PHYSICAL REVIEW VOLUME 153, NUMBER 1 5 JANUARY 1967

Inelastic Collisions between Excited Alkali Atoms and Molecules. I. Sensitized Fluorescence and Quenching in Cs–N_2 and Cs–H_2 Systems[*]

D. A. McGillis[†] and L. Krause
Department of Physics, University of Windsor, Windsor, Canada

(Received 22 July 1966)

Excitation transfer between the $6\,^2P_{1/2}$ and $6\,^2P_{3/2}$ resonance states in cesium, induced by Cs–N_2 and Cs–H_2 collisions, was observed in the first experiment of its kind, in which techniques of sensitized fluorescence are used to investigate collisional mixing between resonance states of alkali atoms in mixtures with molecular gases. The cesium-vapor–gas system, in which the cesium vapor pressure was low enough to avoid radiation trapping, was irradiated with a single component of the resonance doublet. The fluorescent light, which contained both components of the doublet, was monitored at right angles to the direction of excitation. Measurements of relative intensities of the fluorescent components yielded the following cross sections for excitation transfer and for quenching of resonance radiation. For Cs–N_2 collisions: $Q_{12}({}^2P_{1/2}\rightarrow {}^2P_{3/2})=3.6\,\text{Å}^2$, $Q_{21}({}^2P_{1/2}\leftarrow {}^2P_{3/2})=16.2\,\text{Å}^2$, $Q_{10}({}^2S_{1/2}\leftarrow {}^2P_{1/2})=55.2\,\text{Å}^2$, $Q_{20}({}^2S_{1/2}\leftarrow {}^2P_{3/2})=63.5\,\text{Å}^2$. For Cs–$H_2$ collisions: $Q_{12}=6.7\,\text{Å}^2$, $Q_{21}=29.6\,\text{Å}^2$, $Q_{10}=11.7\,\text{Å}^2$, $Q_{20}=6.7\,\text{Å}^2$. The large sizes of the excitation-transfer cross sections, which are comparable to the corresponding Cs–Cs cross sections, are attributed to resonances with transitions in the molecules.

I. INTRODUCTION

When a glass tube containing cesium vapor at low pressure is irradiated with one component of the cesium resonance doublet, the resulting fluorescence often contains both the component present in the exciting light (resonance fluorescence) and that not present in the exciting light, which is known as sensitized fluorescence and whose presence is due to inelastic collisions between the excited and unexcited cesium atoms.[1] If, instead of pure cesium vapor, a mixture of cesium vapor and an inert gas is introduced into the fluorescence tube, collisions between the excited cesium atoms and the inert gas atoms in their ground states also give rise to a transfer of excitation between the $6\,^2P_{1/2}$ and $6\,^2P_{3/2}$ levels of cesium and cause the appearance of sensitized fluorescence.[2] If a gas consisting of diatomic (or polyatomic) molecules rather than a monatomic inert gas is mixed with the cesium vapor, the inelastic collisions between the excited cesium atoms and the molecules may result in two processes: sensitized fluorescence arising from the ${}^2P_{1/2}\leftrightarrow {}^2P_{3/2}$ excitation transfer, and quenching of resonance radiation, during which an excited cesium atom is transferred to its ground state and all its excitation energy is converted into translational, vibrational, and rotational energy.

Investigations of sensitized fluorescence yield cross sections for the various inelastic collisions and provide insight into the appropriate interaction mechanisms. Although considerable attention has recently been given to studies of sensitized fluorescence in pure alkali vapors and their mixtures with inert gases,[3] no such investigations of systems containing molecular gases have yet been carried out. With the exception of Lochte-Holtgreven's early work,[4] all studies of interactions between excited alkali atoms and molecules dealt with the quenching process[5] and involved measurements of the decrease in the intensity of resonance fluorescence with increasing gas pressure. No allowance appeared to be made for the fact that significant transfer of excitation between the two ${}^2P$ levels does take place, nor were the quenching cross sections expressed as a sum of two terms: one arising from the transfer to the other resonance level, and the other, representing quenching proper, from the transfer to the ground state. In most cases the two components of the resonance doublet were not separated and only the net quenching of both components of the doublet was observed. In the present investigation, which follows studies of sensitized fluorescence in pure cesium and in cesium–inert-gas mixtures, transfer of excitation as well as quenching in Cs-N_2 and Cs-H_2 mixtures have been systematically investigated for the first time. The very low cesium vapor pressure, which was maintained throughout the experiments, insured the absence of radiation trapping and low gas pressures permitted a successful separation of the quenching and sensitized fluorescence effects while maintaining single-collision conditions and minimal pressure broadening of the resonance lines.

II. THEORETICAL

The processes which occur when the mixture of cesium vapor and molecular gas is irradiated continuously with the 8521 Å component of the cesium resonance doublet, are shown schematically in Fig. 1. The solid arrows indicate collisional transitions giving rise to

---

[*] Supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under AFOSR Grant No. 361-65, and by the National Research Council of Canada.

[†] Province of Ontario Graduate Fellow.

[1] M. Czajkowski and L. Krause, Can. J. Phys. 43, 1259 (1965).

[2] M. Czajkowski, D. A. McGillis, and L. Krause, Can. J. Phys. 44, 91 (1966).

[3] L. Krause, Appl. Opt. 5, 1375 (1966).

[4] W. Lochte-Holtgreven, Z. Physik 47, 362 (1928).

[5] See, for example, G. W. Norrish, and W. M. Smith, Proc. Roy. Soc. (London) A176, 295 (1940).

sensitized fluorescence in cesium, and the broken arrows represent collisional deactivation of the ^2P cesium atoms to the ground state, which results from the quenching of resonance radiation.

The various interactions may be represented by the following equations:

$$\mathrm{Cs}(6\,^2S_{1/2})+h\nu_2 \xrightarrow{s_2} \mathrm{Cs}(6\,^2P_{3/2}), \tag{1}$$

$$\mathrm{Cs}(6\,^2P_{3/2})+M \xrightarrow{Z_{21}} \mathrm{Cs}(6\,^2P_{1/2})+M^*, \tag{2}$$

$$\mathrm{Cs}(6\,^2P_{1/2})+M \xrightarrow{Z_{12}} \mathrm{Cs}(6\,^2P_{3/2})+M^*, \tag{3}$$

$$\mathrm{Cs}(6\,^2P_{3/2})+M \xrightarrow{Z_{20}} \mathrm{Cs}(6\,^2S_{1/2})+M^*, \tag{4}$$

$$\mathrm{Cs}(6\,^2P_{1/2})+M \xrightarrow{Z_{10}} \mathrm{Cs}(6\,^2S_{1/2})+M^*, \tag{5}$$

$$\mathrm{Cs}(6\,^2P_{3/2}) \xrightarrow{(\tau_2)^{-1}} \mathrm{Cs}(6\,^2S_{1/2})+h\nu_2, \tag{6}$$

$$\mathrm{Cs}(6\,^2P_{1/2}) \xrightarrow{(\tau_1)^{-1}} \mathrm{Cs}(6\,^2S_{1/2})+h\nu_1, \tag{7}$$

where s_2 is the number of cesium atoms excited per second from the $6\,^2S_{1/2}$ state to the $6\,^2P_{3/2}$ state, τ_1 and τ_2 are the mean lifetimes of the $^2P_{1/2}$ and $^2P_{3/2}$ states (3.8×10^{-8} and 3.3×10^{-8} sec, respectively[6]), and Z_{21}, Z_{12}, Z_{20}, and Z_{10} are the collision numbers for the processes designated in Fig. 1, defined as the numbers of collisions per excited cesium atom per second, leading to the appropriate process of excitation transfer. M is a ground-state diatomic molecule and M^* a molecule which, having participated in an inelastic collision, has become modified in its content of translational, vibrational, and rotational energy.

Collisional mixing of the ^2P states due to Cs–Cs collisions has been neglected since the ratio of sensitized to resonance fluorescent intensities due to such collisions is of the order of 10^{-7} at the vapor pressures used in this experiment (10^{-6} Torr) and does not contribute significantly to the observed sensitized fluorescence.[1]

If it is assumed that the vapor-gas mixture exists in a state of dynamic equilibrium which involves only continuous optical excitation of the Cs($6\,^2P_{3/2}$) state by means of 8521 Å radiation, spontaneous decay, and the various binary collisional processes, Eqs. (1)–(7) may be combined to give the following rate equations:

$$\frac{dN(6\,^2P_{3/2})}{dt}=s_2+N(6\,^2P_{1/2})Z_{12} -N(6\,^2P_{3/2})[(\tau_2)^{-1}+Z_{21}+Z_{20}]=0; \tag{8}$$

$$\frac{dN(6\,^2P_{1/2})}{dt}=N(6\,^2P_{3/2})Z_{21} -N(6\,^2P_{1/2})[(\tau_1)^{-1}+Z_{12}+Z_{10}]=0, \tag{9}$$

where, for example, $N(6\,^2P_{1/2})$ denotes the density of cesium atoms in the $6\,^2P_{1/2}$ state. Two additional rate equations similar to (8) and (9) may be obtained by considering the various processes resulting from optical excitation with the 8944 Å component of the cesium resonance doublet. The four rate equations provide the following connection between the collision numbers Z and experimental observations.

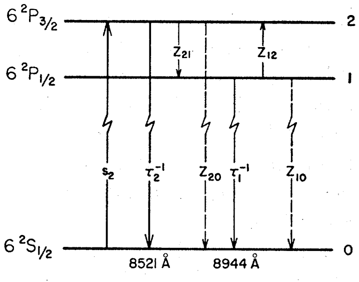

FIG. 1. Energy levels involved in sensitized fluorescence and in the quenching of cesium resonance radiation induced in collisions with molecules.

In the case of excitation with the 8521 Å component:

$$(I_0/I)_2=1+\tau_2Z_{20}+\tau_2Z_{21} -(\tau_1\tau_2Z_{12}Z_{21})/(1+\tau_1Z_{10}+\tau_1Z_{12}), \tag{10}$$

$$Z_{21}=A+Z_{10}B+Z_{20}C. \tag{11}$$

In the case of excitation with the 8944 Å component:

$$(I_0/I)_1=1+\tau_1Z_{10}+\tau_1Z_{12} -(\tau_1\tau_2Z_{12}Z_{21})/(1+\tau_2Z_{20}+\tau_2Z_{21}), \tag{12}$$

$$Z_{12}=D+Z_{20}E+Z_{10}C. \tag{13}$$

$(I_0/I)_2$ is the ratio of the resonance fluorescent intensity (of wavelength 8521 Å) observed in the absence of foreign gas to the intensity observed with the vapor-gas mixture. The quantities A, B, C, D, and E are constants at any given gas pressure:

$$\begin{aligned} A&=(\tau_2)^{-1}\eta_1(1+\eta_2)/(1-\eta_1\eta_2),\\ B&=\tau_1\eta_1(\tau_2)^{-1}/(1-\eta_1\eta_2),\\ C&=\eta_1\eta_2/(1-\eta_1\eta_2),\\ D&=(\tau_1)^{-1}\eta_2(1+\eta_1)/(1-\eta_1\eta_2),\\ E&=\tau_2\eta_2(\tau_1)^{-1}/(1-\eta_1\eta_2), \end{aligned} \tag{14}$$

where η_1 and η_2 are the experimentally measured intensity ratios of sensitized to resonance fluorescence:

$$\begin{aligned} \eta_1&=I(8944\text{ Å})/I(8521\text{ Å}),\\ \eta_2&=I(8521\text{ Å})/I(8944\text{ Å}). \end{aligned} \tag{15}$$

The wavelengths appearing in the denominators are, in each case, the same as those used in the exciting light.

The collision number Z_{ab} for any given process $a\rightarrow b$ may be directly related, by analogy with the gas kinetic cross section, to the total effective cross section Q_{ab} for the corresponding inelastic collision:

$$Z_{ab}=N(M)Q_{ab}V_r, \tag{16}$$

where v_r is the average relative velocity of the colliding partners.

When quenching effects are negligible ($I_0/I\simeq1$), Eqs.

---

[6] Landolt-Börnstein, *Zahlwerte und Funktionen* (Springer-Verlag, Berlin, 1950).

(11) and (13) are reduced to a more straightforward form representing ${}^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer.[7] When an additional condition is satisfied, according to which $\eta \ll 1$, a plot of η against the gas density $N(M)$ should be linear and should pass through the origin. If, on the other hand, there were no ${}^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer, Eqs. (10) and (12) would assume the Stern-Volmer form.[8]

Equation (16) indicates that the collision numbers should vary linearly with the gas density. The collision cross sections Q may be estimated from low-pressure data where quenching effects are small and $\eta \ll 1$. In practice, however, the collision numbers Z were found by iterative solutions of Eqs. (10)–(13) on an IBM 1620 computer.

The above treatment is strictly valid only in the absence of radiation trapping. If resonance radiation is imprisoned, the effective lifetimes of the cesium resonance states are no longer equal to their natural lifetimes, which results in spurious values of the collision cross sections.

III. EXPERIMENTAL

The arrangement of the apparatus is shown in Fig. 2. The cesium resonance doublet, emitted by an rf electrodeless discharge,[9] was separated with a spectral purity of 1 part in 10^6 by means of a Bausch and Lomb grating monochromator in series with a Schott interference filter. The monochromatic beam was then split into two parts: One was condensed into a fluorescence tube containing cesium vapor and the other into a similar tube containing a vapor-gas mixture. The fluorescent light emerging from the latter tube was again resolved into its two spectral components by means of two Spectrolab interference filters in series, which gave a spectral purity of about 1 part in 10^7, and was focused onto the cathode of a liquid-nitrogen-cooled I.T.T. FW118G photomultiplier tube. A second similar photomultiplier served to detect the total fluorescence from the cell containing pure cesium vapor. The output signals of both photomultipliers were directed, through a coaxial switch, to a Keithley picoammeter and were registered with a strip-chart recorder. With dark currents of the order of 10^{-13} A it was possible to detect light signals down to 5×10^{-13} A while maintaining a satisfactory signal-to-noise ratio.

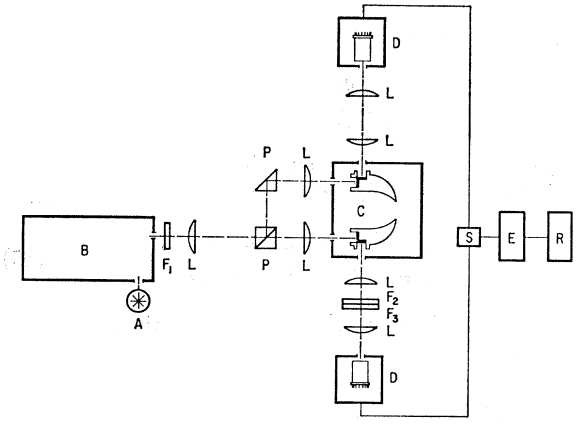

FIG. 2. Schematic diagram of apparatus. A, spectral lamp; B, monochromator; C, oven with fluorescence cells; D, photomultiplier tubes; E, electrometer; R, recorder; S, coaxial switch; F_{1-3}, interference filters; L, lenses; P, prisms.

The details of the fluorescence tubes have been described elsewhere.[2] Both tubes were mounted in a common oven in which temperatures could be maintained constant within ±0.5°C over long periods of time. The tubes had sidearms each containing about 0.5g of cesium metal,[10] which extended through the bottom of the main oven and were enclosed in separate small ovens whose temperatures were kept equal and constant within ±0.2°C by coils through which water was circularted from a Jena ultrathermostat. All temperatures were measured by means of calibrated copper-constantan thermocouples located at various points on the fluorescence tubes and side arms. Although, with 7-cm-long side arms, it would be expected that the vapor pressure in the cells should have a lower value than that predicted by the Taylor and Langmuir formula,[11] this was not an important consideration since, during the experiments, the vapor pressure was kept below 2×10^{-6} Torr while trapping of cesium resonance radiation becomes noticeable only at about 2×10^{-5} Torr.[1] The latter effect was reduced even further by restricting the path lengths of the exciting and fluorescent light inside the cell to about 1 mm.

Each fluorescence tube was connected, by means of a capillary, to a vacuum and gas-filling system. Both cells were baked for 48 h at 200°C and at a vacuum of 6×10^{-8} Torr and then the temperatures of the cells were stabilized at 40°C and those of the side arms at 30°C. When all the liquid cesium migrated to the side arms, the capillaries were flushed with spectroscopically pure argon to free them of accumulated cesium vapor.[2] Finally, the appropriate gas (Linde, spectrograde quality) was admitted in controlled quantities into one of the tubes through its capillary, while the capillary of the other tube remained connected to the vacuum system. Vacuum measurements were carried out with an ionization gauge and gas pressures were determined using a trapped McLeod gauge with a useful range 10^{-3}–10 Torr or a mercury manometer.

When one component of the cesium resonance doublet was made incident on both cells, it was found that the ratio of the resonance fluorescent intensities in the two tubes was independent of the intensity and shape of the

---

[7] R. Seiwert, Ann. Physik **18**, 54 (1956).

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

[9] R. J. Atkinson, G. D. Chapman, and L. Krause, J. Opt. Soc. Am. **55**, 1269 (1965).

[10] Cesium of 99.99% purity was supplied by the A. D. McKay Company of New York.

[11] J. B. Taylor and I. Langmuir, Phys. Rev. **51**, 753 (1937).

exciting line, which could be varied by changing the temperature of the light source.[9] There was a slight dependence on the cesium vapor density which was due to small differences between the geometries of the two cells. Since, however, the temperatures of the two side-ovens were quite stable, no significant error was introduced by this effect. Thus the quenching produced by the gases could be determined by measuring the intensity of the fluorescence emerging from the cell containing the pure vapor and multiplying it by a previously determined conversion factor. In this way, it was possible to obtain the intensity of the fluorescence in the gas-filled cell, which would have been produced in the absence of the gas. This technique, which has also been used by Steacie and LeRoy,[12] was capable of detecting a 3% decrease in fluorescent intensity. The intensity ratios η, appropriate to the $6\,^2P_{1/2} \leftrightarrow 6\,^2P_{3/2}$ excitation transfer in the vapor-gas mixture, were determined by measuring directly the relative intensities of the two resonance components present in the fluorescent light emerging from the cell which contained the vapor-gas mixture.[2]

It is estimated that depolarizing collisions might increase the intensity of the 8521 Å component of the fluorescent light emitted in the direction of the detector by about 4% and thus introduce a slight error into the experimental results.

IV. THE Cs-N$_2$ COLLISION CROSS SECTIONS

The intensity ratios I_0/I, representing the quenching of cesium resonance radiation, are plotted in Fig. 3 against N$_2$ pressure. The curves are of Stern-Volmer type[8] and ought to be linear. The curvature in the plot corresponding to the $^2S_{1/2} \leftarrow {}^2P_{1/2}$ transition is probably due to the fact that the 8944 Å line emitted by the lamp is of smaller width than the 8521 Å line. The pressure broadening due to the N$_2$ molecules in the fluorescence cell causes the width of the 8944 Å absorption line to exceed the width of the exciting line at already quite low gas pressures and renders the excitation process less efficient than in the case of the other resonance line. This additional 'quasiquenching effect' has also been observed in mixtures of cesium and inert gases.[2]

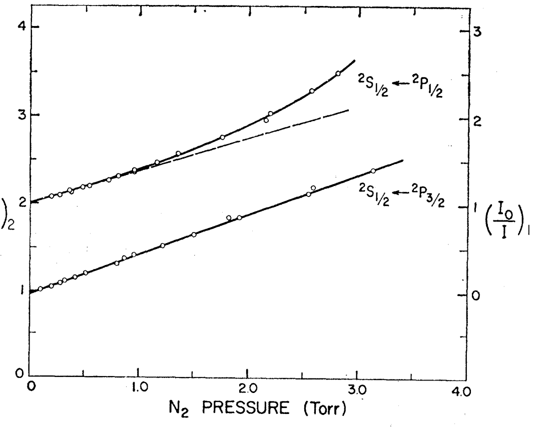

FIG. 3. Plots of intensity ratios I_0/I against N$_2$ pressure showing the quenching of cesium resonance radiation.

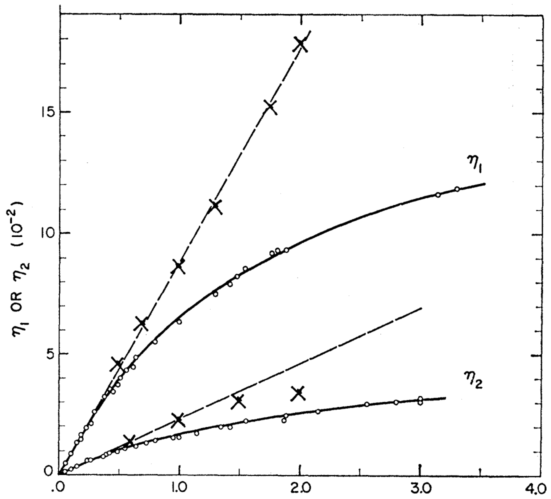

FIG. 4. Plots of intensity ratios η_1 and η_2 against N$_2$ pressure showing sensitized fluorescence in cesium. ○, raw experimental data; ×, data corrected for quenching.

The intensity ratios η, arising from the collisional $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer, are shown as functions of N$_2$ pressure in Fig. 4. The results obtained at very low pressures, which are lost in Fig. 4, are presented in Fig. 5. At low pressures, where the quenching of resonance radiation is not significant, η_1 and η_2 are linear with N$_2$ pressure. At higher pressures, departuret from linearity can be corrected by taking into accouns the quenching effects. The correction factors were obtained from the curves in Fig. 3 and were applied to the η values which, when corrected in this manner, lie on the straight lines extrapolated from low pressures as

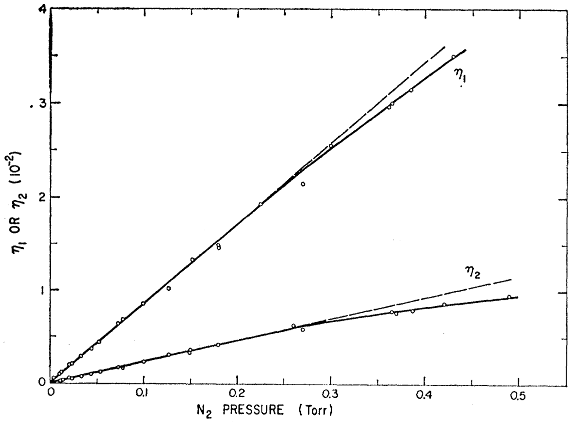

FIG. 5. Plots of intensity ratios η_1 and η_2 against N$_2$ pressure in the very low pressure region.

---

[12] E. W. R. Steacie and D. J. LeRoy, J. Chem. Phys. **11**, 164 (1943).

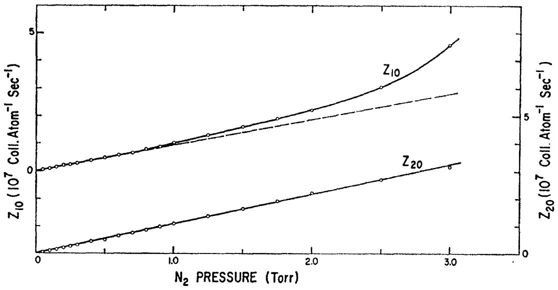

FIG. 6. Plots of quenching collision numbers Z_{10} and Z_{20} against N_2 pressure.

long as $\eta \ll 1$, in conformity with the prediction of Eqs. (11) and (13).

The collision numbers Z_{10} and Z_{20} for quenching, and Z_{12} and Z_{21} for $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer, were obtained from Eqs. (10)–(13), which were solved by means of an iteration carried out on an IBM 1620 computer on the basis of smoothed data read off the curves in Figs. 3, 4, and 5. The plots of the collision numbers for quenching and for excitation transfer against N_2 pressure are shown in Figs. 6 and 7, respectively. The departures from linearity in the cases of Z_{10} and Z_{21} are again due to collision broadening of the cesium absorption lines. Although the η values are not themselves affected by such broadening, the corrections for quenching are, and they, are in turn, introduce nonlinearity in the values of Z_{21} at higher pressures.

The collision cross sections, obtained from the slopes of the Z-P plots, are given in Table I. It is estimated from the scatter of experimental points that the values are accurate to ±10%. It is noteworthy that the cross sections Q_{12} and Q_{21}, yielded by the Z-P plots, lie within 5% of the values obtained directly from the linear portions of the η-P curves at low pressures.

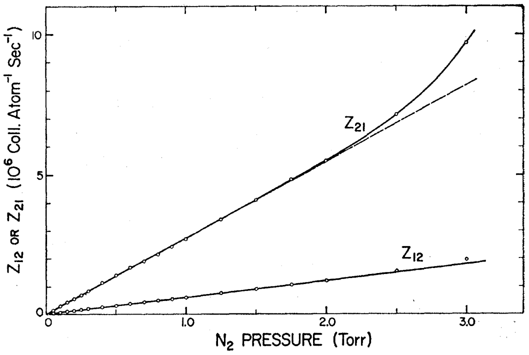

FIG. 7. Plots of collision numbers Z_{12} and Z_{21} for $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer against N_2 pressure.

V. THE Cs–H$_2$ COLLISION CROSS SECTIONS

The quenching of cesium resonance radiation by hydrogen is depicted in Fig. 8, which shows plots of the intensity ratios I_0/I against H_2 pressure for both components of the resonance doublet. The Stern-Volmer diagrams depart from linearity at pressures about one order of magnitude lower than in the case of nitrogen. The nonlinear character of the quenching at pressures above a few microns is shown even more clearly by the behavior of the collision numbers Z_{10} and Z_{20} shown in Fig. 9. These differences in the behavior of N_2 and H_2 are altogether too large to be explained by the difference in the two corresponding line-broadening cross sections.[13] A reduction in the concentration of cesium, caused by a chemical reaction between ground state Cs atoms and H_2 molecules, would account for this effect and such reactions have indeed been reported previously.[5,14] On the other hand, an examination of the sensitized fluorescence in the Cs–H_2 mixture, which should not be affected by such a reaction, leads to a con-

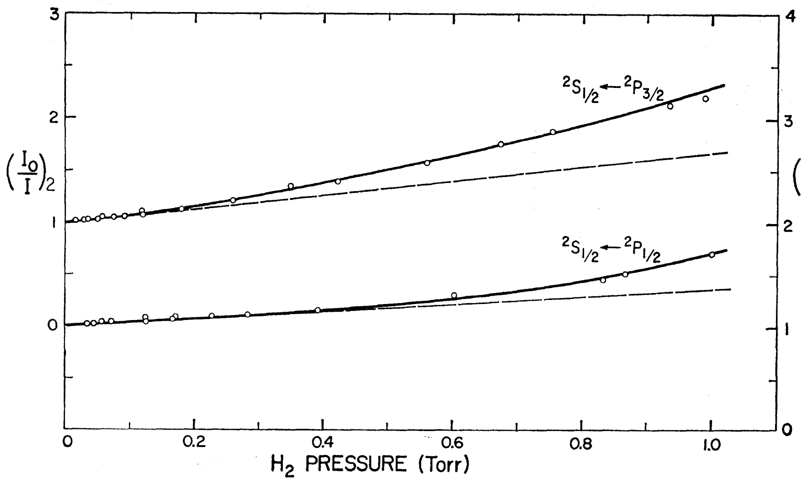

FIG. 8. Plots of intensity ratios I_0/I against H_2 pressure showing the quenching of cesium resonance radiation.

---

[13] S. Ch'en and M. Takeo, Rev. Mod. Phys. 29, 20 (1957).

[14] W. M. Smith, J. A. Stewart, and G. W. Taylor, Can. J. Chem. 32, 961 (1954).

TABLE I. Cross sections for quenching and excitation-transfer collisions.

Designation	Cross sections for various collision partners (Å^2) Cs–N$_2$	Cs–H$_2$	Cs–Cs[a]	Cs–He[b]
$Q_{10}(6\,^2S_{1/2} \leftarrow 6\,^2P_{1/2})$	55.2	11.7	...	...
$Q_{20}(6\,^2S_{1/2} \leftarrow 6\,^2P_{3/2})$	63.5	6.5	...	...
$Q_{12}(6\,^2P_{1/2} \rightarrow 6\,^2P_{3/2})$	3.6	6.5	6.4	5.7×10^{-5}
$Q_{21}(6\,^2P_{1/2} \leftarrow 6\,^2P_{3/2})$	16.2	29.6	31	3.9×10^{-4}

[a] Reference 1.
[b] Reference 2.

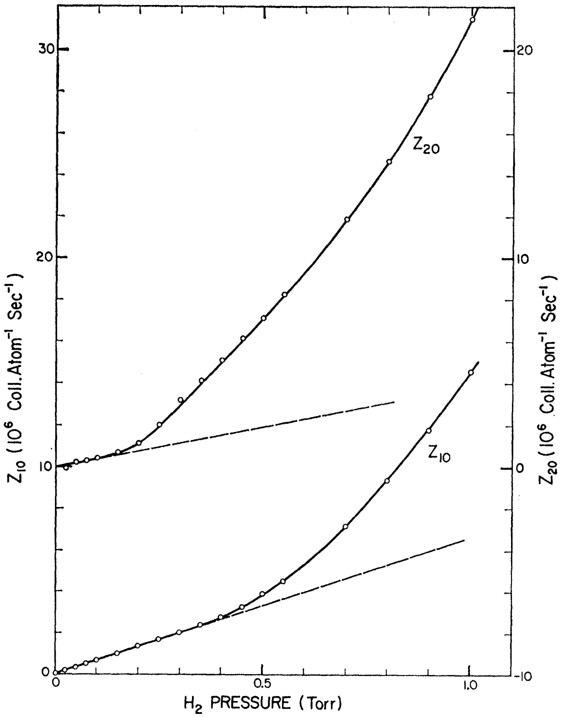

FIG. 9. Plots of quenching collision numbers Z_{10} and Z_{20} against H$_2$ pressure.

clusion that the curvatures in the quenching curves are due to real collisional deactivation processes.

The intensity ratios η of sensitized to resonance fluorescence are shown as functions of H$_2$ pressure in Fig. 10. Many of the experimental points taken at very low gas pressures are not shown and the curves appear similar to those in Fig. 4. An iteration procedure, analogous to that used with Cs–N$_2$ collisions, was used to obtain the collision numbers Z_{12} and Z_{21} which are plotted against the pressure of hydrogen in Fig. 11. If raw experimental data are used in the calculation, the collision numbers exhibit curvatures at quite low gas pressures. A correction, made on the basis of the observed quenching effects, renders the Z-P plots linear to about 0.8 Torr, where collision broadening becomes significant. As with the Cs–N$_2$ system, the 8944 Å component of the doublet is more affected than the 8521 Å component.

Thus it would seem that the rapid nonlinear increase in the quenching at very low H$_2$ pressures, as shown in Fig. 9, is caused by a real collisional deactivation process which might be due to a chemical reaction between excited Cs atoms and H$_2$ molecules with the $6\,^2P_{3/2}$ Cs atoms being somewhat more likely to enter the reaction than the $6\,^2P_{1/2}$ atoms, as is borne out by the appearance of the curves in Fig. 9. Some support to this hypothesis is lent by the results of a subsidiary experiment which showed that the onset of the curvature in the H$_2$

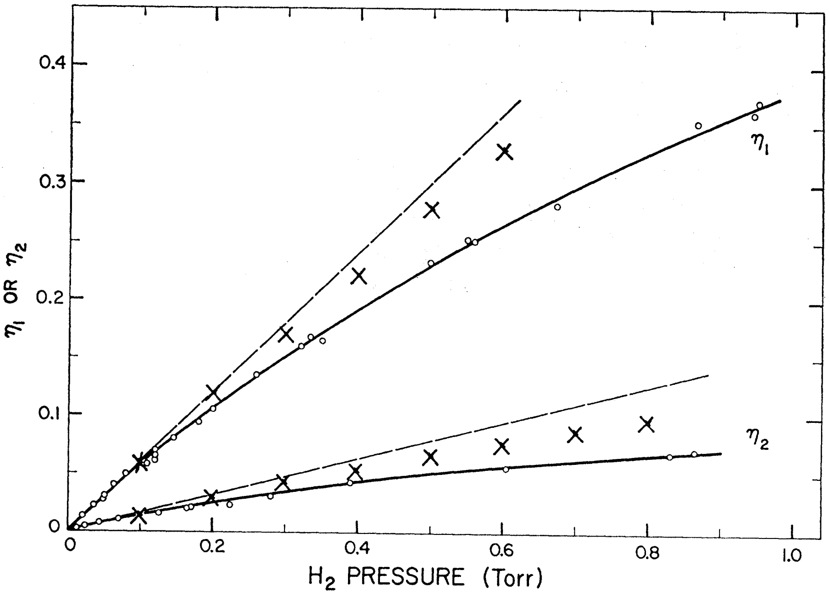

FIG. 10. Plots of intensity ratios η_1 and η_2 against H$_2$ pressure showing sensitized fluorescence in cesium. ○, raw experimental data; ✕, data corrected for quenching.

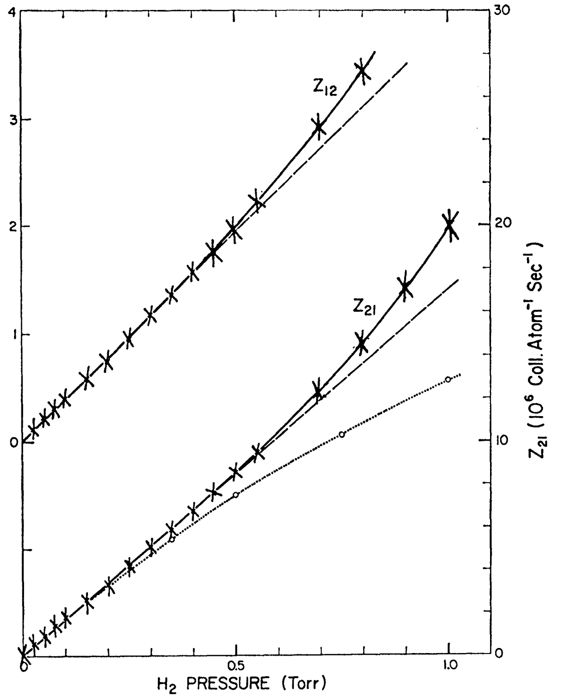

FIG. 11. Plots of collision numbers Z_{12} and Z_{21} for $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer against H_2 pressure. ○, raw experimental data; ×, data corrected for quenching.

quenching curve could be displaced somewhat towards higher H_2 pressures when the mixture was illuminated with the exciting light for very short time periods.

The Cs–H_2 collision cross sections for quenching (Q_{10},Q_{20}) and for the $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer (Q_{12},Q_{21}) were obtained from the linear slopes of the Z-P graphs and are tabulated in Table I. The values are estimated to be accurate within ±15%.

VI. DISCUSSION OF THE RESULTS

The quenching cross sections Q_{10} and Q_{20} are significantly larger for nitrogen than for hydrogen. There is also no conspicuous difference between the two cross sections for any one gas. These two facts imply that resonances between the atomic levels in cesium and particular vibrational levels in N_2 and H_2 do not play a major role in determining the sizes of the collision cross section. The ^2P cesium levels are at 11 181 and 11 735 cm^{-1}, the $v=5$ level of N_2 is at 11 365 cm^{-1}, and the $v=3$ level of H_2 at 11 782 cm^{-1}. If vibrational resonances involving these levels determined the quenching mechanism, the Q_{20} cross section in the Cs–H_2 system would be largest of all; in fact, it is the smallest.

Norrish and Smith, in their study of the quenching of Na resonance radiation,[5] found the cross section for N_2 to be about twice as large as that for H_2, which they ascribed to the presence of a potential unsaturation in the N_2 molecules. Such an unsaturation would make somewhat easier the formation of an atom-molecule transition complex in which the transfer of the atomic excitation energy would take place to all the available degrees of freedom. A similar phenomenon involving the collisional distribution of atomic excitation energy among several vibrational molecular levels has been observed by Karl and Polanyi in their investigation of Hg–CO inelastic collisions.[15]

The cross sections for $^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ excitation transfer, Q_{12} and Q_{21}, are about five orders of magnitude larger than the corresponding cross sections for collisions with inert-gas atoms[3] and are comparable to the corresponding Cs-Cs cross sections. This is not unreasonable if it is considered that the energy defect between the ^2P states, which equals 554 cm^{-1}, falls within the range of the rotational energy levels in H_2 and N_2, giving rise to the possibility of resonances.

The rotational levels in nitrogen are altogether too closely spaced to permit any sharp resonance effect corresponding to a particular $\Delta J=2$ rotational transition. In hydrogen, however, the transition $(J=1) \leftrightarrow (J=3)$ has an energy of 587 cm^{-1}, close enough to envisage the possibility of a resonance. Some evidence in favor of such a resonance is provided by the fact that the Cs–H_2 cross section Q_{21} is larger than the corresponding Cs–N_2 cross section, even though the opposite is true for the quenching cross sections which appear to have no resonance properties. Additional support for a mechanism involving the rotational states of hydrogen is lent by the results of recent investigations of energy transfer in CO–H_2 collisions.[16] It is hoped that experiments which are now in progress in this laboratory will help to clarify the role of molecular rotational levels in collisional excitation-transfer processes.

---

[15] G. Karl and J. C. Polanyi, J. Chem. Phys. **38**, 271 (1963).

[16] R. C. Millikan and L. A. Osburg, J. Chem. Phys. **41**, 2196 (1964).