SODIUM LEVEL POPULATION INVERSION IN EMISSION FROM A MIXTURE OF SODIUM AND MERCURY VAPORS

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As long ago as in 1936 one of us, together with Ferkhmin,[1] observed an appreciable increase in the intensity of the higher terms of the subsidiary series of sodium, resulting from impacts of the second kind in the emission from a mixture of sodium and mercury vapors. Recently Rautian and Sobelman[2] reached the conclusion that in sensitized fluorescence of a mixture of sodium and mercury vapors[3] negative absorption is possible for the 8P → 8S and 8P → 7S 30.2 and 7.77 μ lines. Besides, since the intensities of the lines of the principal series have not yet been measured, these authors made a theoretical estimate of the 8P level population.

We measured the populations of the S, P, and D levels of Na I in the emission from a mixture of sodium and mercury vapors. The emission was excited by a high-frequency discharge (6—50 Mcs) in cylindrical tubes 18—25 mm in diameter and 60—80 mm long, using external electrodes. The tubes were made of glass resistant to sodium vapor, fused quartz, and molybdenum glass with fused-in sapphire windows[4]. For measurements in vapor of pure sodium, we used tubes with one stub, containing metallic sodium. For measurements in a mixture of sodium and mercury vapors, we used tubes with two stubs, one containing mercury and the other sodium. The tubes and the stubs could be heated independently by individual electric furnaces. To maintain a stable discharge, helium was added at a pressure ~ 0.05 mm Hg.

The populations of the S and D levels were determined from the absolute intensities of the lines of the lateral series, which were measured photoelectrically (for the brighter doublet component), by comparison with the continuous spectrum from a calibrated band lamp. To find the population of the P levels we determined the absolute intensity of the doublets of the principal series (summary intensity, the doublets were not resolved) by a photographic method as compared with the intensity of the continuous spectrum from the band lamp and a hydrogen lamp. In both cases corrections were introduced for reabsorption[5] and for absorption in the windows.

In calculating the concentration of the excited atoms of sodium, we used the values of transition probabilities calculated by a group of staff members of the Latvian State University under the leadership of E. M. Anderson, to whom the authors are deeply grateful for these data.

The absolute values of the populations N_i depend strongly on the conditions of the discharge, namely the current density and the partial pressures of the sodium and mercury vapors. The regulation of the partial pressures entails considerable difficulties, since a sodium amalgam is readily formed, the saturation vapor tension over which differs greatly from the vapor tension over the pure metals. Nonetheless the rather characteristic variation of the line intensity on going from the emission of pure sodium to that of a mixture of sodium and mercury vapor was well duplicated.

Table I lists the average level populations of sodium, obtained from several measurements made under similar conditions. For the T and D levels we give the summary values of the populations for both components of the doublet terms. As can be seen from the table, the populations of the sodium levels (except for the highest ones) increase appreciably on going from pure sodium emission to that of a mixture of sodium and mercury vapors. The greatest increase is in the populations of the 7S, 9S, 6D, and 6P levels. Population inversion is observed in all these levels. Accordingly, negative absorption should take place for the infra-red Na I series corresponding to transitions from these levels to the lower ones.

The 8P level is weakly populated, and under the conditions of our experiment one therefore cannot observe negative absorption on the 8P → 8S and 8P → 7S Na I lines with wavelengths 30.2 and 7.77 μ.

The absorption coefficient k_0 for the center of the lines was calculated under the assumption of a Doppler line contour. Table II lists the values of k_0 for those lines for which $k_0 < -0.001$ cm^{-1}.

Finally, we could estimate the absolute values of the effective cross sections of the second kind. In accordance with the previous conclusion[3] it can be assumed that the effective cross sections of impacts of the second kind are appreciable only when the excitation energy differences between the two colliding particles are smaller than 0.1 eV. In this case the effective cross sections are larger when the energy is added at the expense of the kinetic energy of the particle, than in cases when the

Table I. Populations N_i of the sodium levels, in cm^{-3}, in the emission of pure sodium and that of a mixture of sodium and mercury vapors

Level	$10^{-6} N_i$		Level	$10^{-6} N_i$		Level	$10^{-6} N_i$	
	Na	Na + Hg		Na	Na + Hg		Na	Na + Hg
—	—	—	—	—	—	4 *P*	3.04	77.2
—	—	—	5 *D*	2.34	7.24	5 *P*	2.17	22.6
6 *S*	—	10.8	6 *D*	2.22	13.10	6 *P*	1.33	38.6
7 *S*	0.91	28.7	7 *D*	1.80	7.09	7 *P*	0.30	2.41
8 *S*	0.67	2.43	8 *D*	1.10	4.39	8 *P*	—	1.27
9 *S*	0.51	6.40	9 *D*	0.68	2.41	9 *P*	—	0.23
10 *S*	0.26	—	10 *D*	0.39	0.74	10 *P*	—	0.21
11 *S*	0.11	0.09	11 *D*	0.24	—	—	—	—
12 *S*	0.04	—	12 *D*	0.15	—	—	—	—

Table II. Negative absorption coefficients for sodium lines

Transitions	λ, μ	$-10^2 k_0$, cm^{-1}	Transitions	λ, μ	$-10^2 k_0$, cm^{-1}
$7^2S_{1/2} \rightarrow 6^2P_{3/2}$	14.002	1.0	$9^2S_{1/2} \rightarrow 7^2P_{3/2}$	9.678	0.21
$8^2S_{1/2} \rightarrow 7^2P_{3/2}$	23.424	0.21	$6^2P_{1/2} \rightarrow 5^2D_{3/2}$	38.500	0.76
$9^2S_{1/2} \rightarrow 8^2P_{3/2}$	36.31	1.4	$6^2P_{3/2} \rightarrow 5^2D_{3/2,5/2}$	39.279	4.2

excess excitation energy goes over into kinetic energy. An important role in the general process of populating the levels is played by cascade transitions.

According to our measurements, the intensity of the higher terms of both the subsidiary and the principal series of the sodium, for which impacts of the second kind with the mercury atoms do not play any role, do not change appreciably on going over from sodium emission to that of a mixture of sodium and mercury vapors. It follows therefore that the excitation of the sodium levels as a result of collisions with the electrons is approximately the same in either pure sodium vapors or in a mixture of sodium and mercury vapors. On the basis of this circumstance, we can write the following expression for the effective cross section Q of impacts of the second kind:

$$Q = \left\{ [N_k\,(\mathrm{Na}) - N'_k\,(\mathrm{Na})] \times \sum_{r=k-1}^{0} A_{kr} - \sum_{l=k+1}^{\infty} [N_l\,(\mathrm{Na}) - N'_l\,(\mathrm{Na})]\, A_{lk} \right\} \times [N_0\,(\mathrm{Na})\, N\,(\mathrm{Hg}^*)\, \alpha \bar{v}]^{-1},$$

where the prime denotes that the corresponding concentration pertains to pure sodium vapors; $\bar{v}$ is the relative velocity of the gliding particles, and α is a coefficient that determines the fraction of the colliding particles having a sufficient kinetic energy to bring about the given transition.

The concentrations of the excited mercury atoms N(Hg*) for the states $^3P_1$ and $^3P_0$ were determined from the reabsorption of the lines of Hg I with λ = 4358 and 4047 Å; the concentrations of the normal atoms of sodium, N_0(Na), were measured by the method of anomalous dispersion. Under the conditions of our experiments we had:

$$N\,(\mathrm{Hg}^*_{^3P_1}) = 4.8 \cdot 10^{10}\ \mathrm{cm}^{-3}; \quad N\,(\mathrm{Hg}^*_{^3P_0}) = 1.6 \cdot 10^{11}\ \mathrm{cm}^{-3}; \quad N_0\,(\mathrm{Na}) = 1.0 \cdot 10^{13}\ \mathrm{cm}^{-3}.$$

From these data we obtain

$$Q\,(9S) = 0.7 \cdot 10^{-16}\ \mathrm{cm}^2, \quad Q\,(7S) = 5 \cdot 10^{-16}\ \mathrm{cm}^2.$$

It is assumed here that the 9S level of the sodium is excited by collisions with the mercury atoms in the state $^3P_1$ (ΔW = +0.021 eV), and the level 7S is excited in the state $^3P_0$ (ΔW = +0.046 eV).

We could not carry out the corresponding calculations for the excitation of the D levels, since the populations of the F levels from which the intense transitions to D levels took place remained undetermined. The 6P level is populated essentially as a result of cascade transitions from nS and nD levels.

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ON KINETIC TRANSITIONS

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IT is known that when a thermodynamic force X (a gradient of an electric or chemical potential, a temperature gradient, etc.) acts on a system in thermodynamic equilibrium, a generalized flow J develops which is proportional to that force. We wish to note that in many cases when X is increased above a certain critical value X_c the state of the system becomes unstable and several degrees of freedom are created in it—periodic internal motions develop; the function J(X) while remaining continuous, has a break at the point X_c. (We do not consider here transitions in which the function J(X) is itself discontinuous.)

Examples of such a change in the flow J are, for example, the break in the curve of the heat flow upon the start of convection in an ordinary [1] and a conducting [2] (in a magnetic field) fluid, the break in the curve of the "effective viscosity" when eddies form in a fluid between rotating cylinders, [3] the break in hydrodynamic resistance during magnetohydrodynamic flow, [4] the break in the characteristic of a gas discharge in a magnetic field, [5] the break in the dependence of current upon voltage in a magnetic field in a solid, [6] etc.

The physical reason for the appearance of the break is the following: the presence of internal motions in the supercritical region leads to a spatial redistribution of force X in the system, in which the changes in the force δX are proportional, when the supercriticality $X - X_c$ is small, to the square of the amplitude of the internal motions ξ (there is no linear term, owing to the periodicity of the motion); at $X > X_c$, the amplitude increases until the condition $\delta X \sim X - X_c$ begins to be fulfilled, so that $\xi \sim \sqrt{X - X_c}$, and the supplementary flow δJ, quadratic with respect to ξ, is proportional to the supercriticality: $\delta J \sim X - X_c$. Consequently, the function J(X) is continuous at $X = X_c$ but its first derivative has a finite discontinuity.

$$(J)_{X_c+0} - (J)_{X_c-0} = \Delta J = 0 \tag{1}$$

$$(\partial J / \partial X)_{X_c+0} - (\partial J / \partial X)_{X_c-0} = \Delta (\partial J / \partial X) \neq 0, \infty. \tag{2}$$

The critical value X_c depends, generally speaking, on a set of external parameters α. If we differentiate (1) with respect to α, we get

$$\Delta (\partial J / \partial \alpha)_X = - (dX_c/d\alpha)\, \Delta (\partial J/\partial X)_\alpha; \tag{3}$$

thus the partial derivative $\partial J/\partial \alpha$ is also discontinuous at $X = X_c$, the relation (3) can be used both for an experimental check on the nature of the transition [if the two jumps $\Delta(\partial J/\partial X)$ and $\Delta(\partial J/\partial \alpha)$ and the slope of the transition curve $X_c = X_c(\alpha)$ are measured] and to express some discontinuities through others.

When two thermodynamic forces, X_1 and X_2, are present, the kinetic transition takes place on the curve $\Phi(X_{1c}, X_{2c}) = 0$. In that case the jumps $\Delta(\partial J/\partial X)$ are connected by relations analogous to (3):

$$\begin{aligned} \Delta (\partial J_1/\partial X_1)_{X_2} &= - (dX_{2c}/dX_{1c})\, \Delta (\partial J_1/\partial X_2)_{X_1}; \\ \Delta (\partial J_2/\partial X_1)_{X_2} &= - (dX_{2c}/dX_{1c})\, \Delta (\partial J_2/\partial X_2)_{X_1}. \end{aligned} \tag{4}$$

Eliminating dX_{2c}/dX_{1c}, we get

$$\Delta (\partial J_1/\partial X_1)_{X_2}\, \Delta (\partial J_2/\partial X_2)_{X_1} = \Delta (\partial J_2/\partial X_1)_{X_2}\, \Delta (\partial J_1/\partial X_2)_{X_1} \tag{5}$$

Equations (5) are analogous to the Ehrenfest relations [7] between the jumps of the second derivatives of thermodynamic potentials at the point of a second-order thermodynamic transition.

As an example, let us examine the convection of a viscous conducting fluid, heated from below, between horizontal plates in an external magnetic field. In that case the difference in temperatures of the plates Θ plays the role of the generalized force X, and the heat flow between the plates q is the flow J. If we consider the magnetic field H as the parameter α, we get from (3):

$$\Delta \left(\frac{\partial q}{\partial H}\right)_\Theta = - \frac{d\Theta_c}{dH}\, \Delta \left(\frac{\partial q}{\partial \Theta}\right)_H. \tag{6}$$

The flow in the transcritical mode is composed of mo-