Collision Processes in Mixtures of Mercury Vapor and Foreign Gases

DONALD E. CUNNINGHAM*† AND LEONARD O. OLSEN
Case Institute of Technology, Cleveland, Ohio

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An extensive and quantitative study of collision processes occuring in mercury vapor-foreign gas mixtures has been performed. Measurement of the polarization of mercury resonance radiation allows a determination of the probability for quenching, adiabatic depolarizing, and nonadiabatic depolarizing collisions. The use of a photomultiplier circuit in securing the data, and of an IBM 610 computer in analysis of the data, made the breadth of this study possible. The most important result is that no adiabatic depolarization is needed to account for the results obtained for all foreign gases studied. All quenching and depolarizing probabilities obtained in this study, and in earlier studies at this laboratory, are summarized in tabular form.

IN earlier papers[1–3] a semiclassical theory of the processes undergone by atoms in quenching and depolarizing mercury resonance radiation was developed, and data were presented for several common gases. Application of the theory to the experimental results obtained in mixtures of mercury vapor and foreign gases at various pressures and applied magnetic fields allowed the evaluation of the probability for quenching, nonadiabatic depolarizing and adiabatic depolarizing collisions. The probability for these collisions was given by the constants α, α', and α'', respectively. In this earlier work it seemed necessary to introduce a concept which was referred to as "adiabatic depolarization" in order to bring theory into agreement with experiment. Physically this left much to be desired and the present work was undertaken to re-examine this matter with a better experimental approach now available because of technological advances. This new investigation also afforded us an opportunity to extend the study to several new foreign gases.

The experimental setup used is shown in Fig. 1. It does not differ substantially in geometrical configuration from that employed in the earlier work. However, a photomultiplier tube and appropriate circuitry was used as the intensity measurer in this work, while photographic plates were used in the earlier work. The use of the photomultiplier allowed much better control of the experimental conditions and also allows a much more rapid acquisition of data. It is this feature that made possible the breadth of the present study. Otherwise, the same experimental approach was employed as is reported in the earlier papers, and agreement was secured with Olson's[4] data for polarization vs magnetic field with no foreign gas present *before* and *after each series of measurements.*

Ten gases were studied in these experiments. The gases included hydrogen, nitrogen, oxygen, helium, neon, argon, krypton, xenon, carbon monoxide, and carbon dioxide. The first seven of these gases were investigated in the earlier, more cumbersome experiments.[1–3] The probability, per mm of foreign gas pressure, for the various collisions, α, α', and α'' are presented in Table I along with a comparison of the results with those previously reported from this laboratory. The values of the α's were obtained by a least squares technique in which it was required that the square of the deviations between theoretically predicted values and measured values of polarization be a minimum. This requirement is imposed over the entire pressure range of several hundredths of a mm of mercury to several mm of mercury pressure of foreign gas and over the magnetic field range of zero to 1.6 gauss. The technique developed for accomplishing this determination of the α's involved the use of an IBM 610 computer.

Table II displays the cross sections for quenching and depolarization for the ten gases investigated in this particular study. These have been calculated in the usual way as indicated in reference 1.

A typical curve obtained showing polarizations vs magnetic field strength for various pressures of argon is shown in Fig. 2. Only three pressures of argon are indicated for reasons of clarity. The solid curves are the

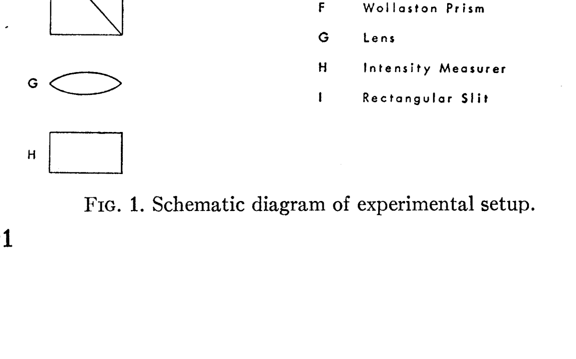

FIG. 1. Schematic diagram of experimental setup.

* Now at American Institute of Physics, 335 East 45th Street, New York 17, New York.
† Summarization of a thesis presented in partial fulfillment of the requirements for a Ph.D. degree at Case Institute of Technology.
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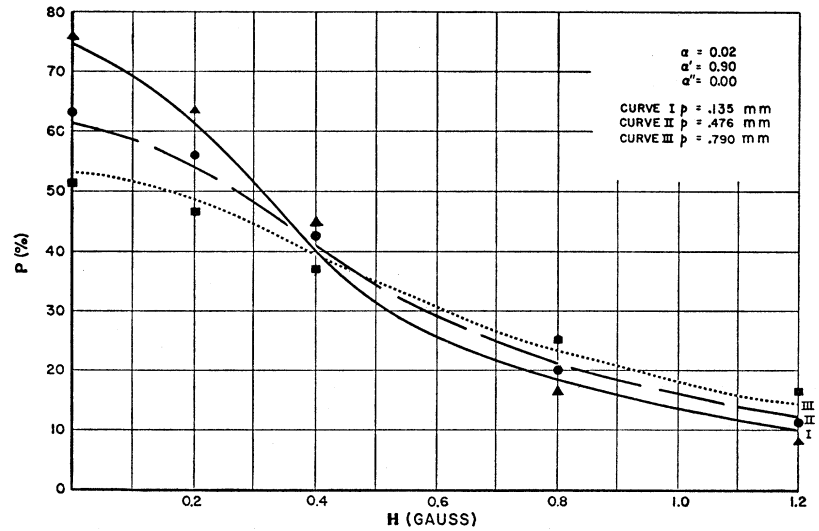

FIG. 2. Polarization $P(\%)$ vs magnetic field H (gauss) for argon.

curves predicted by theory. Experimental points are indicated.

CONCLUSIONS

As is seen by reference to Table I the results obtained are in substantial agreement with those obtained previously in this laboratory. However, in these experiments it has been found that for all gases studied the *probability of adiabatic collisions is zero,* within the limit of experimental error. In previous work considerable doubt existed concerning this point. The investigation reported on here is more extensive and under better control experimentally than the earlier work. As a result it seems possible to state rather conclusively that adiabatic collisions are not needed to account for observed results.

Mercury resonance radiation quenching and depolarization cross sections for some of the gases included in this study were determined by several experimenters some thirty years ago. The results of these experiments are discussed and tabulated in two comprehensive treatises on collision processes and related topics.[5,6] The results reported in this paper differ somewhat from those found by these earlier experimenters. The early results are all suspect principally for the reasons that the temperature of the resonance vessel was too high or the foreign gas pressure was too large. Also the experimental approaches were less direct than that used for this study. Matland[7] has studied quenching of mercury resonance radiation by nitrogen and reports a cross section observed at only one nitrogen pressure which he finds to vary with temperature. He

TABLE I. Quenching and depolarizing collision probabilities [in 10^7 sec^{-1} (mm Hg)$^{-1}$].

Gas	α	α'	α''
Hydrogen	1.40	1.75	0.02
	1.39	1.81	0.00[a]
Deuterium	0.45	0.90	0.00[a]
Nitrogen	0.11	2.35	0.00
	0.10	1.55	0.55[a]
	0.10	2.40	0.00[b]
Oxygen	1.05	0.75	0.02
	0.85	0.78	0.00[a]
	1.1	0.9	0.00[b]
Helium	0.0	1.45	0.05
	0.0	1.40	0.35[c]
Neon	0.02	0.81	0.03
	0.02	0.77	0.14[c]
Argon	0.02	0.90	0.00
	0.01	0.97	0.13[c]
Krypton	0.02	1.15	0.00
	0.00	1.11	0.00[c]
Xenon	0.03	1.30	0.02
Carbon monoxide	0.15	1.54	0.00
Carbon dioxide	0.35	1.89	0.00

[a] See reference 1.
[b] See reference 3.
[c] See reference 2.

TABLE II. Quenching and depolarizing cross sections (in 10^{-16} cm^2).

Gas	σ_{α}^2	$\sigma_{\alpha'}^2$	$\sigma_{\alpha''}^2$
Hydrogen	7.59	9.48	negligible
Nitrogen	2.09	44.6	0.00
Oxygen	21.1	15.1	0.00
Helium	0.00	11.0	negligible
Neon	0.33	13.3	negligible
Argon	0.44	19.9	0.00
Krypton	0.59	33.9	0.00
Xenon	1.03	44.5	negligible
Carbon monoxide	2.85	29.3	0.00
Carbon dioxide	8.05	43.5	0.00

[5] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), Chap. 4.
[6] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, 1952), p. 422.
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reports a lower value than found by our method. Because of the indirectness of his experimental approach and the difficulties he reports in making observations at different gas pressures, we believe our cross section for nitrogen is the better one.

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Effects of Added Gases on the Sensitized Fluorescence Spectrum of a Hg-Tl Mixture*†

RICHARD A. ANDERSON‡ AND ROBERT H. MCFARLAND
Department of Physics, Kansas State University, Manhattan, Kansas
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An investigation of the sensitized fluorescence of a mercury thallium mixture without and with the addition of argon and helium gases is discussed. Data taken without the addition of foreign gases are used to extend the theory of Frish and Karaulinya to a mercury thallium mixture. Relative collision cross sections for the excitation of the thallium energy states, $9\,^2S_{1/2}$, $7\,^2D_{5/2,3/2}$, $8\,^2S_{1/2}$, $6\,^2D_{5/2}$, and $6\,^2D_{3/2}$ were calculated for mercury thallium collisions. Data taken with the addition of argon and helium gases are given to indicate the variation of the intensity of the thallium lines as a function of argon and helium gas pressures at one constant thallium and three mercury temperatures. The explanation of the results depends on the role of mercury $6\,^3P_1$ excited atoms, metastable atoms, and mercury molecules in collision with thallium atoms for energy exchange, and also requires the use of Winans' partial selection rule and other generally accepted ideas concerning energy transfer, emission, and absorption.

INTRODUCTION

FRANCK[1] first extended the ideas of Klein and Rosseland[2] to the collisions of excited atoms of one kind with unexcited atoms of another kind. If this second atom had energy levels below the excited energy state of the first atom, energy exchange could occur followed by the emission of characteristic spectral lines of this element. Franck called this phenomenon sensitized fluorescence.

Shortly after Franck and Cario[3] completed this work, both Donat[4] and Loria[5] performed experiments in sensitized fluorescence using a mercury thallium mixture with added foreign gases. The results of these investigators did not completely agree, but both authors attributed the behavior of the thallium lines to the increased formation of metastable $6\,^3P_0$ mercury atoms caused by the addition of argon and nitrogen. In this paper the work of Donat and Loria will be repeated for argon and extended to helium. Their experiments will be repeated with improved vacuum and measurement techniques. The data obtained in this investigation will be discussed in light of recent data obtained on the role of metastable atoms,[6–9] mercury molecules,[10–13] and the HgTl quasi-molecules,[8,14,15] in sensitized fluorescence; and in light of recent studies on mercury resonance radiation.[16–20]

The recent theory of Frish and Karaulinya[21] will be extended in this paper to a mercury thallium mixture without the addition of foreign gases. This theory was the first quantitative theory to explain the phenomenon of sensitized fluorescence.

THEORY OF FRISH AND KARAULINYA

The experimental apparatus for this discussion consisted of a resonance cell having three different reservoirs. One reservoir contained the mercury metal, another the thallium metal, and the central portion of the cell was used for fluorescence studies. Ovens were

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‡ Present address: University of Missouri School of Mines and Metallurgy, Rolla, Missouri.
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