Formation of electron-excited molecules in the photorecombination of potassium atoms in the 4*p* and 4*s* states

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Molecular bands in the λ 10500 Å ($^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$) and λ 6500 Å ($^1\pi_u^+ \rightarrow {}^1\Sigma_g^+$) regions were observed in the luminescence spectrum of potassium irradiated by the $4p \rightarrow 4s$ potassium-atom resonance lines. It is shown that the $^1\Sigma_u^+$ and $^1\pi_u$ electron-excited states are populated in the photorecombination process $K^*(4p) + K(4s) \rightarrow k^*_2 (^1\Sigma_u^+; {}^1\pi_u) + h\nu$. The values obtained for the cross sections of these processes, $\sigma_\Sigma = (1.6 \pm 0.2) \times 10^{-16}$ and $\sigma_\pi = (1 \pm 0.2) \times 10^{-19}$ cm^2, are larger by several orders of magnitude than the cross sections for the known photorecombination reactions accompanied by formation of molecules in the ground electronic state. The regularities of the molecular-band emission from a low-pressure potassium plasma are investigated. It is shown that the intensity of the anomalously bright λ 10500 Å is due entirely to photorecombination of the atoms, and that of the less bright λ 6500 Å band is due to photorecombination of the atoms and electron-excitation of the K_2 molecules.

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INTRODUCTION

Rebbek and Vaughan[1] observed in the emission spectrum of a potassium-discharge plasma an anomalously bright molecular band in the region λ 5725° A. The regularities of its emission as functions of the discharge conditions, investigated by us earlier,[2] suggest that this band stems from photorecombination of two resonantly excited potassium atoms. According to preliminary estimates the cross section of the indicated process is very large, $\approx 10^{-16}$ cm^2. More accurate values are presently sought for this quantity.

In an investigation of the longer-wavelength part of the spectrum of a low-pressure potassium discharge (10^{-3}–10^{-2} Torr), we observed that a molecular band with an abrupt boundary in the region λ 10 500 Å has a high integrated intensity, lower only than the intensity of the resonance lines of the K atoms. An indication of the existence of this band under discharge conditions is contained in a paper by Sorokin and Lankard,[3] where its absolute intensities were not determined, nor were the excitation mechanisms investigated.

Simultaneously with the λ 10 500 Å band, we observed a much less intense (by almost three orders of magnitude) molecular band in the region of λ 6500 Å.

These two bands were observed long ago in the absorption spectrum of potassium vapor by Loomis *et al.*[4] According to their identification, these bands correspond to the electronic transitions $^1\Sigma_u^+ - {}^1\Sigma_g^+$ for λ 10 500) and $^1\Pi_u - {}^1\Sigma_g^+$ (for λ 6500). The dissociation products of both excited states were taken to be atoms in the 4*P* and 4*S* states.

The observed intensity of the λ 10 500 Å band cannot be ascribed to the excitation of the K_2 molecules by electrons, the usual mechanism for discharge conditions, since the concentration of these molecules at the indicated potassium vapor pressure are very low.[5] As will be shown below, the recourse to only this mechanism to explain the laws governing the emission of the λ 6500 Å band also produced no results. It is these facts which served as the principal motivation for the present study, in which we determined the predominant processes that populate the states $^1\Sigma_u^+$ and Σ_u^1 in a potassium discharge plasma, as well as the cross sections of these processes. The decisive role in reaching this target was played by experiments in optically excited potassium vapor.

EXPERIMENTS IN A POTASSIUM DISCHARGE PLASMA

The potassium-discharge plasma was produced in a cylindrical tube of 2 cm diameter with an incandescent cathode. Flat diagnostic windows were sealed into the end faces of the tube. In the course of the measurement, the tube was placed in a thermostat whose temperature T set the pressure p of the saturated potassium vapor.[5] The experiment was performed at discharge currents $J_d = 0.02$–0.6 A and pressures $p = 2.4 \times 10^{-3}$–2.6×10^{-2} Torr. Under these conditions, the temperatures T_e and the concentrations n_e of the plasma electrons were determined in Ref. 6, where the mechanisms of the generation of K_2^+ ions were investigated. The characteristic ranges of variation of the plasma parameters were the following: at $p = 2.4 \times 10^{-3}$ Torr, the concentration n_e increased with increasing J_d in the indicated range from 10^9 to 8×10^{10} cm^{-3}, while the temperature T_e decreased from 13 000 to 7200° K. At $J_d = 0.4$ A, with decreasing pressure in the indicated range, the concentration n_e increased from 4×10^{10} to 1.1×10^{11} cm^{-3}, and the temperature T_e decreased from 8600 to 3500° K.

The optical system used for the measurement is illustrated in Fig. 1a. Radiation was incident from the end face of the discharge tube on the input of an MDR-3 diffraction momochromator. The light flux was registered with a photomultiplier (FÉU-79 in the visible region of the spectrum, FÉU-62 in the infrared). To increase the sensitivity of the measurements, the well known method of modulating the radiation followed by

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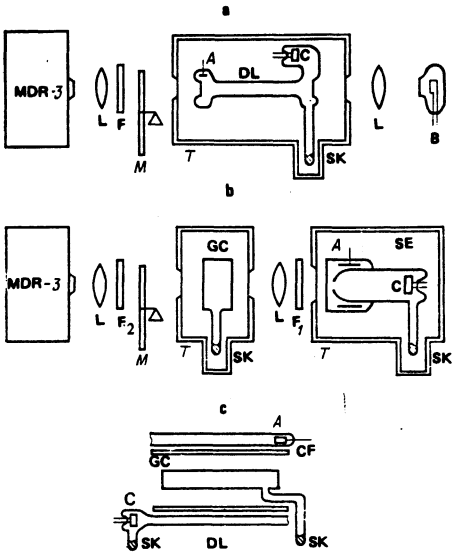

FIG. 1. Diagram of experimental installations and instruments: MDR-3—diffraction monochromator, DL—discharge lamps, C—cathodes, A—anodes, SK—stubs with potassium, T—thermostat, M—modulators, L—lenses, F—light filters, CF—cylindrical light filters, GC—cells, SE—surface emitter.

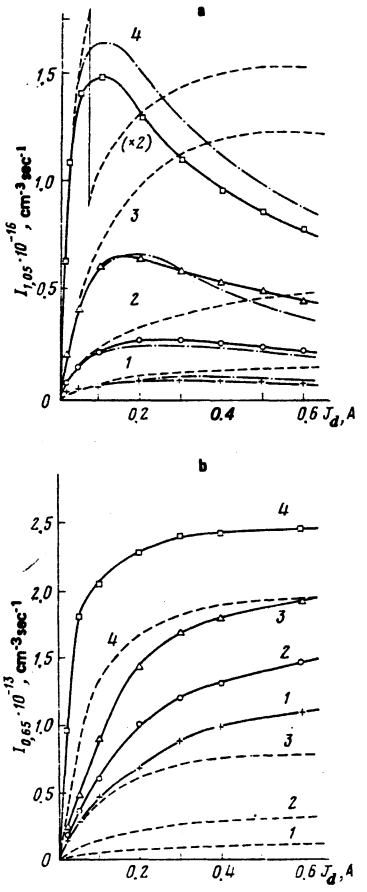

FIG. 2. Dependence of the intensities of the molecular bands on the discharge current and on the potassium-vapor pressure: *a*—λ10 500 Å, *b*—λ6500 Å; solid lines—experiment, dashed—calculation without allowance for quenching by the electrons, dash-dot—with allowance for the quenching by the electrons. Curves 1, 2, 3, and 4 correspond to $p = 2.4 \cdot 10^{-3}$, $4.4 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ and 2.6×10^{-2} Torr.

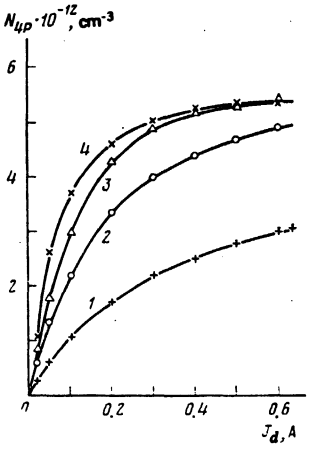

FIG. 3. Concentration of the potassium atoms in the $4P_{1/2,\,3/2}$ states. Curves 1, 2, 3 and 4 correspond to $p = 2.4 \cdot 10^{-3}$, $4.4 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ and 2.6×10^{-2} Torr.

sychronous detection, was used.[7] The spectrum was recorded with an electronic automatic potentiometer. A light filter placed between the discharge lamp and the monochromator cut out the intense resonance-line light scattered in the monochromator and hindering the registration of the weak light fluxes. An SZS-23 light filter was used in the investigation of the λ 6500 Å band, and an IKS-5 filter was used at 10 500 Å. Each filter passed the corresponding molecular band and attenuated potassium line (λ 7665/99) by hundreds of times.

The absolute intensities of the bands were measured by the known method of comparison with radiation from a standard source—a ribbon-filament lamp. The same lamp was used to determine the concentration of the potassium atoms in the $4P_{1/2,3/2}$ states from the temperature of the reversal of the spectral lines. Reversal was reached only at small discharge current J_d, when the values of N_{4P} were small. These values of N_{4P} were determined for each pressure p and were used to normalize the dependences of the relative values of N_{4P} on J_d in the entire range of variation of J_d. The concentration N_{4S} of the atoms in the ground state was calculated from the values of p.

The results of the measurements of the absolute intensities $I_{1.05}$ and $I_{0.65}$ of the molecular bands λ 10 500 and 6500 Å, radiated from 1 cm^3 of plasma and averaged over its volume, are represented by the solid curves on Fig. 2 as functions of J_d for four values of pressure $p = 2.4 \cdot 10^{-3}$, $4.4 \cdot 10^{-3}$, $1 \cdot 10^{-2}$, and 2.6×10^{-3} Torr. For the same regimes, Fig. 3 shows the concentrations N_{4P} averaged over the volume of the plasma and summed over the components of the doublet structure of the states $4P_{1/2,3/2}$.

We begin the analysis of the plots shown in Fig. 3 with a formulation of the balance equation for electron-excited molecules in the plasma. To simply the comparison, we analyzed the lifetimes of the $^1\Sigma_u^+$ and $^1\Pi_u$ states relative to all possible processes that cause their deactivation:

a) the lifetime τ_e relative to spontaneous emission is known only for the $^1\Pi_u$ states and is equal to $\tau_{e\Pi} \approx 10^{-8}$ sec[8];

b) the lifetime $\tau_2 = 1/\sigma_2 n_e v_e$ with respect to electron

impact of the second kind, at the maximum value $n_e \approx 4 \times 10^{11}$ cm^{-3} of our experiments, is equal to $\approx 3 \times 10^{-6}$ sec (if we assume that $\sigma_2 \approx 2 \times 10^{-14}$ cm, i.e., the same as in the case of electron quenching of excited alkali atoms[9]; v_e is the average thermal velocity of the electrons);

c) the lifetime τ_{exc} with respect to excitation by electrons into a higher molecular state should be larger than τ_2 because these de-activation channels have energy thresholds;

d) the lifetime τ_w with respect to departure to the wall of the discharge tube is not less than $2R/v_m \approx 5 \cdot 10^{-5}$ sec (v_m is the thermal velocity of the molecules and R is the radius of the discharge tube);

e) the lifetime τ_a with respect to de-exciting collisions with the potassium atoms in the reaction

$$K_2^*(^1\Sigma_u^+, {}^1\Pi_u) + K \rightarrow K^*(4P) + K_2 \qquad (1)$$

should be long enough, since the latter is characterized by a potential-energy defect and its cross section can therefore not be large; in fact, measurements[8] of the natural lifetime of the $^1\Pi_u$ state at pressures corresponding to the present study revealed no quenching influence of the reaction (1).

It follows from the foregoing that for the state $^1\Pi_u$ the times τ_a, τ_w, τ_{exc} and τ_2 are much longer than $\tau_{e\Pi}$, and the balance equation takes in this case the form

$$\Gamma_\Pi = N_{m\Pi}/\tau_{e\Pi}, \qquad (2)$$

where Γ_Π is the combined rate of all the possible channels of the population of the $^1\Pi_u$ state, and $N_{m\Pi}$ is the concentration of the molecules in this state.

The lack of information on the natural lifetime $\tau_{e\Sigma}$ of the $^1\Sigma_u^+$ state and the observed drop of curve 4 of Fig. 2a at large J_d induce us in this case to include in the balance equation a term that characterizes the de-excitation due to impacts of the second kind, and consequently

$$\Gamma_\Sigma = N_{m\Sigma}/\tau_{e\Sigma} + N_{m\Sigma}/\tau_2. \qquad (3)$$

The curves of Fig. 2a show qualitatively that $\tau_{e\Sigma}$ cannot greatly exceed the value of τ_2 at large J_d, i.e., the value $\approx 3 \times 10^{-6}$ sec, and as a result the times τ_a, τ_w, τ_{exc} are all much longer than $\tau_{e\Sigma}$. This justifies the neglect of all other de-exciting processes in (3). A quantitative estimate of $\tau_{e\Sigma}$, which confirms this conclusion, will be obtained below.

Assume that Γ_Σ and Γ_Π are due only to excitation of the K_2 molecules by the electrons. The rates of these processes Γ_n' (the index n corresponds to excitation to the $^1\Sigma_u^+$ or $^1\Pi_u$ state in the case of the Maxwellian energy distribution of the electrons are given by the expression

$$\Gamma_n' = a_n N_m n_e v_e (U_n + 2kT_e/e) \exp(-eU_n/kT_e), \qquad (4)$$

where U_n are the potentials of the excitation of the $^1\Sigma_u^+$ or $^1\Pi_u$ states, a_n are the initial slopes of the electronic excitation functions of the molecules (there are no published values); N_m is the concentration of K_2 molecules in the ground state (the dependence of N_m on N_{4S} and T, according to Lapp and Harris, [10] is given by

$$N_m = BN_{4S}^2 \exp(D/kT),$$

where B is a constant and D is the dissociation energy of the K_2 molecule).

The changes of the quantities Γ_Σ' and Γ_Π' with increasing J_d and p, calculated from (4) using the experimental values of n_e and T_e, are shown by the solid curves in Figs. 4a and 4b. We note that according to (2) $\Gamma_\Pi' = I'_{0.65}$ under all experimental conditions, and $\Gamma_\Sigma' = I'_{1.05}$ only at small discharge currents, when the second term in (3) can be neglected ($I'_{0.65}$ and $I'_{1.05}$ are the band intensities due only to the electron excitation of the molecules). Therefore a comparison of the experimental and calculated curves of Figs. 2 and 4 can be carried out for the band λ 6500 Å and the entire range of variation of J_d, while for the λ 10 500 Å band it is possible only in the region of small discharge currents ($J_d \lesssim 100$ mA). It is seen from this comparison that the considered excitation mechanism cannot account for the observed experimental growth of $I_{1.05}$ and $I_{0.65}$ with increasing pressure.

Analysis of the regularities of the experimental curves of Fig. 2a has revealed an important circumstance that reduces greatly the number of the possible mechanisms of population the $^1\Sigma_u^+$ state. It turns out that $J_d \lesssim 100$ mA the intensity $I_{1.05} \propto N_{4P} N_{4S}$. This has made it possible to assume that the $^1\Sigma_u^+$ state is populated by the photorecombination process

$$K^*(4P) + K(4S) \rightarrow K_2^*(^1\Sigma_u^+) + h\nu. \qquad (5)$$

To verify this assumption it is necessary to perform an experiment that is not made complicated by the presence of electrons and proves directly the possibility of the reaction (5).

Although no such regularity was observed for the curves of Fig. 2b, we have nevertheless included among the possible mechanisms of populating the $^1\Pi_u$ state the process

$$K^*(4P) + K(4S) \rightarrow K_2^*(^1\Pi_u) + h\nu. \qquad (6)$$

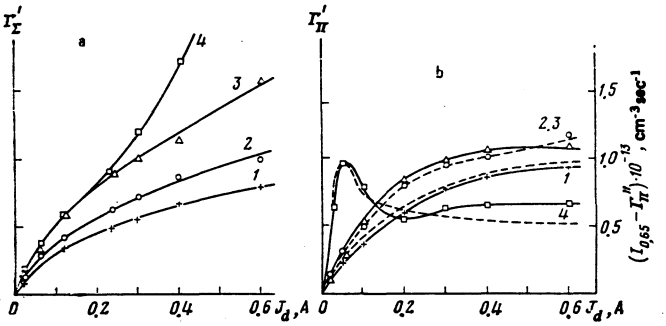

FIG. 4. Relative rates of excitation of the K_2 molecules by electrons. Curves 1, 2, 3, and 4 correspond to pressures $p = 2.4 \cdot 10^{-3}$, $4.4 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ and 2.6×10^{-2} Torr; in case b, the dashed curves are plots of the quantity $I_{0.65} - \Gamma_\Pi''$.

EXPERIMENTS IN OPTICALLY EXCITED POTASSIUM VAPOR

To prove the feasibility of the processes (5) and (6) and to determine their cross sections, we performed two supplementary experiments. The setup for the first of them is shown in Fig. 1b. A cell with potassium vapor was irradiated by an external potassium discharge source. To increase the intensity of the $4P \to 4S$ resonance lines the irradiating lamp had a special construction (surface radiator). Light filters F_1 were placed between the lamp and the cell in a combination such that all the resonance lines could be separated from the radiation spectrum, and the λ 10 500 and 6500 Å bands were attenuated by several orders of magnitude. Conversely, the light filter F_2, placed between the cell and the diffraction monochromator, cut off the resonance lines and passed the investigated bands. Thus, the aggregate of the filters F_1 and F_2 constituted effectively a system opaque to the entire emission spectrum of the source. In fact, when the cell was kept at room temperature ($p \approx 10^{-7}$ Torr) and the source was turned off, neither bands nor lines were registered in the spectral regions 10 500 and 6500 Å at the maximum sensitivity of the measuring circuit. When the cell was heated to 230–300° C, corresponding to $p = 2.5 \times 10^{-2} - 3 \times 10^{-1}$ Torr, an intense λ 10 500 Å molecular band appeared, together with a λ 6500 Å band which was less intense by approximately three orders of magnitude. Their origin is uniquely connected with the population of the atomic $4P$ states in the cell.

By placing stepped attenuators between the lamp and the cell, we obtained a linear dependences of $I_{1.05}$ or $I_{0.65}$ on the intensities of the resonance lines, and consequently on the concentration N_{4P} at constant p.

When the concentration N_{4S} (the pressure p) increased, $I_{1.05}$ and $I_{0.65}$ increased while N_{4P} was kept approximately constant. It was impossible to establish rigorously the character of this dependence, since the values of N_{4P} could be maintained only very approximately. It is necessary, however, to obtain this relation if the reactions (5) and (6) are to be separated from the possible three-particle process of generation of excited molecules.

$$K^*(4P)+2K(4S) \to K_2^*(^1\Sigma_u^+, {}^1\Pi_u)+K(4S), \qquad (7)$$

the yield of which is proportional N_4S^2.

This question was solved by the next experiment, in which measurements of the absolute intensities of the bands emitted resonantly by the excited potassium vapor were accompanied by measurements of the concentrations N_{4P} at various values of N_{4S}.

A cylindrical cell with potassium vapor (Fig. 1c), 20 cm long and 2 cm in diameter, was placed in a cylindrical cavity along the surface of which were located six potassium discharge tubes which produced a uniform radiation flux over the entire lateral surface of the cell (the figure shows only two of these radiating tubes). A cylindrical light filter with a pass band 7000–8500 Å was placed between the radiators and the cell, i.e., just as in the preceding case, the resonant radiation was passed to the cell but the molecular bands were cut off. The entire described system replaced the discharge lamp of the measurement setup of Fig. 1a. The procedure for the optical measurements was the same as before. The intensity of the populating flux from the radiator was chosen such that, at each value of N_{4S}, the concentrations N_{4P} could be measured by the reversal method. The described construction of the instrument ensured spatial homogeneity of the values of N_{4P} in the cell.[11]

The measurements were performed in the range $N_{4S} = 1 \cdot 10^{14} - 3 \cdot 10^{15}$ cm^{-3}, which corresponds to variation of T from 467 to 553 K. The results for each of the bands are shown in Fig. 5 in the form of plots of $I_{1.05}/N_{4P}$, and $I_{0.65}/N_{4P}$ against N_{4S} (the ordinate axis represents the absolute values of the indicated quantities). The linear character of the plots in Fig. 5 demonstrates that the generation of the electron-excited molecules is the result of the two-particle processes (5) and (6).

When the experiment is performed in a cell, there is no quenching of the excited molecules by the electrons (the concentrations of the latter are smaller by several orders of magnitude than the value of n_e under discharge conditions[11]), and consequently the absolute band intensities $I''_{1.05}$ and $I''_{0.65}$ are equal to the rates of the processes (5) and (6), which in turn are given by

$$\Gamma_\Sigma'' = \langle \sigma_\Sigma v_0 \rangle N_{4P} N_{4S} = I''_{1.05}, \quad \Gamma_\Pi'' = \langle \sigma_\Pi v_0 \rangle N_{4P} N_{4S} = I''_{0.65}, \qquad (8)$$

where σ_Σ and σ_Π are the cross sections of the processes and v_0 is the relative thermal velocity of the atoms. In accordance with (8), the slopes of the lines in Fig. 5 yield the following rate contants of the photorecombination processes

$$\langle \sigma_\Sigma v_0 \rangle = (8 \pm 1) \cdot 10^{-12}, \quad \langle \sigma_\Pi v_0 \rangle = (5 \pm 0.6) \cdot 10^{-15} \text{cm}^3 \text{ sec}^{-1}.$$

At $T \approx 500$ K. These values lead to the effective cross sections

$$\bar{\sigma}_\Sigma = \langle \sigma_\Sigma v_0 \rangle / \bar{v}_0 = (1.6 \pm 0.2) \cdot 10^{-16},$$
$$\bar{\sigma}_\Pi = \langle \sigma_\Pi v_0 \rangle / \bar{v}_0 = (1 \pm 0.2) \cdot 10^{-19} \text{cm}^3.$$

The indicated errors of $\bar{\sigma}_\Sigma$ and $\bar{\sigma}_\Pi$ correspond to the deviations of the experimental points from the straight lines in Fig. 5. These deviations do not exceed the total error of the method of measuring the absolute intensities of the bands and of the method of determining the con-

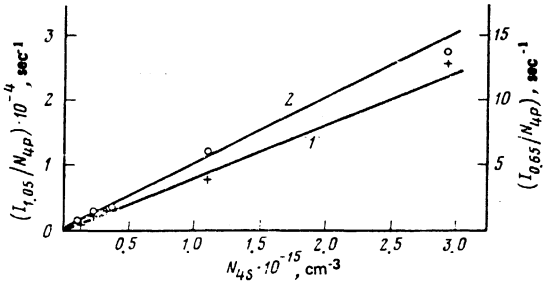

FIG. 5. Plots of $I_{1.05}/N_{4P}$(1) and $I_{0.65}/N_{4P}$(2) against N_{4S}.

centrations N_{4P} by reversal of the spectral lines.

Attention is called to the very large cross section of the process (5). We know of only one qualitative result that attests to high effectiveness of photorecombination of atoms in optically excited cesium vapor—the data of Bonch-Bruevich *et al.*[12], who attribute its feasibility to the existence of prolonged quasi-finite motions of the particles next to one another. In our opinion, the experimental cross section given in Ref. 12 for the recombination process is strongly overestimated ($\approx 10^{-14}$ cm^2). In fact, at this value of the cross section, a cesium discharge, under perfectly ordinary conditions ($p = 0.1$ Torr and $N_{6P} = 5 \times 10^{12}$ cm^{-3}, see Ref. 9), would emit the molecular bands observed in Ref. 12 at an intensity commensurate with the intensity of the $6P - 6S$ resonance line, but this was not observed in the experiment. If we compare the rate constant of the process (5) with the constants of photorecombination processes accompanied by formation of molecules in the electronic ground state (see, e.g., the review[13]), then in the largest of them ($\approx 10^{-17}$ cm^3 sec^{-1} for the reaction $N + O \rightarrow NO(X^2\Pi) + h\nu$) turn out to be smaller than many orders of magnitude.

The possible channels of populating the $^1\Pi_u$ and $^1\Sigma_g^+$ states are shown schematically in Fig. 6 (the molecular terms of this figure were taken from Ref. 1). As already noted, in accordance with the identification of Ref. 4, the molecular band λ 6500 Å corresponds to the electronic transition $^1\Pi_u \rightarrow \Sigma_g^+$ (dashed arrow 1), and the λ 10 500 Å band corresponds to its transition $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ (dashed arrow 2). The population of the state $^1\Sigma_u^+$ in the photorecombination of the atoms in the $4P$ and $4S$ states can result from radiative transitions from quasimolecular states, corresponding to both attraction (arrow 1) and repulsion (arrow 2). The population of the state $^1\Pi_u$ can come only from the repulsion state (arrow 3). The photorecombination rate of the atoms via an attracting quasibound molecular state greatly exceeds the photorecombination rate via a repulsion state,[13] and this appears to be the reason why the cross section of the process (5) is larger by three orders of magnitude than the cross section of the process (6). This explanation is only tentative, and the cause of the high effectiveness of the process (5) calls for further experimental and theoretical studies.

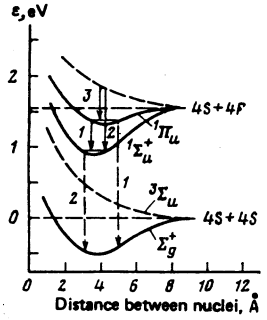

FIG. 6. Terms of the K_2 molecule.[1]

CONCLUSION

The dashed curves of Figs. 2a and 2b show the rates of the processes (5) and (6), calculated from (8) on the basis of the cross sections obtained above and the concentrations N_{4P} measured in the discharge (from Fig. 3). The calculated values of Γ_Σ'' at low discharge currents agree fully with the experimental values of $I_{1.05}$ both as to their dependence of J_d and p, and in absolute magnitude, i.e., in this case $\Gamma_\Sigma = \Gamma_\Sigma''$. The reason why Γ_Σ'' exceeds the intensities $I_{1.05}$ at large discharge currents is the quenching of the $^1\Sigma_u^+$ states by the plasma electrons.

Allowance for this process in accordance with (3) leads to the following expression for the intensity of the λ 10 500 Å band:

$$I_{1.05} = \langle \sigma_2 v_0 \rangle N_{4P} N_{4S} / (1 + \sigma_2 \tau_{e\Sigma} n_e v_e).$$

Substituting in this expression the value $\sigma_2 \tau_{e\Sigma} = 1.5 \cdot 10^{-19}$ cm^2 and the values of n_e and v_e measured by a probe method, we obtain full agreement between the experimental and calculated curves of Fig. 2a in the entire range of J_d (dash-dot curves). If we now tentatively put $\sigma_2 \approx 2 \times 10^{-14}$ cm^2 then we obtain from $\sigma_2 \tau_{e\Sigma}$ the value $\tau_{e\Sigma} \approx 7 \cdot 10^{-6}$ sec. This time is unusually long compared with the lifetimes of the electron-excited alkali molecules with respect to allowed radiative transitions. For example, it exceeds the radiative lifetimes of the $^1\Pi_u$ state of the K_2 molecule by almost three orders of magnitude.

This circumstance can be due to the fact that the estimated value of $\tau_{e\Sigma}$ does not characterize the natural lifetime of the $^1\Sigma_u^+$ state, and pertains to a longer-lived intermediate state, through which it is populated in the course of photorecombination of the atoms. In accordance with the calculations made by Roach[14] for the terms of the alkali molecules, such an intermediate state can be the triplet state $^3\Sigma_g^+$, which lies somewhat higher than the state $^1\Sigma_u^+$. The intercombination transitions between these states can result from lifting of the forbiddeness in collisions of molecules with atoms (a similar lifting of forbiddeness for other singlet-triplet transitions is observed experimentally in cesium and rubidium vapors[3,15]). If the indicated situation is indeed realized, then the lifetime 7×10^{-6} sec estimated by the method described above pertains to the state $^3\Sigma_g^+$, and the lifetime of the state $^1\Sigma_u^+$ can be much shorter. Inasmuch as under these conditions the intensity $I_{1.05}$ should be equal to the intensity of the intercombination transitions, we are justified in ascribing the effective photorecombination cross section σ_Σ obtained in the present study to the population of either the $^1\Sigma_u^+$ or the $^3\Sigma_g^+$ state. It is important to note that the population of the excited state (be it $^3\Sigma_g^+$ or $^1\Sigma_u^+$) to which a lifetime $\approx 7 \times 10^{-6}$ sec corresponds is approximately equal to $7 \times 10^{-6} I_{1.05}$ cm^{-3} and exceeds by almost six orders of magnitude the population of the $^1\Pi_u$ state, which is equal to $10^{-8} I_{0.65}$ cm^{-3}. From the intensities $I_{1.05}$ shown in Fig. 2a we see that the population of the long-lived electron-excited molecules under the conditions of our experiment reaches $\approx 10^{11}$ cm^{-3}. A prelim-

inary analysis shows that the ionization of these states by electrons can play an essential role in the generation of K_2^+ ions in a potassium low-pressure discharge plasma.

As seen from Fig. 2b, the process (6) predominates in the population of the $^1\Pi_u$ state only at the largest pressure p of the potassium vapor in our experiment. With decreasing p, the relative role of this process decreases. The difference values $I_{0.65}-\Gamma_\Pi''=\Gamma_\Pi-\Gamma_\Pi''$, determined from Fig. 2b, are shown by the dashed curves in Fig. 4b as functions of J_d and p. The relative values of Γ_Π' calculated from (4), shown in Fig. 4b, are normalized in a single regime ($J_d=0.3$ A and $p=4.4\times 10^{-4}$ Torr) to the absolute values of $\Gamma_\Pi-\Gamma_\Pi''$. It is seen that the dashed and solid curves of Fig. 4b are in satisfactory agreement, so that we can put $\Gamma_\Pi'=\Gamma_\Pi-\Gamma_\Pi''$. It follows therefore that in the region of lower values of p the predominant mechanism of populating the $^1\Pi_u$ state is electron-excitation of the molecules from the ground electronic state. If we now use the values of N_m from Ref. 10, then the normalization performed above yields $a_\Pi\approx 4\times 10^{-17}$ cm^2 eV^{-1}.

Thus, our experimental investigations have shown that the population of the $^1\Sigma_u^+$ state of the molecule K_2 is due to an intense photorecombination of the potassium atoms in the $4P$ and $4S$ states, and this of course, is the cause of the anomalously large brightness of the λ 10 500 Å band emitted by the potassium discharge. The less intense λ 6500 Å band is due to photorecombination of the $^1\Pi_u$ state and to electronic excitation of the molecules. Since the electron-excited molecules intensely generated in the process (5) go over spontaneously to the ground molecular state $^1\Sigma_g^+$, one should expect the concentrations of the dimers of K_2 in potassium vapor to deviate from their thermodynamic-equilbrium values.

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