Quenching and Depolarization of Resonance Radiation by Collisions with Molecules of a Foreign Gas

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A semi-classical theory describing the quenching and depolarization of resonance radiation by collisions with foreign gas molecules is presented. The total depolarizing probability is divided into two parts to allow for adiabatic and nonadiabatic depolarization. The equations for polarization are generalized in order to apply to the case in which the observed polarization results from several lines belonging to a hyperfine group. The effect of a magnetic field applied along the direction of observation is also included in the treatment. Experimental results on the polarization of the λ2537A mercury line as a function of gas pressure and as a function of magnetic field at various fixed gas pressures show good agreement with the theory. Cross sections for quenching and depolarization have been calculated for the gases investigated and are presented in Table VI.

THEORY

When resonance radiation is excited in a gas at pressures such that the probability of collision is of the same order of magnitude as that for the emission of radiation, the polarization and intensity of the emitted radiation are affected.[1,2] Collisions with atoms of a foreign gas may result in either depolarization or quenching. In collisions of atoms of the resonating gas, the passing on of excitation and all the phenomena connected with the possibility of coherent excitation of neighboring atoms complicate the situation. The present paper deals with the effect of foreign gases only. Clearly, in this case, it makes sense to speak of quenching collisions and a cross section for quenching. We shall assume that the mechanism of depolarization is such that after a depolarizing collision the excited atom, on the average, emits isotropic and unpolarized radiation. Quenching collisions obviously shorten the mean life of the excited state. With depolarizing collisions this is not necessarily true, as the depolarization may be the result of an adiabatic process.

If, however, depolarization is the result of a nonadiabatic process, the excited atom, while still excited after the collision, is in a new excited state having no coherence with the state which existed before the collision. Collisions giving rise to such noncoherent excited states must be counted as transitions from the original excited state and so lead to a shortening of the mean life of the excited atom. To sum up, an atom in an excited state may emit radiation with probability $1/\tau_0$, or it may suffer a collision of any of three types: (1) Quenching, probability αp proportional to the pressure of foreign gas; (2) Adiabatic depolarizing leading to no loss of coherence, probability $\alpha'' p$; (3) Nonadiabatic depolarizing, leading to a noncoherent excited state, probability $\alpha' p$. The total transition probability from the original excited state is then

$$1/\tau = 1/\tau_0 + \alpha p + \alpha' p. \tag{1}$$

By exciting resonance radiation with plane polarized light in a weak magnetic field parallel to the magnetic vector of the exciting light and observing either the polarization or rotation of the plane of maximum polarization of the radiation emitted along the applied magnetic field we may measure τ. For we have

$$P = P_{0,p}/[1+(eHg\tau/mc)^2],$$

TABLE I.

ATOM TYPE	N_r	A_r	B_r
Nonspin	0.613	1	0
199 $f=\frac{1}{2}$	0.211	0.111	0.111
199 $f=\frac{3}{2}$	0.211	0.444	0.111
201 $f=\frac{1}{2}$	0.176	0.050	0.050
201 $f=\frac{3}{2}$	0.176	0.182	0.075
201 $f=5/2$	0.176	0.260	0.120

* Deceased. Data for hydrogen and oxygen were obtained by Mr. Petersen.
[1] R. W. Wood, Phil. Mag. **44**, 1109 (1922).
[2] V. Von Keussler, Ann. d. Physik **87**, 793 (1927).

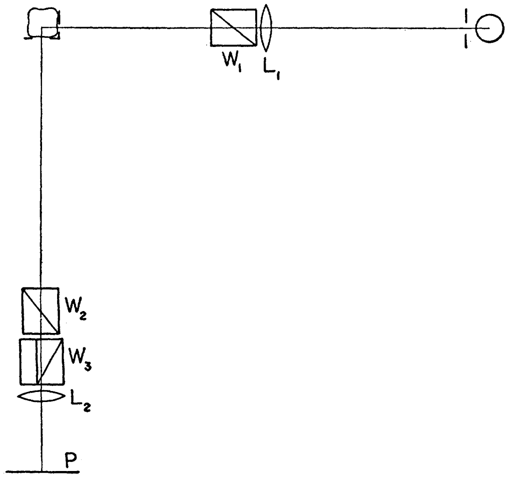

FIG. 1. Diagrammatic sketch of apparatus.

where $P_{0,p}$ is the polarization of the radiation in zero magnetic field at a pressure p of the foreign gas, and H is the magnetic field strength. For the angle of rotation of the polarization maximum ϕ

$$\tan 2\phi = eHg\tau/mc. \tag{3}$$

In order to obtain the dependence of P upon p we must estimate the relative amounts of radiation coming from atoms in the original excited state, before suffering collision of *any* type, and from atoms which have suffered either type of depolarizing collision. The competing processes have probabilities $1/\tau_0$ and $(\alpha+\alpha'+\alpha'')P$, so that a fraction $(1/\tau_0)/[1/\tau_0+(\alpha+\alpha'+\alpha'')p]$ emits before collision. A fraction

$$\frac{(\alpha'+\alpha'')p}{1/\tau_0+(\alpha+\alpha'+\alpha'')p}$$

is left in a condition such that the atoms either emit unpolarized light or are quenched. The fraction emitting is $(1/\tau_0)/(1/\tau_0+\alpha p)$ so that the ratio of the numbers of emissions giving rise to polarized and nonpolarized radiation is

$$\beta=\frac{1/\tau_0+\alpha p}{(\alpha'+\alpha'')p}. \tag{4}$$

Excited atoms emitting before collision give rise to intensities A, polarized parallel to the electric vector of the exciting light, and B, perpendicular thereto. If they emit after a depolarizing collision the intensity plane polarized in any azimuth is $\frac{1}{3}(A+2B)$. The relative intensities of radiation polarized parallel and perpendicular to the electric vector of plane polarized exciting light are then:

$$\frac{I_{\parallel}}{I_{\perp}}=\frac{A\beta+\frac{1}{3}(A+2B)}{B\beta+\frac{1}{3}(A+2B)}, \tag{5}$$

so that

$$P_{0,p}=P_{0,0}\Big/\left[1+(1-\tfrac{1}{3}P_{0,0})\frac{(\alpha'+\alpha'')p}{1/P_0+\alpha p}\right]. \tag{6}$$

For sufficiently small gas pressures, $\alpha p \ll 1/\tau_0$

$$P_{0,p}=\frac{P_{0,0}}{1+(1-\frac{1}{3}P_{0,0})(\alpha'+\alpha'')p\tau_0}. \tag{7}$$

Von Keussler[2] attempted to represent his data on polarization *vs.* gas pressure with an equation of this form. If it is fitted merely to the initial part of the curve, or if quenching is negligible, it will give good values for the total depolarizing efficiency. If quenching is not negligible, such a curve will not fit at higher pressures. As pressure increases, the polarization will not approach zero but will approach

$$P_{0,\infty}=\frac{P_{0,0}}{1+(1-\frac{1}{3}P_{0,0})(\alpha'+\alpha'')/\alpha}. \tag{8}$$

The equations above require modification if the observed polarization is due to several lines having different g values and different initial polarizations. Equation (5) will apply to any one line and the modification required is merely that the polarization is now

$$P=(\sum I_{\parallel}-\sum I_{\perp})/(\sum I_{\parallel}+\sum I_{\perp}), \tag{9}$$

where $\sum I_{\parallel}$ and $\sum I_{\perp}$ signify the total radiation due to all lines polarized in the specified azimuth. If, in zero magnetic field at zero gas pressure, the normalized parallel and perpendicular intensities due to the sth line of the rth isotope are A_{rs} and B_{rs}, respectively, and N_r the relative number of atoms of this isotope present, then for a broad line exciting source we have

$$P_0=\frac{\sum_r \sum_s N_r\left(\dfrac{A_{rs}-B_{rs}}{1+\left(\dfrac{e}{m}\dfrac{H}{c}\tau g_{rs}\right)^2}\right)}{\sum_r \sum_s N_r\left[A_{rs}+B_{rs}+\frac{2}{3}(A_{rs}+2B_{rs})\dfrac{(\alpha'+\alpha'')p}{1/\tau_0+\alpha p}\right]}. \tag{10}$$

The corresponding generalization of Eq. (3) may be written

$$\tan 2\phi=\frac{\sum_r N_r \sum_s \dfrac{(eHg_{rs}/mc)(A_{rs}-B_{rs})}{[(\alpha+\alpha')p+1/\tau_0]^2+(eHg_{rs}/mc)^2}}{\sum_r N_r \sum_s \dfrac{[(\alpha+\alpha')p+1/\tau_0](A_{rs}-B_{rs})}{[(\alpha+\alpha')p+1/\tau_0]^2+(eHg_{rs}/mc)^2}}. \tag{11}$$

In applying the above equation to the λ2537A mercury resonance line we have used values of N_r given in Table I. These are not in agreement with Aston's[3] isotope ratios—the relative number of atoms of nonspin isotopes has been arbitrarily reduced in order that $P_{0,0}$ may be brought into agreement with the observed value. It should be mentioned that the values of the quantities α are not very sensitive to change in the N_r. The use of the simple equations (2), (3) with $g=\frac{3}{2}$ and $P_{0,0}=0.80$ will give values of the α's differing from those obtained with Eqs. (10), (11) by ten percent, at most.

Experimental Procedure

A diagrammatic sketch of the apparatus is shown in Fig. 1. The earth's magnetic field was counteracted in the vicinity of the resonance bulb by means of a large Helmholtz coil, the axis of which was parallel to the direction of the earth's field. The necessary current to reduce the field to zero was determined by means of a flip coil operated in the position to be occupied by the resonance bulb.

The applied field was produced by a smaller Helmholtz coil which was accurately calibrated. The current in this coil was measured with a precision ammeter. The mercury vapor pressure was kept low by means of ice and salt mixtures surrounding the reservoirs. One reservoir containing a drop of mercury consisted of a U-tube bent in the pumping line. The second reservoir was a tube attached to the bottom of the resonance bulb. The resonance bulb was constructed

Table II. *Depolarization in hydrogen for various fields (H) and pressures (p).*

H	p=0.12	0.188		0.442		0.743		2.37	3.67	5.93
0	0.68	0.64		0.57		0.53		0.46	0.45	0.45
0.4		0.44	*0.63*	0.47	*0.44*	0.48	*0.33*			
0.8		0.25	*1.17*	0.33	*0.83*	0.37	*0.58*			
1.2			*1.73*		*1.22*		*0.93*			
1.6		0.10		0.17		0.23				

Table III. *Depolarization in deuterium for various fields (H) and pressures (p).*

H	p=0.19	0.52	0.84	0.86	2.40	3.50	4.54	5.63
0	0.71	0.59		0.55	0.46	0.44	0.40	0.39
0.406	0.33	0.40	*0.46*	0.44				
0.812	0.16	0.24	*0.91*	0.29				
1.218	0.11	0.16	*1.23*	0.20				
1.624	0.08	0.12	*1.44*	0.15				

Table IV. *Depolarization in nitrogen for various fields (H) and pressures (p).*

H	p=0.096		p=0.3		0.47		p=0.58		0.76	2.05	3.16	4.7
0	0.71		0.53		0.47		0.41		0.38	0.23	0.18	0.11
0.203	0.57		0.49		0.44		0.38					
0.406	0.36	*0.96*	0.37	*0.66*	0.34	*0.58*	0.32	*0.54*	0.30			
0.812	0.16	*1.85*	0.21	*1.26*	0.21	*1.10*	0.20	*0.97*	0.21			
1.218		*2.48*		*1.62*		*1.62*	0.13	*1.46*				
1.624	0.07		0.09		0.09		0.10		0.11			

Table V. *Depolarization in oxygen for various fields (H) and pressures (p).*

H	p=0.41	0.99		1.86	3.49
0	0.68	0.61		0.57	0.53
0.4		0.52	*0.37*		
0.8		0.38	*0.82*		
1.2			*1.06*		
1.6		0.20			

[3] F. W. Aston, Proc. Roy. Soc. **126**, 523 (1930).

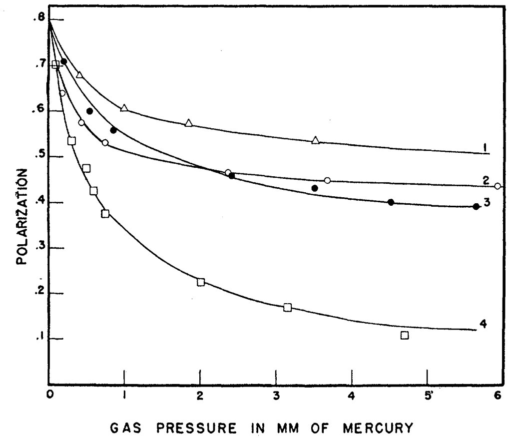

FIG. 2. Polarization of mercury resonance radiation as a function of gas pressure. The curves are drawn using the α's given in Table VI. Curve 1 (△) oxygen; 2 (○) hydrogen; 3(●) deuterium; 4 (□) nitrogen.

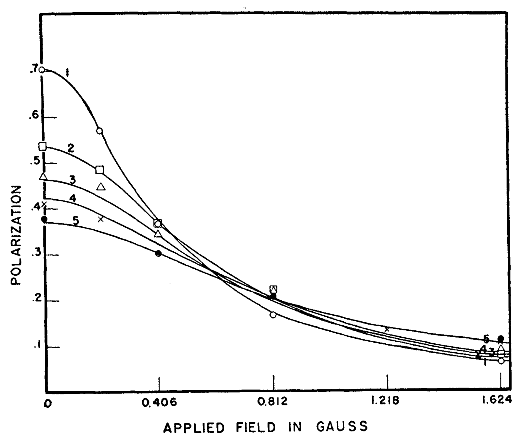

FIG. 3. Effect of magnetic fields on polarization of mercury resonance radiation at fixed nitrogen pressures. The curves are drawn using $\alpha=0.1\times10^7$, $\alpha'=1.55\times10^7$ and $\alpha''=0.55\times10^7$. Curve 1 (○) N_2 pressure$=0.096$ mm of Hg; curve 2 (□) $p=0.305$ mm of Hg; curve 3 (△) $p=0.47$ mm of Hg; curve 4 (+) $p=0.58$ mm of Hg; curve 5 (●) $p=0.76$ mm of Hg.

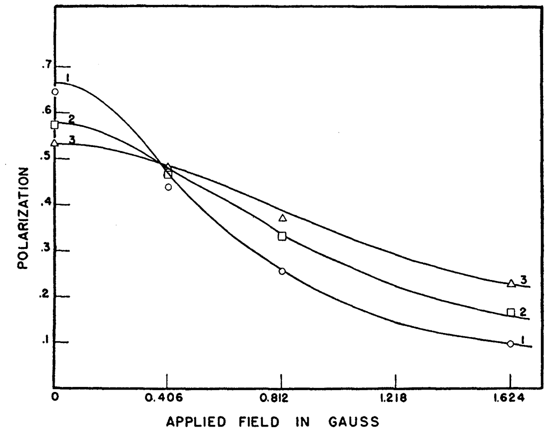

FIG. 4. Effect of magnetic fields on polarization of mercury resonance radiation at fixed hydrogen pressures. The curves are drawn using $\alpha=1.39\times10^7$, $\alpha'=1.81\times10^7$ and $\alpha''=0$. Curve 1 (○) H_2 pressure$=0.188$ mm of Hg; curve 2 (□) $p=0.443$ mm of Hg; curve 3 (△) $p=0.743$ mm of Hg.

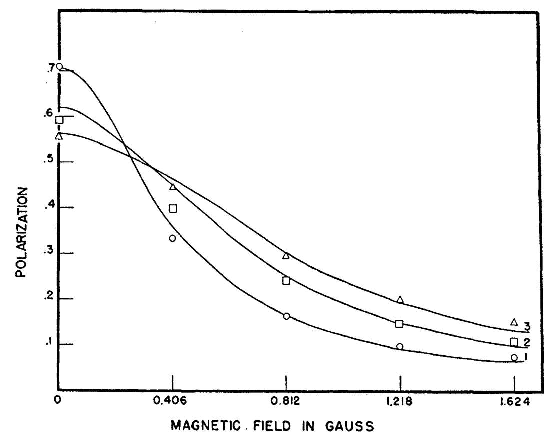

FIG. 5. Effect of magnetic fields on polarization of mercury resonance radiation at fixed deuterium pressures. The curves are drawn with $\alpha=0.45\times10^7$, $\alpha'=0.9\times10^7$ and $\alpha''=0$. Curve 1 (○) pressure$=0.19$ mm of Hg; curve 2 (□) $p=0.52$ mm of Hg; curve 3 (△) $p=0.864$ mm of Hg.

from a round quartz cell (about 70 cc capacity) by flattening four sides, giving it the approximate rectangular shape shown in the figure.

The polarization was determined by the Cornu method. Four images of a small area of the resonance bulb were produced by the Wollastons W_2, W_3 and the quartz lens L_2. W_3 was rotated about the direction of observation until two of the images on the photographic plate were equal in intensity. Experimentally, five photographs were taken near the probable match position. The difference in intensity was plotted against the angle and a straight line drawn through the points. The intersection of this line and the zero intensity line determined the match point.

In order to measure the intensity of the images, which were approximately one-eighth inch square, the images were placed over a square slit of approximately the same size and illuminated from beneath. The transmitted light fell on a photronic cell connected to a galvanometer. The difference in galvanometer readings for the two images was assumed proportional to the intensity difference when working near the match point.

The experimental method was checked by determining the polarization as a function of applied field with no foreign gas present. Good agreement with H. F. Olson's[4] data was obtained.

The nitrogen used was secured by decomposing sodium azide in a vacuum. Deuterium was prepared electrolytically from 99.5 percent pure heavy water.

Results

The observed polarization of the λ2537A mercury line for various pressures of H_2, D_2, N_2, O_2, and in various applied magnetic fields is given in Tables II to V. In these double-entry tables values of the polarization are printed in roman type and tangents of twice the angle of maximum polarization in italics. The same data are presented graphically in Figs. 2 to 7 together with curves computed from Eqs. (10), (11), with values of the α's which appear to give the best fit. These values are presented in Table VI together with cross sections computed in the usual way by means of the relation:[5]

$$\sigma_\alpha{}^2=\frac{\alpha}{2.608}\left(\frac{M_1M_2}{M_1+M_2}\right)^{\frac{1}{2}}\cdot 10^{-22}.$$

It will be noticed that the quenching cross sections given here differ considerably from those obtained by less direct methods. Where depolarizing cross sections differ significantly from those of von Keussler, the difference is due to the fact that the condition $\alpha p \ll 1/\tau_0$ was not always satisfied in his experiments, and to the high mercury pressure in his resonance lamp.

TABLE VI. *Collision probabilities* ($\times 10^{-7}$ *sec.*$^{-1}$) *and cross sections* ($\times 10^{16}$ *cm*^{2}).

Gas	Quenching α	Quenching σ_α^2	Nonadiabatic Depolarizing α'	Nonadiabatic Depolarizing $\sigma_{\alpha'}^2$	Adiabatic Depolarizing α''	Adiabatic Depolarizing $\sigma_{\alpha''}^2$	Total Depolarizing $\sigma_{\alpha'+\alpha''}^2$
Hydrogen	1.39	7.5	1.81	9.80	0.00	0.00	9.80
Deuterium	0.45	3.4	0.90	6.82	0.00	0.00	6.82
Nitrogen	0.10	1.92	1.55	29.60	0.55	10.50	40.1
Oxygen	0.85	17.2	0.78	15.70	0.00	0.00	15.70

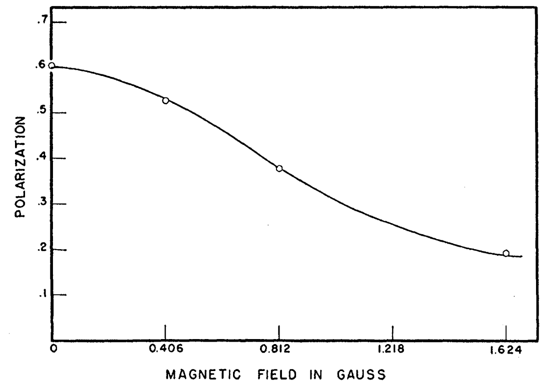

FIG. 6. Effect of magnetic fields on polarization of mercury resonance radiation at an oxygen pressure of 0.994 mm of Hg. The curve is drawn with $\alpha=0.85\times10^7$, $\alpha'=0.78\times10^7$ and $\alpha''=0$.

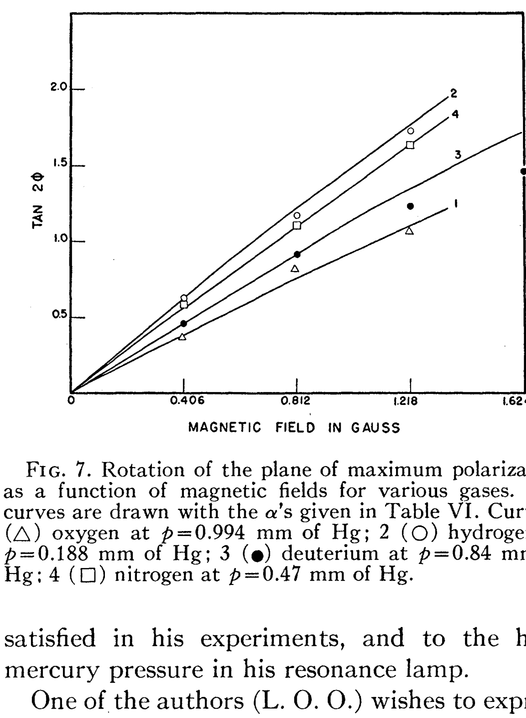

FIG. 7. Rotation of the plane of maximum polarization as a function of magnetic fields for various gases. The curves are drawn with the α's given in Table VI. Curve 1 (△) oxygen at $p=0.994$ mm of Hg; 2 (○) hydrogen at $p=0.188$ mm of Hg; 3 (●) deuterium at $p=0.84$ mm of Hg; 4 (□) nitrogen at $p=0.47$ mm of Hg.

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[4] H. F. Olson, Phys. Rev. **32**, 443 (1928).

[5] Sir James Jeans, *Introduction to Kinetic Theory of Gases* (Macmillan Company, New York, 1940), p. 137.