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Quenching of Cadmium Resonance Radiation by Foreign Gases

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Measurements have been made on the quenching of the cadmium resonance line 3261 by H_2, D_2, CO, NH_3, N_2 and CH_4. The experiment was carried out by comparing the intensity of 3261 emitted from a cell containing Cd vapor and foreign gas with that from a cell containing Cd vapor only. The cells were illuminated simultaneously and the results obtained by the method of photographic photometry. The experiments were performed under conditions (low vapor pressure, short light path through the vapor and small foreign gas pressure) which warrant the application of the Stern-Volmer formula. The quenching cross sections obtained therefrom are: H_2, 0.67; D_2, 0.19; CO, 0.14; NH_3, 0.041; N_2, 0.021; CH_4, 0.012×10^{-16} cm^2.

INTRODUCTION

THE term quenching implies a reduction in the intensity of resonance radiation due to the presence of a foreign gas. Collisions of the second kind between foreign gas molecules and excited atoms lead to a removal of the latter from the excited state before they have time to radiate, thus causing a diminution in the intensity of the emitted radiation. Under certain conditions a quenching collision cross section, σ_Q^2, can be determined, which in turn may be correlated with the particular process taking place, if the energy levels of the foreign gas molecule are known.

After Wood's first discovery[1] of the quenching of resonance radiation, a great deal of work was done on Hg and Na in which the cross sections for various gases were fairly well established, especially in the case of mercury. The first quantitative work in this field was done by Stuart on mercury[2] whose work was repeated and extended by Zemansky[3] and Bates.[4] With apparatus similar to that of Stuart, Mannkopf[5] measured the quenching of sodium resonance radiation. The work of Bates[6] and Bender[7] on the quenching of Cd resonance radiation was purely of a qualitative nature and no attempt was made to determine collision cross sections. Cadmium exhibits a spectrum of the same type as that of mercury, the main difference, as far as this experiment is concerned, is that the energy difference between the normal state and the ^3P levels is less in the case of cadmium (see Fig. 1) than in the case of mercury ($6^3P_2 - 6^3P_1 = 0.57$ v, $6^3P_1 - 6^3P_0 = 0.20$ v, $6^3P_1 - 6^1S_0 = 4.86$ v).

EXPERIMENTAL PROCEDURE

The top view of the full experimental arrangement is represented in Fig. 2. Light from a quartz discharge tube, *S*, containing cadmium vapor, and through which hydrogen was circulated to carry the discharge, was focused by means of a quartz lens, *L*, on two resonance cells placed one above the other. In one arm of each

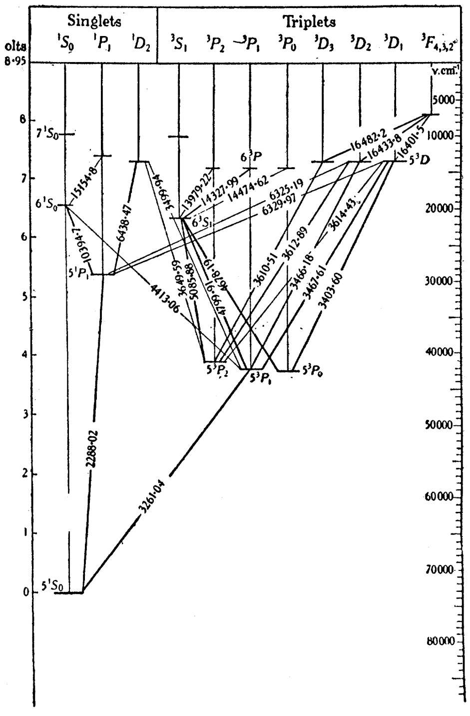

FIG. 1. Energy level diagram of cadmium.

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[1] R. W. Wood, Physik. Zeits. **13**, 353 (1912); Phil. Mag. **27**, 1018 (1914).

[2] H. Stuart, Zeits. f. Physik **32**, 262 (1925).

[3] M. W. Zemansky, Zeits. f. Physik **36**, 919 (1930).

[4] J. R. Bates, J. Am. Chem. Soc. **52**, 3825 (1930); **54**, 569 (1932).

[5] R. Mannkopf, Zeits. f. Physik **36**, 315 (1926).

[6] J. R. Bates, Proc. Nat. Acad. Sci. **14**, 849 (1928).

[7] P. Bender, Phys. Rev. **36**, 1535 (1930).

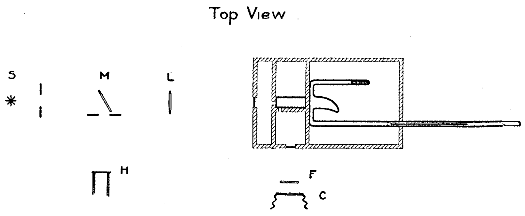

FIG. 2. Diagram of apparatus.

cell pure cadmium was distilled; the other arm was connected to the pumping system and to the source of a foreign gas. The cells could be isolated from the rest of the system by stopcocks and magnetic cut-offs to prevent cadmium from condensing outside the furnace. The vapor pressure of cadmium was determined by the temperature of the side arms which was maintained at 210°C throughout the experiment. A separate electric heating circuit maintained a considerably higher temperature in the front part of the furnace to prevent cadmium from condensing on the windows of the cells. The resonance radiation was taken out at right angles, passed through a filter to cut off the 2288 line, and 3261 was photographed by means of a camera fitted with a quartz lens.

On the photograph there appeared two images, one from each resonance cell. The lower cell usually contained cadmium vapor plus foreign gas while the upper cell contained cadmium vapor alone and served as a standard of comparison. In this manner any fluctuations in the light source were compensated.

Reasonable care was taken to insure purity of the gases used. Hydrogen was admitted to the system by diffusion through a heated palladium tube. Nitrogen was generated by heating sodium azide and was stored over metallic sodium. Carbon monoxide was generated by the action of sulphuric acid on sodium formate, while methane was prepared by heating sodium acetate and sodium hydroxide. Anhydrous ammonia, obtained from a tank, was stored over potassium hydroxide and was further purified by condensing in liquid air and pumping off the residual noncondensible gases. Deuterium (100 percent pure) was obtained through the courtesy of the Frick Chemical Laboratory, Princeton University.

The procedure adopted was first to reflect the light from the arc by a mirror, M, into a Hilger quartz spectograph, H (see Fig. 2) and place intensity-time calibration marks on a photographic plate; then to remove the mirror, allow the light to fall on the two resonance cells and photograph on the same plate the resonance radiation from the two cells, first in the absence of the foreign gas and then in the presence of the varying amounts of the gas in the lower cell. Each pressure change was made slowly and the cadmium vapor was allowed to reach equilibrium before a photographic exposure was made.

The plate blackenings were traced on a microphotometer and then translated into light intensities by means of the calibration marks mentioned above. The quenching, Q, was determined by dividing the intensity of the resonance radiation from the cell containing the foreign gas by the radiation intensity from the cell containing cadmium vapor only and the reciprocal of this quenching was plotted against the foreign gas pressure in mm.

EXPERIMENTAL RESULTS

The experimental results are given in Figs. 3, 4, 5 and 6 and Table I. As is seen in Fig. 3, hydrogen quenches very efficiently, the effect being first noticeable at pressures as low as 0.01 mm and the

TABLE I. *Quenching slopes and collison cross sections for the quenching of Cd resonance radiation by foreign gases.*

Gas	H_2	D_2	CO	NH_3	N_2	CH_4
Slope (mm^{-1})	2.45	0.50	0.15	0.063	0.022	0.016
$\sigma_Q^2(\times 10^{16}\ \text{cm}^2)$	0.67	0.19	0.14	0.041	0.021	0.012

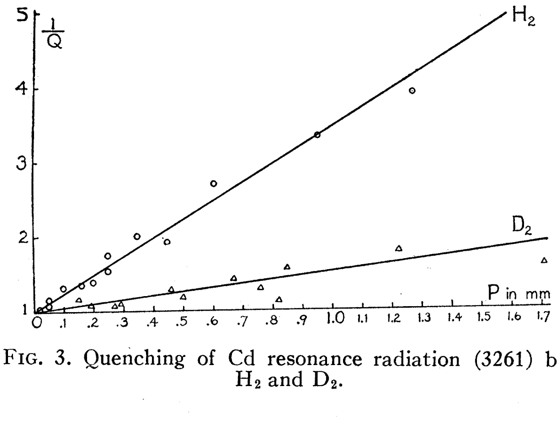

FIG. 3. Quenching of Cd resonance radiation (3261) by H_2 and D_2.

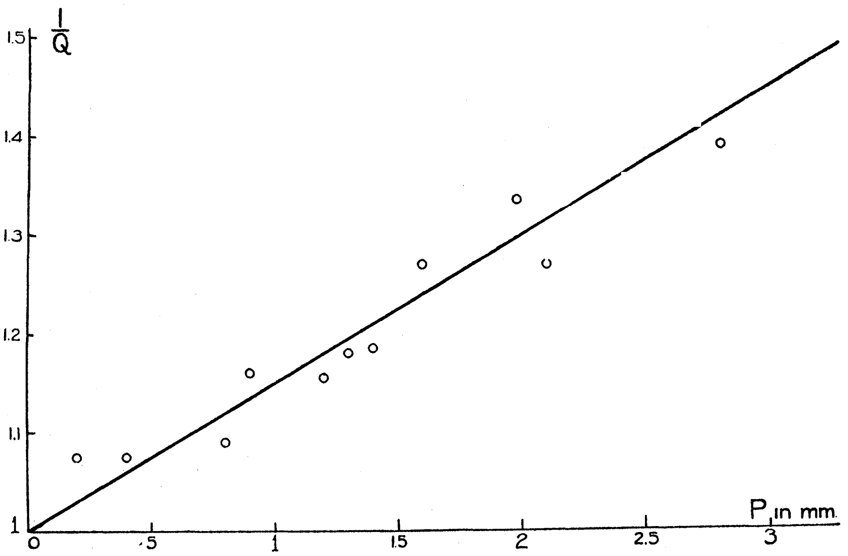

FIG. 4. Quenching of Cd resonance radiation (3261) by CO.

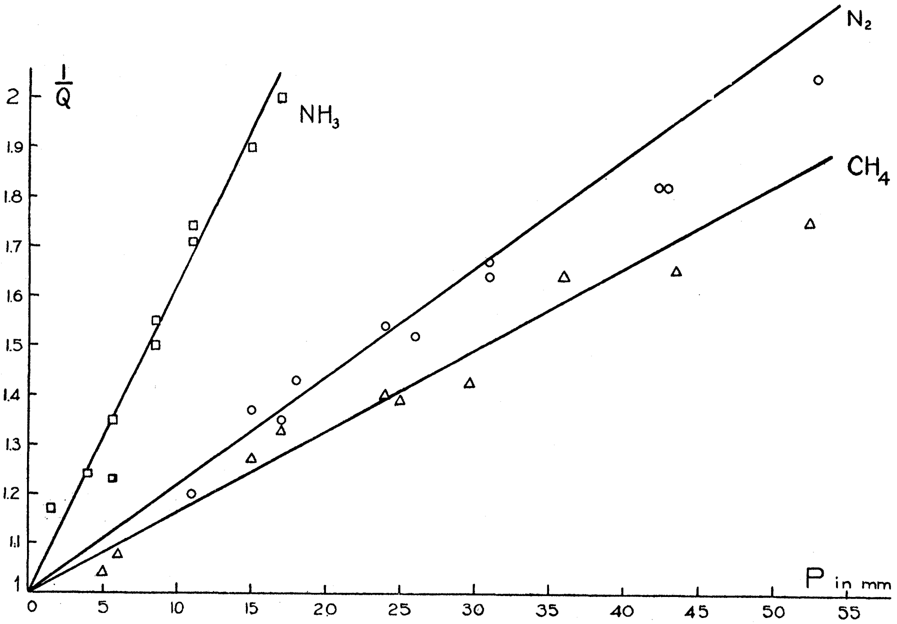

FIG. 5. Quenching of Cd resonance radiation (3261) by N_2, CH_4 and NH_3

intensity of the resonance radiation being reduced to half of its original value at about 0.4 mm of H_2. The quenching by deuterium is of the same order of magnitude as that of hydrogen although the "half-value" occurs at 1.5 mm. Carbon monoxide, Fig. 4, is less efficient than hydrogen, 0.4 mm decreasing the resonance radiation intensity to only about 95 percent of its maximum. Ammonia, Fig. 5, quenches moderately, the curve lying between those of nitrogen and carbon monoxide. Nitrogen and methane are very ineffective as quenching agents, the phenomenon not being observed until a pressure of a few millimeters was reached and the intensity

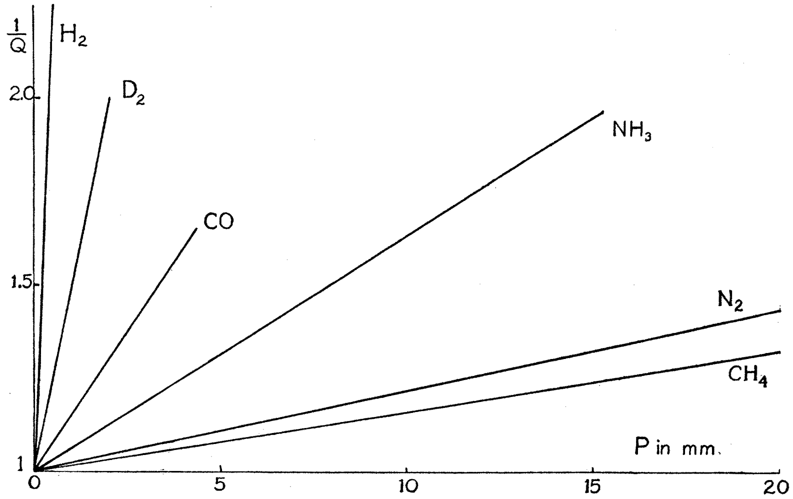

FIG. 6. Quenching of Cd resonance radiation (3261) by foreign gases.

dropping to approximately half-value at 45 mm in the case of N_2 and 60 mm in the case of CH_4. The relative quenching efficiency of all the gases is shown in form of slopes in Fig. 6.

DISCUSSION AND INTERPRETATION OF RESULTS

The correct interpretation of quenching experiments is affected mainly by two factors:

1. The diffusion of imprisoned resonance radiation, i.e., reabsorption of the emitted resonance radiation on its way out through the gas to the exit window, giving rise to secondary radiation, which absorbed again will produce tertiary radiation, and so on.
2. The alteration of the width and the position of the absorption line relative to the exciting line, which is due to the collisions of atoms with foreign gas molecules (Lorentz broadening).

Unless the above difficulties are overcome, a quenching curve can give no information leading to the computation of collision cross sections and in some cases[3, 5] it is not even evidence that quenching takes place at all.

The present work was performed under conditions in which these two effects were largely eliminated. Thus, Lorentz broadening was reduced by operating with pressures of foreign gas as low as was compatible with the quenching process. As to diffusion of the imprisoned resonance radiation this was eliminated, first by keeping the cadmium vapor pressure low (5.6×10^{-4} mm corresponding to 210°C at which the absorption coefficient at the center of the 3261 line is about 0.4) and second, by placing both the entrance and the exit window of the resonance cell near a common edge, so that only a small portion of the Cd vapor was exposed to the incident radiation, thus permitting only the primary resonance radiation to be re-emitted.

The fulfilment of the above conditions warrants an application of the Stern-Volmer formula:[8]

$$Q = 1/(1+\tau Z_Q) \qquad (1)$$

where Q = quenching of the resonance radiation, τ = the lifetime of the excited atom, and Z_Q = the number of quenching collisions per sec., per cc, per excited atom.

Since Z_Q varies linearly with the foreign gas pressure, p, a plot of the reciprocal of Q against p should result in a straight line. This was found to be true in the present investigation, as attested by the above graphs. Above a certain pressure, the deviation from straight lines can probably be accounted for by Lorentz broadening.[9]

The quenching collision cross sections, σ_Q^2, were determined as follows:

The Stern-Volmer formula, (1), gives a relation between the quenching Q and the total number of quenching collisions Z_Q. The latter can be calculated on the basis of the Maxwellian distri-

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[8] O. Stern and M. Volmer, Physik. Zeits. **20**, 183 (1919).

[9] Mitchell and Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Co., 1934), p. 224.

bution of velocities, resulting in the equation

$$Z_Q = 2Nn\sigma_Q^2[2\pi kT(1/M_1+1/M_2)]^{\frac{1}{2}} \quad (2)$$

where M_1 and M_2 = molecular weights of the colliding particles, N and n = their molecular concentrations, and k = universal gas constant or expressed in terms of the pressure in mm of Hg

$$Z_Q = 2666.6\sigma_Q^2[2\pi N/kT(1/M_1+1/M_2)]^{\frac{1}{2}}\cdot p. \quad (3)$$

From (1) and (3) it follows that the collision cross section is given by

$$\sigma_Q^2 = \frac{1/(Q\cdot p)}{\tau 2666.6[2\pi N/kT(1/M_1+1/M_2)]^{\frac{1}{2}}}. \quad (4)$$

The values $1/(Q\cdot p)$ are the slopes of the quenching curves and could be read for each gas from Figs. 3, 4 and 5; they are given in Table I. The temperature of the cadmium vapor was 210°C and the mean life for the 5^3P_1 state of Cd was taken as $\tau = 2.5\times 10^{-6}$ sec.[10] The values of the quenching collision cross sections thus computed from (4) are given in the same table.

The high quenching efficiency of hydrogen was interpreted by Bender[7] as due to a collision of an excited Cd atom in the 5^3P_1 state with a normal H_2 molecule, resulting in a formation of an unexcited cadmium hydride molecule and an atom of hydrogen

$$\begin{matrix} \mathrm{Cd}\ (5^3P_1) + & H_2 \rightarrow & \mathrm{Cd\,H} + \mathrm{H} \\ 3.78\ \mathrm{v} & 4.44\ \mathrm{v} & 0.67\ \mathrm{v} \end{matrix} \quad (5)$$

This process seems to be highly probable, as indicated by the energy balance of the equation, in which the energy required for the above reaction differs from the energy available by less than half of one percent. This was further substantiated in Bender's experiment by the appearance of CdH bands in the resonance cell and the formation of atomic hydrogen found as water frozen out by the liquid air trap, due, probably, to a reduction by atomic hydrogen of some oxide present in the Cd supply.

However, simple calculations made on the basis of the data given by Jevons[11] indicate that H_2 has a vibrational level of the normal electronic state at 3.73 volts, which, from purely energetic considerations makes the following process also possible: upon collision, the excited Cd atom gives up 3.78 volts to raise the H_2 molecule to a 3.73-volt vibrational level:

$$\begin{matrix} \mathrm{Cd}\ (5^3P_1) + H_2 \rightarrow \mathrm{Cd}\ (5^1S_0) + & (H_2)_v \\ 3.78\ \mathrm{v} & 3.73\ \mathrm{v} \end{matrix} \quad (6)$$

Although in this reaction the energy discrepancy is larger (about 1.5 percent), still the above process seems to be very plausible.

Similar considerations can probably apply to deuterium (energy of dissociation of D_2 is the same as that of H_2; there is also a vibrational level at 3.72 volts) although no attempt was made to detect the existence of the CdD bands.

The quenching by CO, N_2 and CH_4 cannot be accounted for by a dissociation process, since the energies of dissociation of these molecules are far in excess of the energy available (10.0 volts for CO, 9.1 for N_2, 16.3 for CH_4). However, the carbon monoxide molecule has a vibrational level at 3.83 volts, which being near the excitational level of the 3261 Cd line makes the following reaction possible:

$$\begin{matrix} \mathrm{Cd}\ (5^3P_1) + \mathrm{CO} \rightarrow \mathrm{Cd}\ (5^1S_0) + & (\mathrm{CO})_v \\ 3.78\ \mathrm{v} & 3.83\ \mathrm{v} \end{matrix} \quad (7)$$

In this case the energy discrepancy is 1.5 percent.

The nearest vibrational level of nitrogen is at 3.48 volts, indicating an energy discrepancy of 8 percent; concerning the CH_4 molecule there are not sufficient band spectra data known to consider the quenching by methane from above point of view. However, at the temperature used (210°C), the average kinetic energy of translation of a molecule ($\frac{3}{2}kT$) is about 0.07 volt, which corresponds to the energy difference between the excited 5^3P_1 and the metastable 5^3P_0 state of Cd. Thus, perhaps, the quenching by N_2 and CH_4 can be explained in terms of a transfer of the excited Cd atom to the metastable state, resulting in a loss of 0.07 volt to the molecules in a form of a translational kinetic energy, e.g.,

$$\begin{matrix} \mathrm{Cd}\ (5^3P_1) + N_2 \rightarrow & \mathrm{Cd}\ (5^3P_0) + & (N_2)\ \mathrm{K.E.} \\ 3.78\ \mathrm{v} & 3.71\ \mathrm{v} & 0.07\ \mathrm{v} \end{matrix} \quad (8)$$

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[10] Reference 9, p. 147.

[11] W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (The Physical Society, London, 1932), p. 269.

Of course, the reverse process is plausible and undoubtedly takes place also, in which a collision between a metastable atom and the gas molecule results in a transfer of the Cd atom back to the 5^3P_1 state, but as has been shown by Klein and Rosseland[12] this type of a collision (collision of the first kind) is less probable than the former, since a fast molecule will remain in the neighborhood of an atom during a shorter interval of time than a slow one. This point of view seems to be confirmed by Bender's observation of an increase in the relative intensity of the 3404 line over the remainder of the spectrum in the presence of N_2 and CO but not in the presence of H_2. This line results (see Fig. 1) in the absorption of an energy quantum from the 5^3P_0 state to the 5^3D_1 state and a subsequent re-emission, and thus a heavy population of the metastable state will favor an increase in its intensity.

Because of the meager data existing about the energy levels of the ammonia molecule it is not possible to ascribe any definite process to the quenching by ammonia. No evidence was obtained for its decomposition under the influence of excited cadmium atoms, in agreement with Bates and Taylor.[13] The test is not conclusive, however, since the intensity of the source may have been too small to produce a measurable chemical effect, although it was large enough for the measurement of quenching. In view of the fact that some decomposition might have occurred and the resulting products might have had an effect on the intensity of the resonance radiation, exposures were made at the same ammonia pressure, first with a fresh sample of gas and next with a sample which has been irradiated previously for 15 minutes. There was no detectable difference in the quenching between the two cases.

Lastly, the collision between any one of the above molecules and the Cd atom cannot result in raising them either to an excited electronic level or to some rotational level, in the first case, the energies required being too high (the first excitational level of H_2 is 11.1 v, CO$-$4.8 v, N_2 $-$8.5 v) in the second case the energies being only of the order of a fraction of a volt.

In conclusion, it ought to be emphasized that it is difficult to interpret quenching in terms of one process alone, the reactions taking place within the resonance tube being of a very complicated nature. It may be that quenching by a particular gas can be explained by all the processes mentioned above, there being only a degree of effectiveness of one reaction over the other. Thus, perhaps one can venture an opinion that the process, in which the discrepancy between the energy required and the energy available is small, is more responsible for the quenching phenomenon than the one in which a corresponding discrepancy is large.

The authors wish to acknowledge their indebtedness to Dr. R. L. Garman of the Chemistry Department of the Washington Square College for making the microphotometer traces.

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[12] O. Klein and S. Rosseland, Zeits. f. Physik **4**, 46 (1921).

[13] J. R. Bates and H. S. Taylor, J. Am. Chem. Soc. **50**, 771 (1928).