The Pressure Broadening of the Cadmium-resonance Line at 326.1 nm in Ammonia and Argon

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The ratio of the collison-broadening cross-section of ammonia to that of argon for the cadmium-resonance line at 326.1 nm has been estimated to be 2.1 by comparing the experimental data of the transmission measurement with the theoretically calculated numerical table. The table shows the relation between the transmission of a resonance line passing through the system containing absorbing atoms and the ratio of the Lorentz half-breadth to the Doppler half-breadth at different values of two parameters; the optical density, and the ratio of the Doppler half-breadth of the emission line to that of the absorption line. This table may have universal importance for the study of the absorption of atomic spectra.

It is well known from experiments that atomic spectral lines have an observable breadth and are not so sharp as the simple quantum theory predicts. Such broadenings of spectral lines may be classified into four types: natural broadening, Doppler broadening, pressure broadening, and the broadening due to isotopes or hyperfine interaction. If a strong electric or magnetic field is present, the Stark and the Zeeman effects also have to be taken into account.

One of the most fundamental problems in the study of the reactions photosensitized by a certain atom is the quantitative estimation of the light intensity absorbed by the atoms. This quantity is seriously affected by the ratio of the Doppler half-breadth of the emission line to that of the absorption line. This ratio is denoted by α in the treatment of Zemansky.[1] If the optical density, $k_0(\nu_0)l$, at the maximum of the resonance line in the absence of pressure broadening is known, the intensity of the transmitted light is expressed as a function of the ratio of the Lorentz half-breadth to the Doppler half-breadth of the absorption line of the atoms in the system for a given value of α. Yang discussed this effect extensively in the particular case of mercury photosensitization.[2] Experimentally, such an effect has usually been avoided by using an appropriate actinometer or by diluting the system with a large amount of an inert gas which has a negligible quenching cross-section for the excited atoms under consideration.

In this investigation, we attacked two problems. One was the making of a numerical table of the relation between the transmission, T, and the ratio of the Lorentz half-breadth to the Doppler half-breadth at various values of α and $k_0(\nu_0)l$. This table has universal importance for the measurement of atomic spectra. The other was the determination of the collision-broadening cross-sections of ammonia and argon for the cadmium-resonance line at 326.1 nm by using the table obtained above.

Calculation

In order to discuss the pressure dependence of the transmission in terms of line broadening, it is necessary to know the shapes of the emission and absorption lines. Here, the emission line is taken to be a Doppler broadening:

$$E(\nu) = C\exp[-(\omega/\alpha)^2] \tag{1}$$

where C is a constant and where

$$\omega = 2(\nu-\nu_0)\sqrt{\ln 2}/\Delta\nu_D$$
$$\alpha = \Delta\nu_E/\Delta\nu_D$$

Here, $\Delta\nu_D$ denotes the Doppler half-breadth of the absorption line, while $\Delta\nu_E$ is that of the emission line. ν_0 is the frequency at the center of the emission line. The absorption coefficient is taken to be a type combining the Doppler broadening and the Lorentz broadening, ignoring natural broadening.[3]

$$k(\nu_0) = k_0(\nu_0)\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-y^2)}{a^2+(\omega-y)^2}\mathrm{d}y \tag{2}$$

where

$$a = \Delta\nu_L\sqrt{\ln 2}/\Delta\nu_D \tag{3}$$

$\Delta\nu_L$ is the half-breadth of the Lorentz broadening. $k_0(\nu_0)$ is the absorption coefficient at the maximum of the absorption line in the absence of the Lorentz broadening and may be estimated by means of the following equation.[3]

$$k_0(\nu_0) = \frac{\lambda_0{}^3 g_2 N}{8\pi^{3/2}g_1\tau_0 v_0} \tag{4}$$

Here, λ_0 is the wavelength at the center of the absorption line, g_1 and g_2 are the degeneracies of the lower and upper levels, τ_0 is the lifetime, v_0 is the most probable velocity of the atoms, and N is the atomic density. Then, the transmission, T, is expressed as follows:

$$T = \frac{\int_{-\infty}^{+\infty}\exp[-(\omega/\alpha)^2]\exp\left[-k_0(\nu_0)l\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-y^2)}{a^2+(\omega-y)^2}\mathrm{d}y\right]\mathrm{d}\omega}{\int_{-\infty}^{+\infty}\exp[-(\omega/\alpha)^2]\mathrm{d}\omega} \tag{5}$$

The T values were calculated at various α, a, and $k_0(\nu_0)l$ values by using a Facom 230-75 computer. The evaluation of the numerator was carried out using Simpson's formula, with a mesh of 0.05, and the upper and lower limits of integral were taken to be ± 16. The denominator is equal to 1.7725 α. The following is the range of parameters used for the calculations. α: 1.0∼4.5, a: 0.05∼7.0, and $k_0(\nu_0)l$: 0.001∼99.999. A part of the results are shown in Figs. 1—4.

The general features of the calculated results may be summarized as follows:

i) The transmission, T, decreases with the increase in the optical density, $k_0(\nu_0)l$. This is a matter of course.

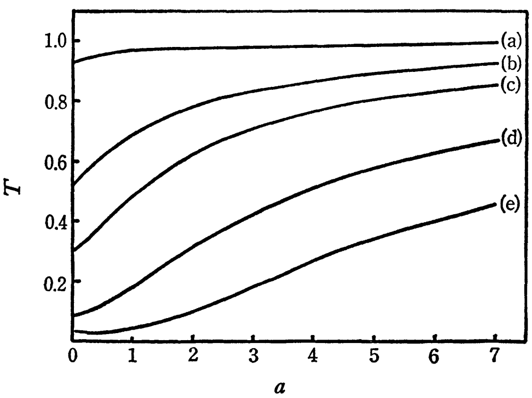

Fig. 1. Relation of the calculated transmission to the value of *a* with several values of optical density in the case of $\alpha=1$.
The optical density is equal to (a): 0.1, (b): 1.0, (c): 2.0, (d): 5.0, (e): 10.0.

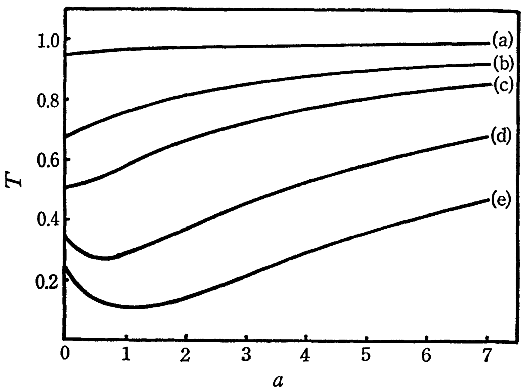

Fig. 2. Relation of the calculated transmission to the value of *a* with several values of optical density in the case of $\alpha=2$.
The optical density is equal to (*a*): 0.1, (b): 1.0, (c): 2.0, (d): 5.0, (e): 10.0.

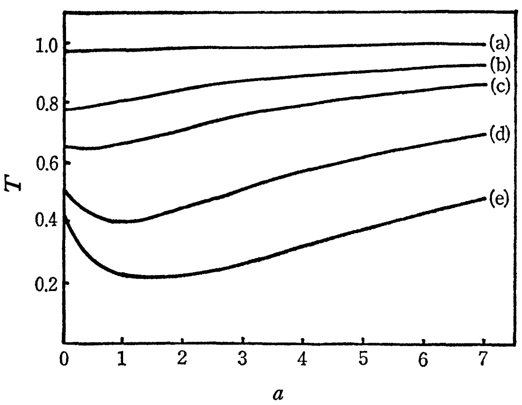

Fig. 3. Relation of the calculated transmission to the value of *a* with several values of optical density in the case of $\alpha=3$.
The optical density is equal to (a): 0.1, (b): 1.0, (c): 2.0, (d): 5.0, (e): 10.0.

ii) As the value of *a* is increased, the effect of α on the T value is reduced: *i.e.*, with the increase in the Lorentz broadening, the effect of the difference in Doppler broadening between emission and absorp-

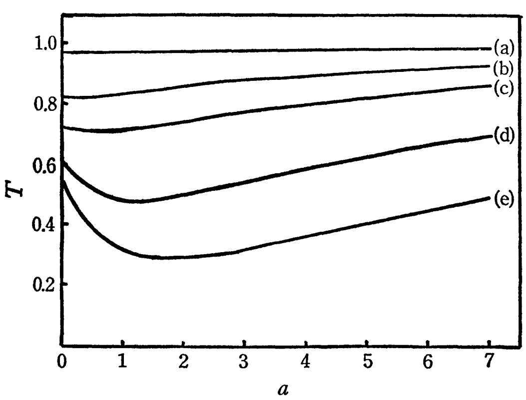

Fig. 4. Relation of the calculated transmission to the value of *a* with several values of optical density in the case of $\alpha=4$.
The optical density is equal to (a): 0.1, (b): 1.0, (c): 2.0, (d): 5.0, (e): 10.0.

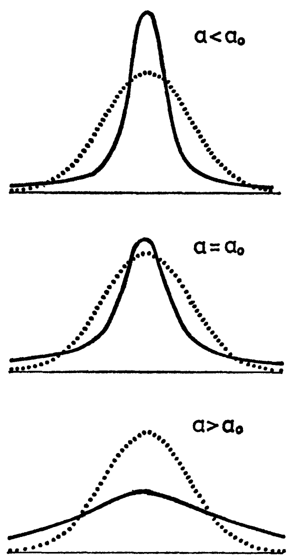

Fig. 5. The variation of the overlap between emission (dotted) and absorption (solid) lines with the increase of *a*. The maximum overlap is obtained at $a=a_0$.

tion lines is reduced.

iii) Similarly, as the α value is increased, the effect of *a* on the T value is reduced.

iv) On the other hand, with the increase in optical density, $k_0(\nu_0)l$, the effect of *a* on the T value is increased.

v) When both α and $k_0(\nu_0)l$ are large, T has a minimum at a certain value of *a*. This relation is qualitatively visualized in Fig. 5.

Measurements

The experimental apparatus was the same as that reported in a previous paper,[4] although the exciting resonance lamp was not used this time. The materials—cadmium, ammonia, and argon—were also the same as those described previously.[4] The furnace was maintained at 191±2 °C, while the cadmium reservoir was kept at 186±2 °C. The furnace for the resonance lamp was kept at 219±2 °C.

The results are shown in Fig. 6. The transmission n-

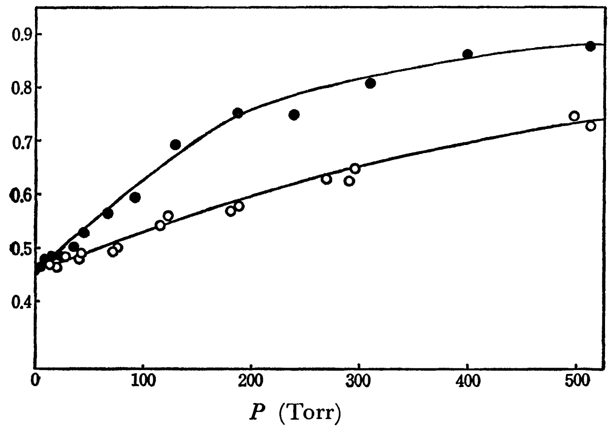

Fig. 6. The intensity of the transmitted light at 326.1 nm as a function of the pressure of argon (○) or ammonia (●).
The vapor pressure of cadmium is 1.48×10^{-4} Torr.

creased with the increase in the pressure of foreign gas. The rate of increase in ammonia was about twice that in argon. The transmission in the absence of any foreign gas, T_0, was 46.2±0.9%.

Discussion

Collision-broadening Cross-section. The $k_0(\nu_0)l$ value in the present experiment was calculated to be 2.3±0.3 by substituting the corresponding values into Eq. (4). However, this value cannot be used directly for the estimation of the collision-broadening cross-section because the presence of isotopes in natural cadmium metal has to be taken into account.

According to the work of Schüler and Westmeyer, the emission line at 326.1 nm of natural cadmium is split into three peaks.[5] Brix and Steudel demonstrated that the main peak observed by Schüler and Westmeyer is further split into three peaks.[6] Figure 7 shows the emission spectrum constructed according to the observations of Schüler and Westmeyer and those of Brix and Steudel, and by considering the Doppler broadening at 191 °C. From this figure, it may be assumed that natural cadmium consists of three imaginary isotopes, the propotions being 16 : 76 : 8.

Unfortunately, the overlap between the two spectra due to the two imaginary isotopes (16 and 76%) is not small. In the following calculations, therefore, we assume two extreme cases. One is Case A, in which the three spectral lines are assumed not to overlap with each other at all. The other is Case B, in which the spectrum of the natural atom is assumed to consist of two separate spectra, the intensities of which are in the ratio of 92 : 8. Consequently, the true collision cross-sections of ammonia and argon will be in between the two values calculated in the two extreme cases.

In the absence of any foreign gas, the transmission, T_0, was 46.2%. The theoretical equation for this value is written as follows:

$$T_0 = \frac{\int_{-\infty}^{+\infty} \exp[-(\omega/\alpha)^2] \exp[-k_0(\nu_0)l \exp(-\omega^2)]d\omega}{\int_{-\infty}^{+\infty} \exp[-(\omega/\alpha)^2]d\omega} \qquad (6)$$

The T_0 value was calculated by Horiguchi and Tsuchiya as a function of $k_0(\nu_0)l$ at different values of α.[7] This T_0 value can also be obtained from the figures shown in the previous section. Using these figures, we can estimate the α and $k_0(\nu_0)_c l$ values. Here, $k_0(\nu_0)_c l$ is the optical density corrected for the

TABLE 1. CALCULATED TRANSMISSION IN THE ABSENCE OF ANY FOREIGN GAS AND THE OPTICAL DENSITY CORRECTED FOR THE PRESENCE OF ISOTOPES

	3 components	2 components	α
T_0	46.2±3.5%		1.04
		46.2±3.2%	1.58
$k_0(\nu_0)_c l$	1.22	1.81	

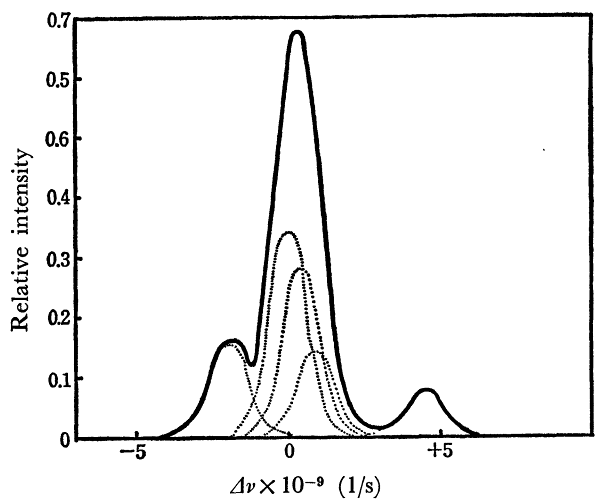

Fig. 7. Hyperfine structure of the cadmium resonance line at 326.1 nm with the Doppler broadening at 191 °C.

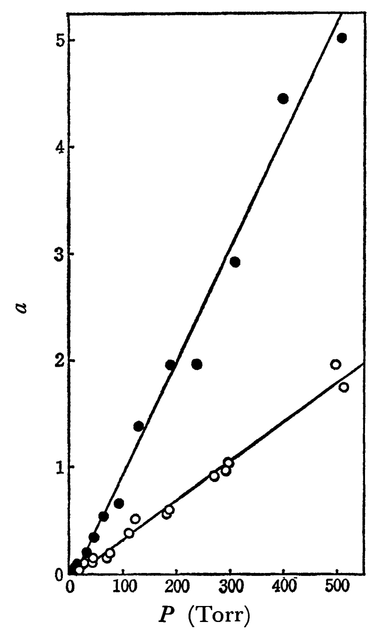

Fig. 8. The values of a as a function of the pressure of argon (○) or ammonia (●).

presence of isotopes; it may be used for the estimation of the collision-broadening cross-sections. The details of the calculation are shown in the Appendix. The results obtained are summarized in Table 1.

Once the α value and the corrected optical density are obtained, we can estimate, by using the numerical table, the value of a for each T value experimentally obtained. Thus, the a values are plotted in Fig. 8 as a function of the pressure of foreign gases. This figure is for Case A. A similar plot has also been obtained for Case B. The linear increase in the a value with the pressure is consistent with the Lorentz theory, which demands that

$$\Delta\nu_L = \frac{1}{\pi}\sigma^2 N(8\pi kT/\mu)^{1/2} \tag{7}$$

Here, σ^2 is the collision-broadening cross-section, N is the number of foreign gas molecules per cm^3, and μ is the reduced mass. Calculation by the least-squares method gives the values for σ^2. The results are listed in Table 2.

TABLE 2. COLLISION BROADENING CROSS SECTIONS (in Å^2) OF ARGON AND AMMONIA

	3 components	2 components
σ^2_{Ar}	49.0	72.9
$\sigma^2_{NH_3}$	100.0	152.6
ratio	2.04	2.09

When we drew the spectrum shown in Fig. 7, we did not take into account any broadening other than the Doppler broadening at 191 °C. Since the resonance lamp was operated at 219 °C and contained about 3 Torr of argon as a carrier gas, the emission line should have been broadened more than that shown in Fig. 7. The α values estimated were 1.04 and 1.58 for Cases A and B respectively. These values correspond to the temperatures of 289 and 885 °C if the broadening is only due to the Doppler effect. Obviously, though, we have to consider the Stark effect in Case B. However, since we cannot estimate the broadening due to the Stark effect in the present experiment, we cannot tell which case is closer to the truth.

On the Dilution with Inert Gases. In the measurement of the quenching efficiency for excited atoms, inert gases have often been used as diluents so as to keep the broadening of the absorption line constant. In a previous paper,[4] we ourselves also used argon as a diluent gas in the measurement of the quenching efficiency of ammonia for the cadmium resonance line at 326.1 nm. One of the most severe conditions was: $k_0(\nu_0)l=0.71$ with 40 Torr of argon and 10 Torr of ammonia. The difference between the light intensity absorbed by this system and that absorbed by the system containing 50 Torr of argon without ammonia was estimated to be within 1%.

Generally speaking, the collision-broadening cross-section does not seem to depend greatly on the kind of molecule as compared with the quenching cross-section for excited atoms. Therefore, if a certain gas which has a negligible quenching cross-section for the excited atoms under consideration is found, we can probably use it as a diluent for keeping the broadening of absorption line constant.

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Appendix

The optical density for a separate spectrum, the proportion being denoted by x, is obviously $xk_0(\nu_0)l$. If the value of α is known, we can estimate the transmission, T_{ox}, for each spectrum by using the numerical table of T_0 against $k_0(\nu_0)l$. Such a relation is shown in Fig. 9. The total transmission is the average of these transmissions:

$$T_0 = \sum xT_{ox}$$

This value should be equal to the experimentally obtained value, 46.2%. Thus, the value of α was obtained by trial and error. By replacing the final value of α in Eq. (6), we can estimate the corrected optical density, $k_0(\nu_0)_c l$.

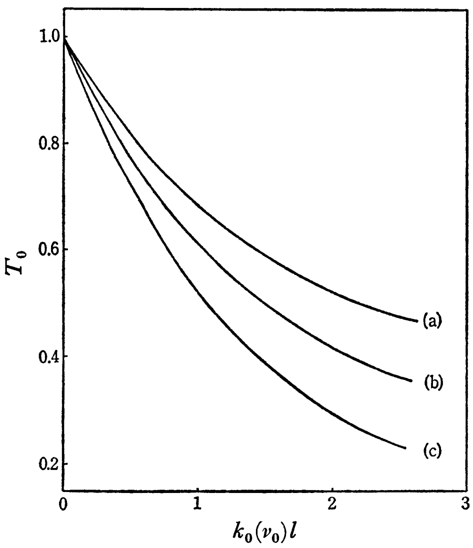

Fig. 9. Relation of the calculated transmission in the absence of any foreign gas to the optical density, $k_0(\nu_0)l$, with several values of α. (*a*): $\alpha=2.0$, (b): $\alpha=1.5$, (c): $\alpha=1.0$.

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