cs(8P) + Cs(6P), c—Cs(6P) + Cs(6P) and Cs(6D) + Cs(6S), d—Cs(7P) + Cs(6S); +—experiment, ○—calculated.

sitivity of this chamber was higher (by roughly two orders) as compared with chamber II, so that we were able to perform the measurements at much lower values of the flux Φ and thus exclude contributions due to parasitic processes (7) and (8). For reactions (2), (3), (5), and (6), the measurements were performed at $N_{6S} = 6.1 \times 10^{13}$ whereas, for reaction (4), at $N_{6S} = 1.4 \times 10^{15}$ cm^{-3} .

Process (2). Both fine-structure components of the $9P$ state were populated. Since the $9P \rightarrow 6S$ lines re-emitted by the chamber were partially absorbed, we measured the absolute intensities of lines due to the $7D \rightarrow 6P$ transitions, the upper levels of which were populated from the $9P$ states. The absolute intensities were then used to determine the concentrations N_{7D} . By using the balance of fluxes populating and deexciting the $7D$ states, we were then able to calculate the concentrations N_{9P} summed over the components of the doublet structure. The transition probabilities were taken from the literature.¹⁹ The ion current corresponding to $N_{9P} = 1.8 \times 10^4 \text{ cm}^{-3}$ was $J_m = 1.7 \times 10^{-12}$ A.

Process (3). Both components of the $8P$ state were populated. We measured the absolute $86 \rightarrow 6P$ line intensities and then, by analogy with the previous case, calculated the concentration N_{8P} . The value of the ion current corresponding to $N_{8P} = 5.5 \times 10^4 \text{ cm}^{-3}$ was found to be $J_m = 1.5 \times 10^{-12}$ A.

Process (4). The population of the $7P$ states was determined by the inversion method. The ion current corresponding to $N_{7P} = 1.6 \times 10^6$ was $J_m = 2 \times 10^{-12}$ A.

Processes (5) and (6). The resultant ion current due to these processes is given by

$$J_m = e \langle \sigma_{ik} v_i \rangle N_{6D} N_{6S} V + 0.5 e \langle \sigma_{ik} v_i \rangle N_{6P}^2 V. \quad (9)$$

The concentrations N_{6P} were determined by the inversion method and N_{6D} from the absolute intensity of the $6D \rightarrow 6P$ lines. By varying the ratio of the intensities populating the $6P$ and $6D$ states, we were able to set up two regimes with equal values $J_m = 7.4 \times 10^{-13}$ A and different concentrations of excited atoms: $N_{6P} = 6.5 \times 10^9$ and $N_{6D} = 7.3 \times 10^4 \text{ cm}^{-3}$ in one case, and $N_{6P} = 3.5 \times 10^9$ and $N_{6D} = 1.4 \times 10^5 \text{ cm}^{-3}$ in the other. Substitution of these values in (9) yields the values of $\langle \sigma_{ik} v_i \rangle$ for processes (5) and (6).

The rates of associative processes determined in this way are listed in Table I. The table includes our previous estimates⁶ and the measurements by Klyucharov *et al.*⁵ It also indicates the resultant potential energies E_i of the interacting atoms.

We have obtained an improved value for the rate of the process



the possibility and high efficiency of which was indicated in a previous paper.⁶ The concentration of the $5D$ states was determined by examining the absorption of the $5F \rightarrow 5D$ and $6F \rightarrow 5D$ lines in the fundamental series. This was done by replacing the strip lamp (Fig. 1c) with the cesium source operated at very low discharge-current densities for which these lines were subject to practi-

TABLE I. Rate Constants and Cross Sections for Associative Ionization at $T = 700$ K.

Process	$E_i, \text{ eV}$	$\langle \sigma_{ik} v_i \rangle, \text{ cm}^3 \text{ sec}^{-1}$			$\bar{\sigma}_{ik}, \text{ cm}^2$	
		[5]	[6]	present work		
$7P - 6S$	2.72	—	—	$1.6 \cdot 10^{-14}$	$4 \cdot 10^{-19}$	
$6P - 6P$	2.85	$2 \cdot 10^{-13}$	$1.6 \cdot 10^{-13}$	$2.5 \cdot 10^{-13}$	$5 \cdot 10^{-18}$	
$8P - 6S$	3.20	$1.2 \cdot 10^{-12}$	$1.6 \cdot 10^{-11}$	$8 \cdot 10^{-12}$	$2 \cdot 10^{-16}$	
$9P - 6S$	3.43	—	—	$2 \cdot 10^{-11}$	$5 \cdot 10^{-16}$	
$9P - 6S$	3.43	—	—	—	—	
$10P - 6S$	3.56	—	—	—	—	
$11P - 6S$	3.65	—	$1.2 \cdot 10^{-10}$	—	$3 \cdot 10^{-15}$	
$12P - 6S$	3.70	—		—		—
$6D - 6S$	2.80	$\leq 1 \cdot 10^{-12}$	—	$9 \cdot 10^{-13}$	$2 \cdot 10^{-17}$	
$5D - 6P$	3.22	—	$8 \cdot 10^{-11}$	$1 \cdot 10^{-10}$	$2.5 \cdot 10^{-15}$	
$7D - 6S$	3.23	$1.2 \cdot 10^{-10}$	$4 \cdot 10^{-11}$	—	$1 \cdot 10^{-15}$	
$8D - 6S$	3.45	$\leq 1 \cdot 10^{-10}$	$6 \cdot 10^{-11}$	—	$1.5 \cdot 10^{-15}$	
$9D - 6S$	3.57	—	$4 \cdot 10^{-10}$	—	$1 \cdot 10^{-14}$	
$10D - 6S$	3.65	—	—	—	—	
$11D - 6S$	3.71	—	$6 \cdot 10^{-10}$	—	$1.5 \cdot 10^{-14}$	
$8S - 6S$	3.01	$\leq 1 \cdot 10^{-11}$		—		—
$9S - 6S$	3.34	$\leq 1 \cdot 10^{-10}$		—		—

cally no reabsorption. We used the light filters to vary the population of only the $5D$ states (for constant N_{6P} , N_{6D} , and so on) and, by determining the variation in the current J_m , we were able to isolate the signal due to process (10). These measurements resulted in the rate constants given in the table.

The table does not give the rate constant for the process $\text{Cs}(6D) + \text{Cs}(6S)$ estimated previously.⁶ This exceeds the result obtained in the present work by a factor of 15. This discrepancy cannot be explained by experimental errors in J_m and N_{6D} . It is due to the parasitic process (8), which was not corrected for, whose intensity under the conditions of the experiment described previously⁶ was very high because of the high concentration $N_{6P} = 1.6 \times 10^{11} \text{ cm}^{-3}$. Our estimates show that such a strong distorting effect of (8) would be expected if its cross section is approximately $5 \times 10^{-14} \text{ cm}^2$. The fact that this figure is realistic is, to some extent, confirmed by the cross section ($6 \times 10^{-14} \text{ cm}^2$) for the process $\text{Hg}(6P) + \text{Cs}(6S) \rightarrow \text{Hg}(6S) + \text{Cs}^+ + e$, reported by Brodskii *et al.*²⁰ The influence of the $\text{Cs}(6P) + \text{Cs}(nD) \rightarrow \text{Cs}^+ + \text{Cs} + e$ processes on our previous estimate⁶ of the rate of associative processes involving the participation of higher nD states is unimportant because of the substantial increase in $\langle \sigma_{ik} v_i \rangle$ with n .

When the excited nP ($n \geq 7$) and nD ($n \geq 6$) states are pumped, this is accompanied by a cascade population of levels with smaller n . Their contribution to the rate of associative ionization was always much smaller than the rate of processes involving the participation of the primary excited state.

The precision with which the constants $\langle \sigma_{ik} v_i \rangle$ was established in our present experiments is largely determined by uncertainties in the measured concentrations N_i and the absolute intensity of the flux Φ_{Hg} . The latter uncertainty does not exceed $\pm 10\%$. The absolute intensity of the lines reemitted by the cesium atoms was determined with the same precision. However, in a subsequent calculation of N_i , we used theoretical values¹⁹ for the oscillator strength f , whose precision was very difficult to establish. By using different transitions to determine N_i , we obtained results differing from one another by factors of two. This spread exceeded all the

other errors, and we therefore estimate that our values of $\langle\sigma_{ik\nu_0}\rangle$ are good to within a factor of two.

The data listed in the table show that the rates of associative ionization are very dependent on the quantum states of the interacting atoms. When their total potential energy E_i is reduced from 3.6 to 2.7 eV, the quantity $\langle\sigma_{ik\nu_0}\rangle$ decreases by more than four orders (from 6×10^{-10} to 1.6×10^{-14} cm²/sec), whereas the transition from the nP to the nD state for roughly equal values of E_i is accompanied by an increase in $\langle\sigma_{ik\nu_0}\rangle$ by a factor of a few units.

3. DISCUSSION

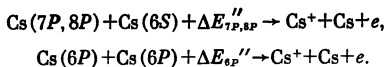
Associative ionization is possible if the resultant energy of the colliding partners is not less than $E_m = E_{ia} - D_m^*$, where E_{ia} is the atomic ionization energy. If $E_m - E_i = \Delta E_i > 0$, the reactions have a threshold energy and one expects an exponential increase in $\langle\sigma_{ik\nu_0}\rangle$ with increasing T . The form of $\langle\sigma_{ik\nu_0}\rangle = f(T)$ is shown in Fig. 5 and can be explained if it is assumed that $\Delta E_{0P} = 0$ for reaction (2), whilst, in reactions (3)–(6), the ionization process occurs along two channels in one of which the energy threshold is $\Delta E_i' = 0$ for reactions (3), (5), and (6), and $\Delta E_i' \geq 0$ for reaction (4), whereas, in the other channel, the threshold $\Delta E_i''$ is large and increases with decreasing potential energy E_i of the excited atom [or two atoms in the case of reaction (5)]. The first channel predominates for $T = 475$ – 600 °K with ionization cross section σ_{ik}' , whereas, for $T = 600$ – 713 °K, the second channel predominates with cross section $\sigma_{ik}'' \gg \sigma_{ik}'$.

In view of the relatively small range of T , we may suppose that $\sigma_{ik} = \bar{\sigma}_{ik}$ and is independent of T . For a Maxwellian distribution of velocities of the atoms, we then have, in accordance with the foregoing considerations,

$$\langle\sigma_{ik\nu_0}\rangle = \bar{\sigma}_{ik}' \bar{v}_0 \left(1 + \frac{\Delta E_i'}{kT}\right) \exp\left(-\frac{\Delta E_i'}{kT}\right) + \bar{\sigma}_{ik}'' \bar{v}_0 \left(1 + \frac{\Delta E_i''}{kT}\right) \exp\left(-\frac{\Delta E_i''}{kT}\right). \quad (11)$$

By varying the parameters $\Delta E_i'$, $\Delta E_i''$, and $\bar{\sigma}_{ik}''/\bar{\sigma}_{ik}'$, we succeeded in achieving complete agreement between the experimental values of $\langle\sigma_{ik\nu_0}\rangle$ as a function of T and those calculated from (11) (the calculated values are represented by the open circles in Fig. 5). This agreement was achieved for the following values of the parameters: $\Delta E_{0P}' = 0$, $\Delta E_{0P}'' = 0.7$, and $\bar{\sigma}_{0P}''/\bar{\sigma}_{0P}' = 3 \times 10^3$ for reaction (3); $E_{6P,6D}' = 0$, $\Delta E_{6P,6D}'' = 1$ eV, and $\bar{\sigma}_{6P,6D}''/\bar{\sigma}_{6P,6D}' = 6.4 \times 10^6$ for reactions (5) and (6); and $\Delta E_{7P}' \approx 0.1$ eV, $\Delta E_{7P}'' = 1.2$ eV, and $\bar{\sigma}_{7P}''/\bar{\sigma}_{7P}' = 7 \times 10^7$ for reaction (4).

The energy threshold $\Delta E_i''$ obtained in this way for reactions (3), (4), and (5) in the second ionization channel gives the following results for the cesium atom: $\Delta E_i'' + E_i = 3.9$ eV $= E_{ia}$. This may be regarded as a very substantial argument in favor of the assumption that the ion current generated in this case is not connected with associative ionization and may be due to the production of atomic ions in the following processes:



This assumption will require further experimental veri-

fication, accompanied by mass-spectrometric identification of the reaction products. In the present situation, however, only the first of the above channels, which predominates at temperatures up to 300 °K, can be clearly connected with the associative process of generation of molecular ions.

The above threshold energy $\Delta E_{7P}' \approx 0.1$ eV for the associative reaction (4) leads to $D_m^* = E_{ia} - E_{7P} - \Delta E_{7P}' = 1.10 \pm 0.05$ eV. Freudenberg¹⁵ obtained a similar value for the dissociation energy of the ions Cs_2^+ by varying the relative value $\langle\sigma_{ik\nu_0}\rangle$ for T between 540 and 713 °K. It is clear from Fig. 5d that this temperature range corresponds to a 14-fold increase in $\langle\sigma_{ik\nu_0}\rangle$, whereas the corresponding factor recorded by Freudenberg¹⁵ was two. This was due to methodologic errors in the work of Freudenberg¹⁵ connected with possible nonlinearity of the detector, the influence of the parasitic process (7), which was not taken into account, and the reduction in the transparency with increasing T of the glass through which the excited states were pumped up. The agreement between the values of D_m^* is, therefore, fortuitous. The much smaller value of D_m^* for the Cs_2^+ ion (≈ 0.73 eV) is obtained from the relation $\langle\sigma_{ik\nu_0}\rangle = f(T)$, obtained experimentally by Klyucharev *et al.*¹⁶ for $T = 405$ – 470 °K in the case of reaction (5). In our view, the reason for the above discrepancy lies in the fact that the leakage between the measuring electrodes decreases with increasing T , and the procedure induced by Klyucharev *et al.*¹⁶ was very sensitive to this leakage.

The theoretical values of D_m^* obtained for Cs_2^+ are very contradictory. For example, recent calculations^{21,22} yield $D_m^* = 0.593$ and 0.85 eV (obtained by the pseudopotential method). They are both much smaller than the values reported here.

The initial segments of the functions $\langle\sigma_{ik\nu_0}\rangle = f(T)$ in Fig. 5 thus show that all the associative ionization processes investigated in the present work (with the exception of the reaction $\text{Cs}(7P) + \text{Cs}(6S)$) do not have threshold energies, and the reduction in the absolute values of $\langle\sigma_{ik\nu_0}\rangle$, accompanying transition to atomic states with lower excitation energies E_i , is due to the reduction in σ_{ik} .

The variation in σ_{ik} corresponding to the interaction between atoms in different excited states can be described in terms of the qualitative picture of the behavior of attractive terms of electronically excited quasimolecules. In accordance with the discussion of Marr and Wherrett¹³ (there are no rigorous potential curves for excited alkali metal molecules in the literature), an excited electron located at a large distance from the nuclei produces a relatively small effect on the residue $\text{Cs}_2^+(X^2\Sigma_g^+)$. The Cs_2^+ terms should approach asymptotically the ground state term of Cs_2^+ as $n \rightarrow \infty$. The crossing of the potential curves is not essential for the transition $\text{Cs}_2^+ - \text{Cs}_2^+ + e$ to take place.⁹ A sufficient condition is the overlap of the vibrational wave function. Since the efficiency of process (4) is low, one would expect that, for a stationary molecular term made up of the atomic 7P and 6S states, the overlap would occur in the region of the exponentially decaying tail of the wave function of the lowest vibrational level of the molecular

ion. Transition to the higher electronically excited states is accompanied by an increase in the overlap which, in turn, is accompanied by the observed increase in σ_{ik} .

Associative processes may be characterized by effective cross sections $\bar{\sigma}'_{ik} = \langle \sigma_{ik} v_0 \rangle / \bar{v}_0$. Their values, determined from the present work and from previous data,⁶ are given in the last column of the table for $T \approx 500$ °K.

¹Preliminary measurements for reactions (3) and (4) were reported in a previous paper.¹⁸

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Higher-order perturbation theory effects in the shift and width of atomic levels in an optical field

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The quasienergy method, developed earlier for the interaction of a system with a periodic field in which the level broadening effects are neglected, is reformulated for the calculation of quasistationary states in a strong optical field. The perturbation theory is developed for the real and imaginary parts of complex quasienergy and singularities which appear on allowance for corrections to the first nonvanishing order are considered. The cases of an isolated level and of a group of resonance levels are discussed separately. The shift and width of a level subjected to short-range and Coulomb potentials are analyzed in detail, including terms of the second and fourth orders in the field. At frequencies higher than the ionization potential the expressions obtained give, in particular, the corrections to the cross section of the classical photoelectric effect, proportional to the optical wave intensity. The exponential decay law of the system in a periodic field is considered. The possibility of experimental detection of the higher-order effects in the shift and width of levels is discussed.

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§1. INTRODUCTION

In considering the processes of direct and resonance ionization of atoms in a strong field, and also the shifts and widths of atomic levels, it is usual to confine calculations to the first nonvanishing order in the perturbation theory of the interaction between a given system and the field. Inclusion of higher-order corrections makes it possible, on the one hand, to identify the range of validity of the results obtained in the first

nonvanishing approximation, and, on the other, to obtain a modified functional dependence of the shifts and widths on the field intensity. Calculations of the higher-order terms by the usual transient perturbation theory methods is fraught with difficulties typical of the higher orders of the perturbation theory in the case of finite level widths¹ and associated, in particular, with the need to allow for the contribution made to the width by the shift effects in lower order (and vice versa); there are also difficulties in integration of the singular ex-