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Fluorescence Intensity Ratio of Sodium Doublet Observed in the Optical Dissociation of Sodium Iodide Vapor*

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The intensity ratio D_2/D_1 for the sodium doublet has been measured for radiation from excited sodium atoms which result from the optical dissociation of sodium iodide vapor by ultraviolet light in the 2082→2500 A region. With shorter wavelength ultraviolet light as exciting source, the D_2/D_1 ratio is 0.98 and increases to above 1.5 with longer exciting wavelengths. Addition of foreign gases cause the observed D_2/D_1 ratio to increase to 1.89 for large foreign gas pressure. Cross sections for the transfer of excited sodium atoms from the $3^2P_{\frac{3}{2}}$ to the $3^2P_{\frac{1}{2}}$ state and vice versa due to collisions with foreign molecules have been measured as they depend on the relative velocity between excited sodium atom and foreign molecule. The Doppler broadening of the separate D lines emitted in the atomic fluorescence of sodium iodide has been estimated from absorption measurements. Both lines show equal broadening within the experimental error of the observations. Measurements were made with a photomultiplier tube. The sodium doublet was resolved with a reflection grating monochromator.

I. INTRODUCTION

THE fluorescence of Na atoms resulting from the optical dissociation of sodium iodide has been studied by several investigators.[1–6] This study is concerned with the ratio of the D_2 and D_1 spectral lines excited in the atomic fluorescence. This ratio is found to depend on the energy of the ultraviolet photon which dissociates the sodium iodide molecule and excites the sodium atom. The cross sections in collision with various gas molecules for transfer of excited sodium atoms from the $3^2P_{\frac{3}{2}}$ state to the $3^2P_{\frac{1}{2}}$ state and the reverse as they depend on the velocity of the sodium atoms have also been measured. Previous studies of the transfer by collision with foreign molecules between the upper states of the D lines have been made by Wood[7,8] and Lochte-Holtgreven.[9] The effects of Doppler broadening of the D_2 and D_1 lines were measured to discover whether there is a significant difference of velocity of dissociation for the excited sodium atoms in the $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$ states respectively. The Doppler broadening due to velocity of dissociation of the unresolved D lines in atomic fluorescence has previously be investigated by Hogness and Franck.[2]

II. EXPERIMENTAL

The method of excitation of the atomic fluorescence of sodium iodide was similar to that described previously.[6] An evacuated vertical fused quartz tube containing sodium iodide was heated in an electric furnace. The furnace and tube were made with fused quartz windows to allow the ultraviolet light to enter the region above the salt in the tube. Temperatures of 600° to 650°C provide sufficient vapor pressure of the salt so the fluorescence can be measured. Diffusion of the salt toward the end of the tube connected to the vacuum system eventually forms a porous salt plug which prevents further rapid sublimation of the salt. If the central portion of the tube where the ultraviolet light enters is kept hotter than the ends of the tube, no condensation of salt occurs on the windows. Since the middle of the tube is hotter than the ends, the surfaces of the salt supply and the porous plug adjust their relative position in the furnace by sublimation and condensation until the surfaces are almost at the same temperature.

The fluorescence was excited by either a water-cooled hydrogen arc or by a condensed spark using zinc, cadmium or iron electrodes. A fused quartz condensing lens focused a cone of ultraviolet light into the tube. The fluorescence, consisting of the two D lines, was resolved by a 500-mm focal length Bausch & Lomb reflection grating monochromator with a dispersion of 16.5 A per mm. The slits were set at 0.25 mm. A cam arrangement allowed rapid change of setting between the D_2 and D_1 lines. A 1P21 photomultiplier tube at the exit slit of the monochromator responds to the fluorescent light. The amplified signal from the photomultiplier was either displayed and photographed on an oscilloscope screen or recorded by an $x-y$ recorder. To determine a D_2 to D_1 ratio for one experimental condition, ten to twenty recordings, depending on the stability of the source, were made by rapidly alternating between the D_2 and D_1 lines. The error due to the small difference in spectral sensitivity of the 1P21 photomultiplier tube for the D_2 and D_1 lines was considered smaller than the errors due to experimental conditions and no correction was made for this difference in spectral sensitivity. The linearity of response of

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[2] T. R. Hogness and J. Franck, Z. Physik **44**, 26 (1927).

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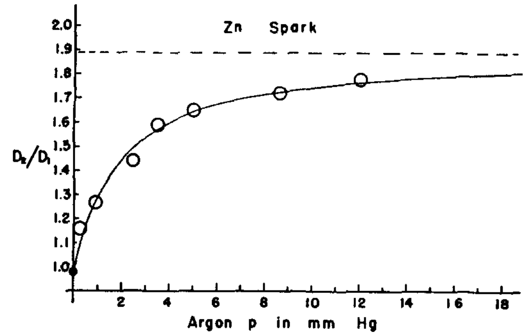

FIG. 1. Ratio of intensity D_2/D_1 of sodium D lines from atomic fluorescence of sodium iodide excited by Zn spark in the presence of different pressures of argon gas.

the photomultiplier tube in the spectral range used and of the recording circuit was checked by varying the slit widths of the monochromator using a steady source and found to be well within the limit of errors set by the stability of the fluorescence to be measured. The background due to scattered light and furnace glow was checked by placing a glass plate in the exciting ultraviolet beam to stop the fluorescence. The background which remained was found to be too small to measure. With the salt tube cold and the ultraviolet source on, no signal was detected.

The Doppler broadening effect on the D_2 and D_1 lines caused by the velocity of dissociation of the excited sodium atoms was studied by measuring the absorption of the two lines in passing through a tube containing sodium vapor. The sodium vapor pressure was controlled by changing the temperature of the absorption tube. The k_0l values[10] were kept low enough so that only the Doppler broadening would have an appreciable effect. The output of a thermocouple which measured the temperature of the sodium absorption tube was connected directly to the $x-y$ recorder so that the intensities of the D_2 and D_1 lines after passing through the absorption tube could be recorded directly as a function of temperature of absorption cell.

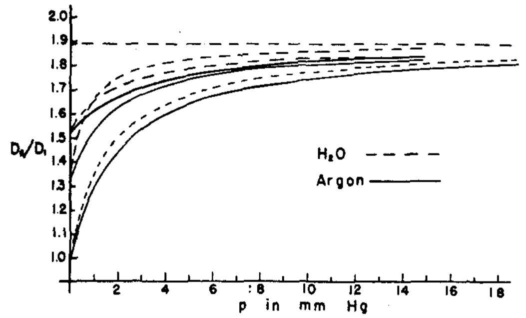

FIG. 2. Experimental curves of intensity ratio D_2/D_1 of sodium D lines from atomic fluorescence of sodium iodide in the presence of different pressures of water vapor and argon gas. Values at zero pressure for different sources: Zn spark 0.98, Cd spark 1.33, Fe spark 1.52.

The measurements of the pressures of the argon gas and water vapor used in studying transfers by collision between the upper states of the D lines were made with a mercury manometer or a McLeod gauge for argon and by a controlled temperature bath for the water vapor pressure.

III. RESULTS AND INTERPRETATION

Figure 1 shows a typical result of the variation of the D_2/D_1 ratio for the atomic fluorescence of sodium iodide in the presence of different pressures of argon. With no argon gas present, the D_2/D_1 ratio when excited by a zinc spark was 0.98. The ratio approach 1.89 at high pressures (200 mm Hg) of argon gas.

Figure 2 shows the curves without experimental points for water vapor and for argon gas when the fluorescence was excited by three separate spark sources. The effective wavelengths of the exciting sparks were taken as: zinc 2082 A, cadmium 2232 A, and iron 2400 A. From reference 6 this means that zinc and cadmium sources correspond to dissociative transitions at internuclear distances for the sodium iodide molecule which are less than the equilibrium internuclear distance. The iron source corresponds to dissociative transitions at greater than equilibrium internuclear distance. Different trends of the upper repulsive potential curve for sodium in the $3^2P_{3/2}$ or $3^2P_{1/2}$ states together with the normal iodine atom are apparently responsible for the different D_2/D_1 ratios measured when no foreign gas was present but when the different spark sources were used to excite fluorescence. It is clear from the data that low excess energies of dissociation favors the $3^2P_{3/2}$ state for the sodium atom resulting from dissociation of the sodium atom by an ultraviolet photon.

In order to calculate the cross section for transfer by collision with foreign molecules between the upper states of the two D lines reference is made to Fig. 3. For any steady exciting source, let N_2 and N_1 represent the number per second of sodium atoms resulting from dissociation entering the $3^2P_{3/2}$ state and $3^2P_{1/2}$ state respectively in the volume observed. For any source (Zn, Cd, Fe spark)$N_2/N_1=K_{\text{source}}$. The atoms can leave either of the excited states by emission of a D line, or by collision and transfer to the other state without emission. Equilibrium populations n_2 and n_1 will result for the two states as shown very shortly after the source of excitation is turned on. The coefficients a_2 and a_1 are defined as the number of expected inelastic collision with foreign molecules per second per excited sodium atom per mm Hg of pressure of foreign gas present for the $3^2P_{3/2}$ and $3^2P_{1/2}$ state, respectively. τ is the mean life of the excited states taken as being 1.61×10^{-8} sec for both states. D_2 and D_1 represent the variable intensities (in photons per second for the volume observed) of the two D components under

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[10] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, England, 1934), first edition, p. 102.

varying pressures of foreign gas. In equilibrium, the number entering and leaving a state per second are equal.

$$N_2+n_1a_1p=n_2a_2p+\frac{1}{\tau}n_2,$$

$$N_1+n_2a_2p=n_1a_1p+\frac{1}{\tau}n_1,$$

which can be written

$$\frac{D_2}{D_1}=\frac{n_2}{n_1}=\frac{(K_{\text{source}}+1)a_1p+K_{\text{source}}}{(K_{\text{source}}+1)a_2p+1}. \tag{1}$$

K_{source} is measured experimentally for each of the sources with zero foreign gas pressure. (Values of K_{source} obtained from Fig. 2 are Zn spark 0.98, Cd spark 1.33, and Fe spark 1.52.) At very large pressures, it can be seen from Eq. (1) that

$$[D_2/D_1]_{\text{large }p}\cong\frac{a_1}{a_2}.$$

Within experimental error, the value of a_1/a_2 for both argon and water vapor as foreign gas and for all spark sources was found to $a_1/a_2=1.89$. This value is indicated by the dashed horizontal asymptote in Figs. 1 and 2. The value 1.89 can be compared with the value 2.00 for the ratio of the statistical weights of the $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$ states. By using $a_1=1.89\ a_2$, one can eliminate a_2 from Eq. (1). The experimental value of a_1 can then be determined for each experimental point of measured foreign gas pressure and D_2/D_1 ratio. The average of these a_1 values for each different exciting source and different foreign gas was used to plot the solid curves shown in Figs. 1 and 2 by the use of Eq. (1).

From the definition of a_1, we have $a_1p=Z_1$ where Z_1 is the expected number of collisions per second per atom in the $3^2P_{\frac{1}{2}}$ state that leads to transfer to the $3^2P_{\frac{3}{2}}$ state. Similarly, $a_2p=Z_2$. Let the gas kinetic expression[11] for Z_1 be

$$Z_1=\pi^{\frac{1}{2}}N_F\sigma_1^2\alpha\psi(X)/X, \tag{2}$$

where N_F is the number of foreign molecules per cm³, $\pi\sigma_1^2$ is the collision cross section for transfer from the $3^2P_{\frac{1}{2}}$ to the $3^2P_{\frac{3}{2}}$ state, α is the most probable speed of the foreign molecules, $V_{\text{Na}'}$ is the most probable speed of the excited sodium atoms, and $X=V_{\text{Na}'}/\alpha$ and

$$\psi(X)=X\exp[-X^2]+(2X^2+1)\int_0^X\exp[-y^2]dy.$$

The values of $V_{\text{Na}'}$ were found to be the same by measurements of Doppler broadening for both excited states and were calculated from the data in reference 6 as $V_{\text{Na}'}$ (Zn) = 24.3×10⁴ cm/sec, $V_{\text{Na}'}$ (Cd) = 15.9×10⁴ cm/sec, and $V_{\text{Na}'}$ (Fe) = 5.74×10⁴ cm/sec. The temperature of the fluorescence tube was 607°C. From Eqs. (1) and (2) and kinetic theory, we obtain

$$\pi\sigma_1^2=1.83\times10^{-20}a_1TX/\alpha\psi(X), \tag{3}$$

where T is the absolute temperature. Values of α at 607°C, were $\alpha(H_2O)=9.01\times10^4$ cm/sec and $\alpha(A)=6.05\times10^4$ cm/sec. The values of $\pi\sigma_1^2$ were calculated from Eq. (3).

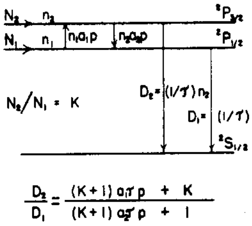

FIG. 3. Schematic energy level diagram and transitions by collision and radiation for the D lines of sodium resulting from the atomic fluorescence of sodium iodide in the presence of nonquenching gas. For definitions of symbols see text.

The most probable relative speed of approach of excited sodium atom and foreign molecule V_R was calculated. Figure 4 shows $\pi\sigma_1^2$ plotted against V_R. With the exception of one point, the cross sections tend to decrease with increase in V_R as other quenching cross sections[6] have been found to decrease.

It will be seen from the foregoing that $\pi\sigma_1^2(3^2P_{\frac{1}{2}}\rightarrow3^2P_{\frac{3}{2}})=1.89\pi\sigma_2^2(3^2P_{\frac{3}{2}}\rightarrow3^2P_{\frac{1}{2}})$. This is not in agreement with the estimate made in reference 10, p. 214, on the data taken from Lochte-Holtgreven's[9] work using argon. Lochte-Holtgreven's measurements, however, were made at lower relative velocities of excited atoms and foreign molecules. Both the previous and present work give values for the cross section of the order of 10^{-14} cm which corresponds to energy transfers at an average distance of approach of 6 A. The cross sections for the $(3^2P_{\frac{1}{2}}\rightleftarrows3^2P_{\frac{3}{2}})$ transitions are approximately two times as large as the quenching cross sections for the $(3^2P\rightarrow2^2S)$ transitions observed in previous studies.[6]

A study of the Doppler broadening of the two D lines was made by comparing the absorption of each line in passing through a layer of sodium vapor. The absorptions were all observed at approximately the same k_0l values (corresponding to 7 cm thickness of sodium vapor at 110°C) and are shown in Table I.

Within the experimental error, the ratio of absorption of the D_2 to the D_1 line is 2:1 for all sources. Thus there can be no large difference in the individual Doppler

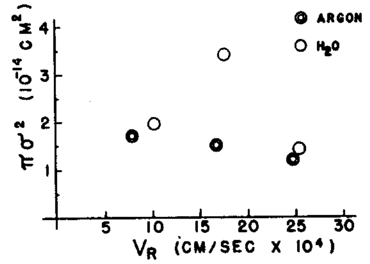

FIG. 4. Transfer collision cross sections $\pi\sigma_1^2(3^2P_{\frac{1}{2}}\rightarrow3^2P_{\frac{3}{2}})$ for excited sodium atoms from atomic fluorescence of sodium iodide as they depend on V_R the most probable relative speed of approach of excited sodium atom and argon atom or water molecule. $\pi\sigma_2^2(3^2P_{\frac{3}{2}}\rightarrow3^2P_{\frac{1}{2}})=1/1.89\times\pi\sigma_1^2(3^2P_{\frac{1}{2}}\rightarrow3^2P_{\frac{3}{2}})$.

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[11] L. B. Loeb, *The Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1934), second edition, p. 102.

TABLE I. Absorption of sodium D lines.

Source	Absorption of D_2	Absorption of D_1
Resonance radiation from Na tube at 230°C	0.23	0.11
Atomic fluorescence excited by H_2 discharge tube (effective $\lambda=2300$ A)	0.17	0.085
Atomic fluorescence excited by Zn spark (effective $\lambda=2082$ A)	0.12	0.065

broadening of the two D lines. The most probable speed due to optical dissociation of the excited sodium atoms from sodium iodide must be essentially the same in the $3^2P_{\frac{3}{2}}$ and $3^2P_{\frac{1}{2}}$ states when excited by the same source.

No great significance can be attached to the relative values of absorption in Table I for different exciting sources. The absorption path in the sodium vapor in the absorption tube is very sensitive to temperature changes and temperature gradients. Since only comparative values of absorption for the two D lines under the same absorption conditions for the same source were desired, no great effort was made to keep these conditions identical for different sources. However, average speeds of the excited sodium atoms calculated from the absorption data in Table I agree quite well with the dissociation speeds calculated in reference 6.

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Free Energy Functions for 54 Gaseous Elements*

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Tables of the free energy functions for 54 elements, each considered as an ideal monatomic gas, were calculated using a Los Alamos Scientific Laboratory IBM 704 computer for the temperature range 0 to 8000°K.

THE steadily increasing interest in the high-temperature behavior of metals and alloys has made the need for convenient tables of the thermodynamic functions of the gaseous elements very great. Recently we have completed at Los Alamos the calculation of the thermodynamic properties of the 54 elements considered as ideal monatomic gases. This LA report[1] contains tables of the partition functions, the enthalpy, the entropy, the free energy function, and the specific heat for each element for 150 temperatures between 10°K and 8000°K. A short table of the harmonic oscillator functions is also included.

Because of the particular interest in the free energy functions, we are presenting in Table I these functions *vs* T and the heat content at 25°C for each of the 54 elements for which detailed energy levels have been compiled by the National Bureau of Standards,[2] including those of the new Vol. III. The free energy functions listed are $-[(F^0-H_0{}^0)/T]$, where F^0 is the free energy, $H_0{}^0$ is the heat content, and T is the absolute temperature. The subscript 0 means H is evaluated at 0°K. The superscript 0 means the functions are referred to the conditions of an ideal gas at one atmosphere pressure. The heat content function at 25°C listed is $H_{298.16}{}^0-H_0{}^0$.

The calculations were performed using the methods described by Giauque.[3] The value of R used was 1.98780 cal mole^{-1} deg^{-1}, the value of hc/k was 1.43880 cm deg, and the free energy Sackur-Tetrode constant was -7.28632 cal deg^{-1} mole^{-1}.[4]

It is realized that these physical constants are on the physical atomic weight scale. However, we have used the chemical scale molecular weights (1949), and 298.16°K for 25°C in computing the tables. If one wishes to correct the present free energy values to values consistent with some other set of physical constants, one should subtract the present Sackur constant, multiply by the ratio of the R desired to the present R, and add the desired Sackur constant. Changes in hc/k are harder to correct for, but are usually negligible for five-figure accuracy.

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* This work was supported by the U. S. Atomic Energy Commission.

[1] Los Alamos Scientific Laboratory Report LA-2110 (Office of Technical Services, U. S. Department of Commerce, Washington, D. C., 1957).

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