The Quenching of Mercury Resonance Radiation (2537A) by Nitrogen

C. G. MATLAND
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania
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When a mercury atom in the resonance 6^3P_1 state collides with a nitrogen molecule, it may be transferred to the metastable 6^3P_0 state. The cross section for this reaction has been measured by a new method. Mercury vapor, in the presence of a known pressure of nitrogen gas, is excited by 2537A radiation. After the source of the excitation is cut off, the decay time of the imprisoned radiation is observed. The quenching collision cross section σ_Q is calculated from the measured decay time and the known value of the imprisonment time in the absence of the quenching gas. Measurements have been taken over the temperature range 325–525°K; σ_Q is found to increase from 5.0×10^{-17} cm² at the lower temperature to 1.0×10^{-16} cm² at the upper temperature.

I. INTRODUCTION

WHEN an atom in an excited state undergoes an optical transition to the ground state, the light emitted is called resonance radiation. If a beam of such light is incident on an enclosure containing normal atoms, the incident quanta may be absorbed by some of these atoms, exciting them to a resonance state. After the natural lifetime of the excited state, the quanta are re-emitted with the atoms returning to the ground state. If the density of the absorbing vapor is sufficiently high, the quanta may be repeatedly emitted and absorbed before finally escaping the enclosure; the resonance radiation is then said to be "imprisoned."[1]

In the event that certain foreign gases are present in the enclosure containing the absorbing vapor, a mechanism is available for the destruction of the resonance states. An excited atom may collide with a foreign gas molecule and transfer some or all of its energy to the latter. The excited atom is thereby reduced to a lower state of excitation while the foreign gas molecule may be raised to a higher vibrational state or in some cases may be completely dissociated. This collision process is referred to as a "quenching" collision since the resonance radiation is thus effectively "quenched."

An example of a quenching mechanism that may occur between excited mercury atoms and nitrogen molecules is given by the reaction[2]

$$\mathrm{Hg}(6^3P_1)+\mathrm{N_2}\rightarrow\mathrm{Hg}(6^3P_0)+\mathrm{N_2}^*-0.07\ \mathrm{ev}. \quad (1)$$

The nitrogen is thought to be excited to its first vibrational level which requires an additional energy of 0.070 ev. It has been shown by optical absorption experiments[3] that as a result of the collision the excited mercury atom is lowered to the metastable $^3P_0$ state.

An early investigation of the quenching of mercury resonance radiation was carried out by Zemansky in 1930.[4] In his experiment he observed the reduction (quenching) of scattered resonance radiation from a tube containing mercury vapor when a foreign gas was introduced to known pressures. By an extension of the existing theory of imprisonment,[5] he was able to derive a relationship between the amount of quenching and the collision frequency of the excited atoms. However, it has since been shown[1] that the early theory of imprisonment is incorrect. Hence the quenching cross sections obtained by Zemansky and other early workers[6,7] who used this theory to evaluate imprisonment effects are in error.

The recent theoretical work of Holstein[1,8] on the imprisonment of resonance radiation has been experimentally verified by Alpert, McCoubrey, and Holstein.[9] Therefore, it is now possible to make quenching measurements in which the imprisonment effects can be correctly evaluated. Furthermore, with the modern gas-handling techniques now available it is felt that gas impurities can be kept at a lower level than ever before. In the present paper we describe a new method with which measurements were obtained of the cross section for the quenching of the 2537A resonance radiation of mercury by nitrogen over the temperature range 325–525°K.

II. PRINCIPLE OF THE EXPERIMENT

Alpert, McCoubrey, and Holstein measured the decay time of imprisoned resonance radiation in the following way. They irradiated a sealed-off vessel (resonance tube) containing mercury vapor with the 2537A resonance line. At the time t_0 they turned off the incident light and observed the decay in intensity of the scattered light from the resonance tube. In the absence of quenching, the rate of decay of excited atoms is[1]

$$dn/dt=-n/T_i, \quad (2)$$

where n is the density of excited atoms, and T_i is the decay time for the imprisoned resonance radiation.

[1] T. Holstein, Phys. Rev. **72**, 1212 (1947).
[2] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge University Press, Cambridge, 1934), Chap. IV.
[3] Reference 2, pp. 250–252.
[4] M. W. Zemansky, Phys. Rev. **36**, 919 (1930).
[5] E. A. Milne, J. London Math. Soc. **1**, 1 (1926).
[6] E. W. Samson, Phys. Rev. **40**, 940 (1932).
[7] V. S. Duffendack and J. S. Owens, Phys. Rev. **46**, 417 (1934).
[8] T. Holstein, Phys. Rev. **83**, 1159 (1951).
[9] Alpert, McCoubrey and Holstein, Phys. Rev. **76**, 1257 (1949).

Equation (2) has the solution

$$n=n_0 \exp(-t/T_i). \tag{3}$$

Experimentally one observes the intensity of the escaping radiation which, since it is proportional to dn/dt, has the same exponential variation as Eq. (3).

The present experiment is based on the fact that the introduction of known quantities of a foreign "quenching" gas into the resonance tube reduces the decay time of the imprisoned radiation by destroying resonance states. Another term must be added to Eq. (2) to account for this loss of excited atoms brought about by the quenching collisions. The rate of destruction of excited atoms is equal to the product of the density of the excited atoms and the quenching collision frequency $1/T_Q$. Under these circumstances Eq. (2) becomes

$$dn/dt=-n/T_i-n/T_Q, \tag{4}$$

which has the solution

$$n=n_0 \exp[-(1/T_i+1/T_Q)t]. \tag{5}$$

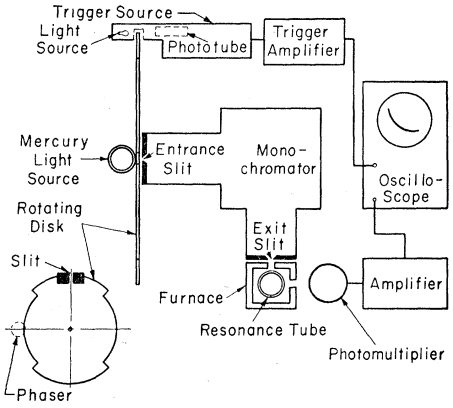

FIG. 1. Schematic diagram of apparatus.

The new decay time T is then given by the relation

$$1/T=1/T_i+1/T_Q. \tag{6}$$

From kinetic theory the expression for the quenching collision frequency is given by[10]

$$1/T_Q=N\sigma_Q \bar{v}, \tag{7}$$

where N is the density of the quenching gas, σ_Q is the cross section for the quenching collision process, and $\bar{v}$ is the mean relative speed.

The value of the imprisonment time in pure mercury is given by the experimentally verified relation[11]

$$T_i=\tfrac{5}{8}k_0R(\pi \ln k_0R)^{\frac{1}{2}}\tau, \tag{8}$$

where k_0 is the absorption coefficient at the center of the Doppler-broadened resonance line, R is the radius of the resonance tube, and τ the natural lifetime of the 6^3P_1 state of mercury. The presence of the nitrogen gas modifies T_i due to the pressure broadening of the mercury absorption line. This has the effect of reducing T_i according to the relation

$$1/T_i' \cong 1/T_i+\Delta\beta_p, \tag{9}$$

where T_i' is the imprisonment time corrected for pressure broadening. The quantity $\Delta\beta_p$ is given by[12]

$$\Delta\beta_p=0.5a_N\gamma_p/(\ln k_0R)^{\frac{1}{2}}, \tag{10}$$

where $a_N=\lambda_0/(4\pi v_0\tau)$, in which λ_0 is the wavelength of the radiation and v_0 the most probable speed. The factor γ_p is equal to twice the pressure-broadening collision frequency and is calculated using the broadening cross section measured by Zemansky.[13] Under our experimental conditions T_i is reduced approximately 10–20 percent by the addition of the nitrogen. From the corrected imprisonment time T_i' and the measured decay time T, the quenching cross section may be calculated from Eqs. (6) and (7).

III. APPARATUS

The apparatus for measuring resonance radiation decay times in the presence of a foreign gas is identical to that used by Alpert *et al.*[9] A schematic diagram of their apparatus is shown in Fig. 1. Light from a mercury discharge source is periodically interrupted by a disk rotating at about 10 000 rpm and directed into the resonance tube through a monochrometer which selects the 2537A line. The radiation escaping from the resonance tube is detected by the photomultiplier and amplified. The output of the amplifier is fed onto the vertical axis of the oscilloscope. The horizontal trace of the oscilloscope is initiated by the trigger source. Timing markers on the oscilloscope trace are obtained from a calibrated oscillator. The oven surrounding the resonance tube is composed of two independent sections so that the mercury vapor temperature and density can be controlled independently. The decay times are obtained from analysis of photographs of the decay trace taken at various vapor densities and temperature.

Temperature control of the ovens surrounding the resonance tube was obtained by operating them on a 110-volt ac regulated source. For every run the upper section of the oven was maintained at a higher temperature than the lower section to insure that no mercury condensed on the walls of the upper part of the resonance tube. A temperature constant within ± 0.1°C was maintained for a minimum period of fifteen minutes before any data for a given point was taken.

IV. PREPARATION OF RESONANCE TUBES

An important requirement for the measurement of quenching is the elimination of all contaminating gases.

[10] Earle H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 112.
[11] Holstein, Alpert, and McCoubrey, Phys. Rev. **85**, 985 (1952), Eq. (1).
[12] Reference 1, Eq. (5.15) and following text.
[13] Reference 2, Table XIX, p. 171.

The gas-handling techniques are therefore of paramount importance; hence, we describe in some detail the preparation of the resonance tubes used in our experiment.[14]

The nitrogen used in the present experiment was obtained from Air Reduction Company, Inc. and supplied with the following mass spectrographic analysis: argon, 2 parts in 10^5; neon, 6 parts in 10^5; all other gases not greater than 2 parts in 10^4. The mercury was chemically pure (99.98 percent) triply distilled mercury. This material was again triply distilled at 200°C in our own vacuum system. The pressure of noncondensible gases during the final distillation of the mercury into a glass break-off capsule was $\sim 10^{-8}$ mm Hg.

The resonance tubes are formed of Vycor[15] tubing 13 mm i.d., with 1-mm thick walls and an over-all length of 15 cm. The tubing is closed at one end and to the other end is joined a quartz-to-Pyrex transition seal for attachment to the Pyrex glass of the vacuum manifold. The tubes are sealed off in the softer glass to minimize the contaminating gases driven out of the glass.

A schematic diagram of the vacuum system used for the preparation of the resonance tubes is shown in Fig. 2. The three valves in the figure are of all metal construction.[14] The manometer shown is a null-reading balance type with a movable metal diaphragm that separates the clean side of the vacuum system from a liquid manometer.[16] Both the vacuum valves and manometer are designed to withstand high-temperature (400–500°C) bakeout.

The vacuum and gas handling procedure used in the preparation of the resonance tubes is as follows. The entire vacuum system is baked out for 12 hours at 400–450°C. After the bakeout both ion gauges are outgassed concurrently for two to four hours. When normal operating voltages are applied to the ion gauges, a pressure of $\sim 10^{-8}$ mm Hg is observed, and in a few minutes the ion gauges pump down the system to a pressure of 5×10^{-9} mm Hg or less. With the manifold isolated from all pumping action, one observes a typical rate of rise of pressure in the system of 2×10^{-10} mm Hg/min.

When filling at low pressures, the expansion volume of the system (see Fig. 2) is filled to the proper pressure, the mercury distilled into the resonance tube, the expansion valve opened, and the tube sealed off. By this method, mercury resonance tubes containing various nitrogen pressures were prepared.

V. ANALYSIS OF DATA

A typical photograph of the oscilloscope trace is shown in Fig. 3. The width of the decay trace is due to the large random fluctuations which occur because the intensity of the radiation being detected is very low. Some smoothing of these fluctuations is accomplished by making photographic exposures of 8- to 16-seconds duration. Under these circumstances the photographic record represents an average over several thousand separate decay traces. The positive prints made for data analysis are overexposed to facilitate the visual selection of the most dense area of the decay trace. Measurements are made from the most dense region between timing markers to the baseline. The results obtained from the trace of Fig. 3 are shown on Fig. 4.

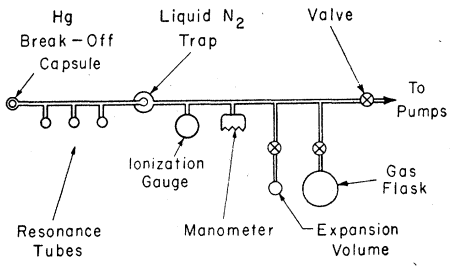

FIG. 2. Schematic diagram of the vacuum manifold used for the preparation of gas-filled resonance tubes.

In these measurements there is a small correction for background intensity which arises from the persistent band fluorescence of mercury molecules.[17] The correction is made by extrapolating the intensity at late times in the decay (due entirely to band fluorescence) back to early times when the resonance radiation predominates.

Since the mean free path for the mercury and nitrogen is small compared to the diameter of the resonance tube, the density in the upper portion of the tube is obtained by equating the pressures of the two temperature regions. The mercury vapor pressure as a function

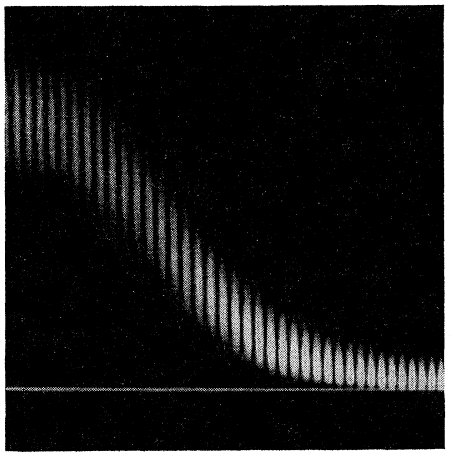

FIG. 3. Photograph of an oscilloscope trace for a nitrogen density of 2.4×10^{16} atoms/cc and a mercury vapor density of 5.7×10^{14} atoms/cc. The blanks in the trace have a 1μsec separation.

[14] For a fuller account of the vacuum techniques employed, see D. Alpert, J. Appl. Phys. **24**, 860 (1953).

[15] An ultraviolet transmitting glass obtained from Corning Glass Company, Corning, New York.

[16] Alpert, Matland, and McCoubrey, Rev. Sci. Instr. **22**, 370 (1951).

[17] A. O. McCoubrey, Phys. Rev. **84**, 1073 (1951).

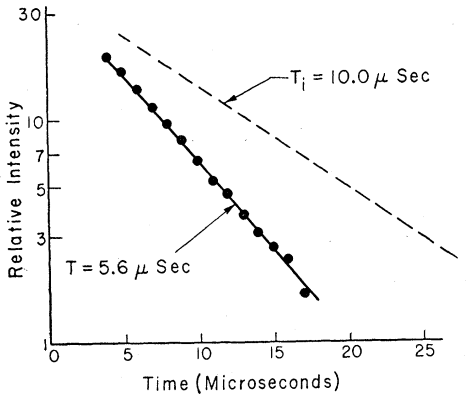

FIG. 4. Experimental results derived from the oscilloscope trace of Fig. 3. The dotted line represents the decay characteristic obtained in the absence of a quenching gas for the same mercury vapor density.

of temperature is taken from tables as given in Landolt-Bornstein.[18]

VI. DISCUSSION OF RESULTS

A plot of the measured quenching cross section *versus* the temperature is shown on Fig. 5. The quenching cross section σ_Q varies from 5.0×10^{-17} cm^2 at 325°K to 1.0×10^{-16} cm^2 at 525°K. The solid curve of the figure is obtained in the following way. As indicated in Eq. (1), if the nitrogen molecule is assumed to be excited to its first vibrational level, an energy of 0.07 ev must be supplied by the kinetic energy of the colliding particles. It is assumed that the cross section for the reaction is constant above this threshold energy. The observed cross section is then equal to this constant cross section times the fractional number of molecules with energies in excess of 0.07 ev. From kinetic theory the fraction of molecules with energies greater than ϵ is given by[19]

$$(1+\epsilon/k\theta)e^{-\epsilon/k\theta},$$

where k is the Boltzmann constant, and θ is the temperature of the upper portion of the resonance tube. With the assumption that this function determines the temperature variation of the cross section, a curve is plotted which is fitted to the data at the temperature 340°K. The curve so obtained is close to the best one which could be drawn through the data.

Direct comparison of the measured value of σ_Q with the experiment of Zemansky is not possible because of the temperature difference of the two experiments. He obtained a value of $\sigma_Q=8.5\times10^{-17}$ cm^2 at 298°K. Our extrapolated value is some 50 percent lower. In view of uncertainties in the earlier experiment and theory, it is thought the value obtained by Zemansky is in error. Other measurements of the quenching cross section are those of Sampson[6] giving $\sigma_Q=9.7\times10^{-17}$ cm^2 for $\theta=301$, 374, and 486°K, and the results (obtained by a similar method) of Duffendack and Owens[7] yielding $\sigma_Q=1.92$, 2.48, and 2.62×10^{-16} cm^2 at $\theta=473$, 673, and 873°K, respectively. In both the above experiments, the early theory was used to evaluate the effect of imprisonment. Furthermore, the pressure-broadening effect of the nitrogen was neglected even though the nitrogen pressure was as large as 100-mm Hg. Consequently, these results are also considered to be in doubt.

Although resonance tubes were prepared containing various nitrogen pressures, the measurements reported here are for $p(N_2)=0.74$-mm Hg only. At higher and lower nitrogen pressures, the measurements become difficult. At higher pressures the amplitude of the band fluorescence becomes quite large (as much as $\frac{1}{3}$ of the total amplitude), tending to obscure the resonance radiation decay. In addition, the shorter decay times encountered at higher pressures are more difficult to measure with accuracy. At low foreign gas pressures, where T is nearly equal to T_i, the quenching effect becomes too small to measure accurately.

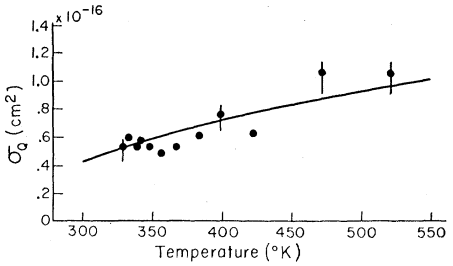

FIG. 5. The quenching cross section σ_Q *versus* temperature. The solid curve is obtained from theory and is fitted to the data at the temperature 340°C. The vertical lines on four data points indicate the variation of the estimated experimental error with temperature.

VII. CONCLUSIONS

When a mercury atom in the resonance 6^3P_1 state collides with a nitrogen molecule, it may be transferred to the metastable 6^3P_0 state. The cross section for this reaction has been obtained from measurements of the decay of resonance radiation following excitation of a resonance tube. The imprisonment effects are taken into account by use of a theoretical formula which has been experimentally verified. A correction has been included for the pressure broadening of the absorption line by the nitrogen gas.

The resonance tubes were prepared using improved vacuum and gas handling techniques. Consequently, it is felt that the impurity contaminations in these tubes is lower than has been achieved before, so that the experimental results may have greater significance than earlier measurements.

The method used for the measurements, while applied to studies of nitrogen, may be used for measuring the

[18] *Landolt-Bornstein Tables* (Verlag Julius Springer, Berlin, 1923), fifth edition, Vol. II, p. 1335.

[19] R. C. Tolman, *Statistical Mechanics with Application to Physics and Chemistry* (The Chemical Catalog Company, Inc., New York, 1927), pp. 67–70.

quenching cross section of such gases as CO, NO, H_2, or O_2. With these gases, the pressure broadening correction would be negligible since a measurable quenching effect is produced at much lower gas pressures. Moreover, for the gases H_2 and O_2 the difficulty arising from the presence of the band fluorescence would be very much reduced. In these cases the quenching processes do not produce metastable mercury atoms, which are the source of the band fluorescence.

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Hyperfine Structures of Silver and Gold by the Atomic Beam Magnetic Resonance Method*

GÜNTER WESSEL† AND HIN LEW
Division of Physics, National Research Council, Ottawa, Canada
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An ionizer of the electron bombardment type has been applied to a beam of atoms in a magnetic resonance apparatus. The ionization efficiency for potassium atoms has been found to be 1 part in 3000. The new ionizer has made it possible to study the hyperfine structures and the g factors of the ground states of silver and gold, two elements which cannot be detected by the surface ionization method commonly used heretofore. The measurements yield the following results:

$$|\Delta\nu(Ag^{107})| = 1712.56 \pm 0.04 \text{ Mc/sec},$$
$$|\Delta\nu(Ag^{109})| = 1976.94 \pm 0.04 \text{ Mc/sec},$$
$$g_J(Ag)/g_J(Cs) = 0.99987 \pm 0.00010,$$
$$|\Delta\nu(Au^{197})| = 6107.1 \pm 1.0 \text{ Mc/sec},$$
$$g_J(Au)/g_J(Cs) = 1.00081 \pm 0.00005.$$

I. INTRODUCTION

A SERIOUS limitation to the scope of the molecular or atomic beam method of radio-frequency spectroscopy has been the difficulty of detecting the neutral atoms or molecules after they have passed through the various deflecting fields of the apparatus. Hitherto there have been two main types of detectors in use. They are the Pirani gauge, which can be used for gases only, and the surface ionization detector. The latter consists of a heated filament on which the atoms to be detected impinge. If the ionization potential of the atom is lower than the work function of the filament, or at most slightly higher, the atom has a high probability of being re-emitted as a positive ion. Thus far, aside from the halogens, only atoms with ionization potentials of 6 volts or less have been detected by this technique. In the case of the halogens,[1] negative ions are formed by electron attachment. Other detectors, as for example one which makes use of the radioactivity[2] of radioactive isotopes, are limited in their applicability to special groups of elements. In an attempt to make a detector that would be applicable to all atoms, we have constructed an ionizer which depends on electron bombardment. The design is based on an ion source developed by Heil[3] and applied to mass spectrometry by Paul.[4] Estimates from Paul's work indicated that the efficiency of such an ionizer should be sufficient even for the low intensities usually encountered in atomic beam work where the density of atoms in the beam may be less than that in the vacuum of the apparatus. Our experiments have confirmed these estimates. However, although the ionizer is probably capable of ionizing any atom or molecule, it cannot be claimed that all detection problems in the field of molecular beams have been overcome. Because of the relatively low efficiency (about 1 part in 3000) and because of the inevitable background resulting from the ionization of the residual gases in the vacuum, a strong source of atoms is required at the source end of the resonance apparatus. The source strength needed is such that the ionizer will probably be restricted to atoms which can be obtained in quantities of appreciable fractions of a gram. The exact amount, of course, will depend on the geometry of the apparatus and the complexity of the spectrum.

Tests of the electron bombardment ionizer have been made with the stable isotopes of silver and gold. These elements are particularly suited for the tests because they cannot be detected by the surface ionization

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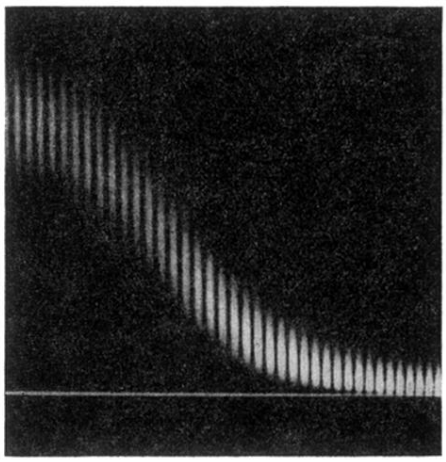
† National Research Laboratories Postdoctorate Fellow.
[1] Davis, Feld, Zabel, and Zacharias, Phys. Rev. **76**, 1076 (1949).
[2] E. H. Bellamy and K. F. Smith, Phil. Mag. **44**, 33 (1953).
[3] H. Heil, Z. Physik **120**, 212 (1943).
[4] W. Paul, Z. Physik **124**, 244 (1948).



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