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## The Quenching of Mercury Resonance Radiation by Compounds Containing Deuterium

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The quenching of mercury resonance radiation by hydrogen, deuterium, ammonia, deuterio-ammonia, water vapor and heavy water vapor has been measured. It has been possible to correlate the differences in quenching efficiencies between the heavy and ordinary compounds with the changes in the vibrational level of the molecules which are brought about by the introduction of deuterium atoms. The quenching cross sections obtained fall on the general type of resonance curve.

THE problem of the transfer of energy between colliding particles is of fundamental importance in the physical chemistry of kinetics. The problem of quenching of resonance radiation by small amounts of foreign gases is a special case of the more general problem of energy transfer. In this case the transfer of energy is one in which energy of excitation may be transferred to the foreign gas molecule either as energy of excitation, or as vibrational energy, and the chemist has been interested in the reactions which molecules undergo subsequent to this transfer of energy. The discovery of the heavy isotope of hydrogen and the formation of compounds in which this isotope is substituted for ordinary hydrogen has given the chemist a means of studying the mechanism of a number of reactions in which hydrogen and its compounds take part. It was the purpose of this research to discover if possible whether the definite changes one could make by the substitution of deuterium for hydrogen would profoundly affect the nature and efficiency of processes involving an exchange of energy, and this special case of energy exchange was chosen as one affording

the most direct method of attack. Further the author had previously carried out an investigation of the rate of the photosensitized reaction between deuterium and oxygen, and for comparison of these results with those obtained for hydrogen and oxygen, it was necessary to know whether there was a difference in the efficiency of hydrogen and deuterium in quenching mercury resonance radiation.

### EXPERIMENTAL PROCEDURE

The experimental method employed was similar to that used by Zemansky<sup>1</sup> and by Bates,<sup>2</sup> full experimental details being given in their publications. The source of mercury resonance radiation used to illuminate the resonance lamp was a Hanovia resonance arc; spectroscopic examination of the light from this source showed it to be very rich in the 2537 line.

The intensities of the resonance radiation were

<sup>1</sup> Zemansky, *Phys. Rev.* **36**, 919 (1930).

Mitchell and Zemansky, *Resonance Radiation and Excited Atoms*, Macmillan Co., 1934.

<sup>2</sup> Bates, *J. Am. Chem. Soc.* **52**, 3825 (1930); **54**, 569 (1932).

measured by means of a platinum photoelectric cell constructed in the manner described by Zemansky, and the photoelectric currents were measured by means of a sensitive Compton electrometer.

The quenching  $Q$  is expressed as the intensity of resonance light emitted in the presence of a definite pressure of foreign gas divided by the intensity of emitted resonance radiation at zero foreign gas pressure

$$Q = I_{R.p.}/I_{R.vac.} \times 100.$$

#### Preparation of gases and vapors used

Hydrogen was prepared by the electrolysis of caustic potash solution, the oxygen and hydrogen being evolved in separate compartments. The hydrogen so formed was passed over a drying train of phosphorus pentoxide and then over heated platinized asbestos to remove traces of oxygen. The gas was then passed through a U-tube packed with charcoal (activated *in situ*) and cooled in liquid air; finally the gas was further dried by passing over phosphorus pentoxide and stored in a glass bulb from which it was admitted into the quenching apparatus.

Deuterium was prepared in a similar way by the electrolysis of 100 percent heavy water, the purification train being, apart from the U-tube of active charcoal, of the same kind as that used for ordinary hydrogen. Ammonia was prepared by the action of caustic potash on synthetic ammonium chloride, the gas being dried first by solid caustic potash, and lime, and finally after repeated condensation and fractional distillation the gas was condensed over phosphorus pentoxide which had been freshly distilled in a stream of oxygen *in situ*, and then was allowed to evaporate into an evacuated bulb in which the gas was stored.

The deuterio-ammonia was loaned by Professor Hugh S. Taylor and Dr. J. C. Jungers and had been prepared in the manner described by them.<sup>3</sup> The heavy water used contained 100 percent deuterium and had a density of 1.1059 at 20°C.<sup>4</sup> The electrical conductivity of the water was  $3 \times 10^{-6}$ .

Gas pressures were measured by means of a McLeod gauge and the water vapor pressures

were maintained constant by means of constant temperature baths. The data given by Lewis<sup>5</sup> for the vapor pressure of heavy water at various temperatures were used to calculate the pressures of heavy water vapor in the apparatus.

#### EXPERIMENTAL RESULTS

Zemansky,<sup>1</sup> employing Milne's theory, has developed an expression for the intensity of scattered radiation emerging from unit area of the face of the absorption cell next to the photoelectric cell. The intensity is given by

$$\pi I_+ = KG(kl, \tau Z_Q),$$

where  $K$  is the intensity of the collimated beam and  $G$  depends on only two quantities  $kl$ , where  $k$  is the absorption coefficient of the gas in  $\text{cm}^{-1}$  for the radiation in question, and  $l$  the thickness of the absorption cell; and on  $\tau Z_Q$  where  $\tau$  is the mean life of the excited mercury atom in the  $^3P_1$  state and  $Z_Q$  is the number of collisions between foreign gas molecules and excited mercury atoms which are effective in bringing about quenching. From a knowledge of  $k(\nu)l$  it is possible to obtain a relationship between the quenching  $Q$  and the quantity  $\tau Z_Q$ . Fig. 1 shows

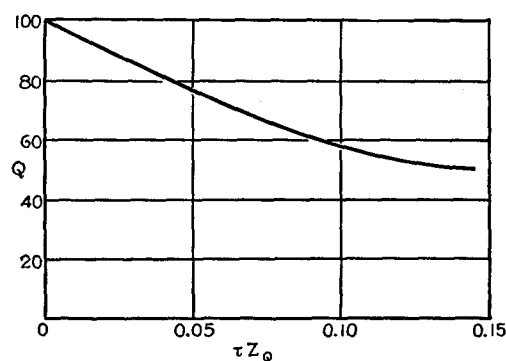


FIG. 1.

graphically the relationship between  $Q$  and  $\tau Z_Q$  which was used in these experiments. The results of the experimental work are tabulated in Table I and values of  $Q$  (the quenching) are plotted against  $p$  in Fig. 2. Table II gives the values of the quenching cross section  $\sigma_Q^2$  cal-

<sup>3</sup> Taylor and Jungers, J. Am. Chem. Soc. **55**, 5057 (1933).

<sup>4</sup> Taylor and Selwood, J. Am. Chem. Soc. **56**, 998 (1934).

<sup>5</sup> Lewis and Macdonald, J. Am. Chem. Soc. **55**, 3057 (1933).

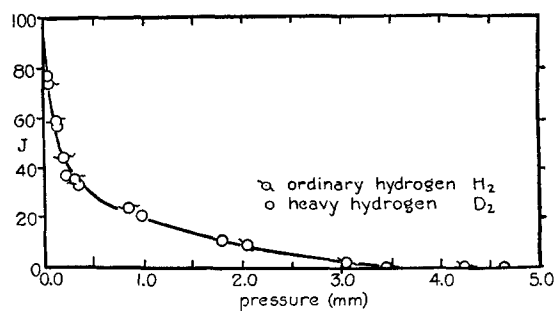


FIG. 2a.

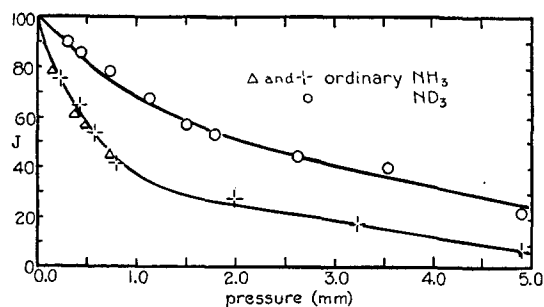


FIG. 2b.

culated from the slopes of the lines obtained by plotting  $\tau Z_Q$  against  $p$  and in the case of hydrogen and ammonia good agreement is obtained with the values for these gases determined by Zemansky. Fig. 3 shows the relationship  $\tau Z_Q$  against  $p$ . The values for deuterio-ammonia and for heavy water vapor fall well below the values obtained for the ordinary compounds. The compounds containing the deuterium being in both cases very much less efficient than the ordinary compounds in quenching mercury resonance radiation. The difference between the heavy and the light compounds is one which is not merely due to the difference in mass, and hence due to the total number of collisions, but, as is seen from the values of the cross sections of

TABLE I.

Hydrogen		Deuterium		Ammonia		Deutero-ammonia	
Pressure in mm	$Q$	Pressure in mm	$Q$	Pressure in mm	$Q$	Pressure in mm	$Q$
0.04	77.0	0.05	74.1	0.16	78.0	0.31	90.0
0.13	58.9	0.12	57.0	0.23	75.1	0.44	85.4
0.22	37.0	0.19	44.3	0.43	64.8	0.72	78.1
0.34	33.1	0.31	35.2	0.49	56.5	1.13	67.2
0.98	21.1	0.84	24.0	0.58	53.4	1.49	56.5
				0.75	45.0	1.79	53.1
				0.80	41.8		

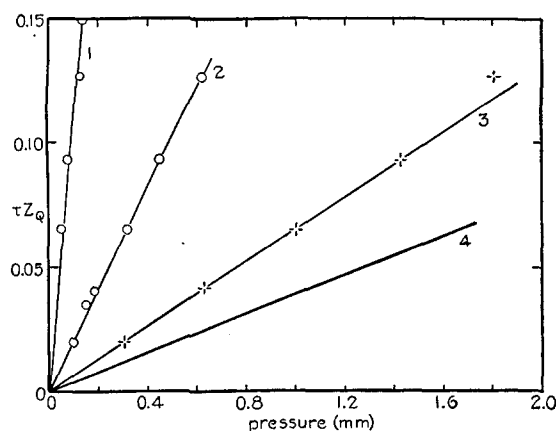


FIG. 3. (1) Hydrogen and deuterium; (2) ammonia; (3) deuterio-ammonia; (4) heavy water.

quenching  $\sigma Q^2$ , where the difference in mass has been taken into account, this difference persists and is due to definite changes in the molecule brought about by the introduction of deuterium atoms.

Deuterium itself on the other hand is within the experimental error of this work equally as efficient as hydrogen in quenching mercury resonance radiation. The values of the quenching obtained for hydrogen and deuterium at various pressures lie practically on the same curve; if a distinction could be made one would say that deuterium showed slightly better quenching than hydrogen.

This result is in accordance with the author's work on the rate of the photosensitized reaction between oxygen and hydrogen or deuterium, and further, some preliminary experiments of Taylor and Jungers have shown that hydrogen and deuterium have apparently the same effect in retarding the rate of photosensitized decomposition of ammonia. Although both these gases give apparently the same  $\tau Z_Q/p$  values because

TABLE II.

Gas	$\tau Z_Q/p$	Normal		$\Delta E$ volts	$E$ volts
		$\sigma Q^2 \times 10^{-16}$	$\sigma^2 \times 10^{-16}$		
Hydrogen $H_2$	1.08	6.01	8.89	4.46	4.86
Deuterium $D_2$	1.08	8.41	8.89	4.54	4.86
Ammonia $NH_3$	0.200	2.94	10.8	0.202	0.218
		3.04			
Deutero-ammonia $ND_3$	0.065	1.09	10.8	0.29	0.218
Water vapor $H_2O$	0.064	1.00	10.0	0.197	0.218
Heavy water vapor $D_2O$	0.038	0.46	10.0	0.15	0.218

of the difference in mass between hydrogen and deuterium the quenching cross section of deuterium is greater than that of hydrogen.

### THEORETICAL DISCUSSION

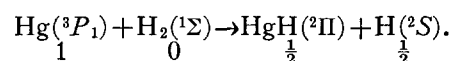
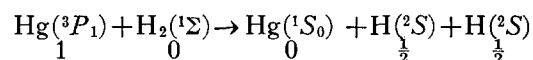
The quantum-mechanical considerations<sup>6</sup> of the problem of the transfer of energy are too general in nature to be applicable quantitatively to any special cases involving relatively complex molecules. There are, however, broad generalizations which emerge from the theoretical treatment.

The efficiency of the process of transfer of energy depends upon the relative positions of the energy levels in the colliding particles, that is on the energy which the excited atom is able to give, and the energy which the colliding molecule is able to receive, either as energy of excitation or as vibrational energy. Any excess energy or deficiency of energy transferred must be adjusted by an adjustment of the kinetic energy of the particles before and after collision. So that the less energy which it is necessary to transfer into kinetic energy, the more efficient will be the transfer of energy.

In the case of excited mercury it is possible that the quenching process may be one of two kinds. The mercury excited to the  $^3P_1$  state may by collision with a molecule be degraded to the  $^1S_0$  ground state, a process which would involve the transfer of 4.86 volts; or on the other hand the mercury may be "quenched" to the metastable  $^3P_0$  state a change involving only 0.218 volt.

In the case of hydrogen it is very evident that the collision is one in which the whole of the energy of full excitation is transferred to the hydrogen, and during or subsequent to this collision the hydrogen is dissociated as a result of the transfer of energy. The dissociation of the hydrogen would involve 4.46 volts. There is, however, abundant spectroscopic evidence for the formation of mercury hydride HgH from hydrogen and mercury when photosensitized by the mercury resonance line. Beutler and Rabinowitsch<sup>7</sup> have found that in the HgH band, which appears when mercury and hydrogen are illuminated with mercury resonance light, the high rotational states of HgH are very intense. This observation being in agreement with their theoretical conclusion that, if during a collision of the type  $A' + BC \rightarrow (AB)^{rot} + C$ ,  $A$  is an atom of large mass,  $AB$  will possess after the collision a large amount of rotational energy. Both the processes suggested for the quenching of excited mercury by hydrogen are energetically possible, and moreover, obey Wigner's<sup>8</sup> rule for conservation of total spin momentum during the process

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It was with the hope that any differences between the efficiencies of deuterium and ordinary hydrogen in quenching excited mercury would give an indication of the mechanism of the process, that the quenching of both hydrogen and deuterium was determined. The collision between an excited mercury atom and a hydrogen molecule and the transfer of excitation energy during this collision may raise the vibrational level of the hydrogen molecule to a level near or above the dissociation level, and in this region the vibrational levels of the hydrogen will be so close together that there will be no difficulty in finding a level which will give an exact correspondence in energy. In other words the transfer of 4.86 volts to the hydrogen will always raise the vibrational level into the continuum where the molecule will always have a vibrational level demanding the exact energy transfer. This, however, would necessitate that the excess energy over that required for dissociation would be accommodated as kinetic energy in the resultant particles and we have stated that the smaller the amount of energy it is necessary to transfer into kinetic energy, the more efficient will be the process of energy transfer. Because of the smaller zero point energy of deuterium the

<sup>6</sup> Kallman and London, *Zeits. f. physik, Chemie* **B2**, 207 (1929).

<sup>7</sup> Beutler and Rabinowitsch, *Zeits. f. physik. Chemie* **B8**, 231, 403 (1930).

<sup>8</sup> Wigner, *Nachr. Götting. Ges.* 375 (1927).

energy of dissociation of the deuterium molecule will be greater than for the hydrogen molecule, and hence, in the case of deuterium, there will be a closer correspondence between the energy transferred from the excited mercury atom, and the energy which the molecule can take up. Hence in the case of deuterium molecule we should expect on this basis a larger quenching cross section than in the case of hydrogen.

If on the other hand the hydride or deuteride of mercury is formed during the process, then, in considering the energy change, not only will the zero point energy difference of the hydrogen and deuterium have to be taken into account, but also the zero point energy difference for mercury hydride and mercury deuteride in the  $^2\Pi$  state. Such a mechanism will naturally diminish the difference between the energies of the two processes with hydrogen and deuterium. Moreover, as has been shown by Rabinowitsch and Beutler the mercury hydride formed will be in a high rotational level and the corresponding compound with deuterium will possess a larger moment of inertia, since in the deuterium compound the center of gravity will not be greatly altered, because of the large mass of the mercury, while the mass of the revolving deuterium particle has been doubled.

The other compounds which have been studied are generally supposed to bring about the transition  $^3P_1 \rightarrow ^3P_0$  in the excited mercury atom. This is a process which involves an energy change of 0.218 volt and this amount of energy is taken up by the colliding molecule in the form of vibrational energy. That this process is not the only one which occurs is evident from the chemical reactions which occur when water vapor and ammonia are illuminated, in the presence of mercury vapor, by mercury resonance light, since the transfer of 0.218 volt is totally inadequate to bring about such chemical decomposition. Several workers have, however, supposed that ammonia and water vapor along with carbon monoxide, nitrogen, carbon dioxide, methane and nitric oxide, are effective in causing predominantly the transition of excited mercury from the  $^3P_1$  to the metastable  $^3P_0$  state, and we shall for the purpose of this discussion adhere to this viewpoint.

It became very evident from the theoretical

work of Morse and Stueckelberg<sup>9</sup> that the form of resonance curve obtained by plotting the quenching cross sections against the energy difference between the levels of the colliding particles, was dependent upon the nature of the interaction between the particles. The use of different potential fields between the colliding particles led to different forms of resonance curve. Furthermore, these workers found that the sharpness of the resonance curve is greater in large molecules, and undoubtedly, as pointed out by Bates when discussing the relative quenching cross sections of butane and heptane, the shape and steric configuration of the molecules probably play a large rôle in determining the efficiency of quenching. Having these considerations in mind a resonance curve made up of quenching cross sections of a variety of molecules can do little more than indicate that the general form of such a curve is obeyed, and a number of factors may very well enter in causing erratic variations from one molecule to another.

In molecules in which ordinary hydrogen atoms can be replaced by deuterium atoms, we have a method of changing the vibrational levels and the mass of the molecule in a well-defined way, and it is probable that in so doing we are not bringing about very profound changes in the nature of the potential field which would affect the quenching cross sections so that we are able to vary the energy levels of the molecules in such a way as to give more significance to comparisons of quenching cross sections.

Let us consider the changes in the vibrational energy levels of ammonia as we successively replace the hydrogen by deuterium. The vibrational levels of ammonia and the various deuterium substituted ammonias are shown in Fig. 4 (a) and Table III. The dotted line in the

TABLE III.

	$\nu_1$	$\nu_2$	$\nu_3$ cm <sup>-1</sup>
Ammonia	938	1631	3336
Deutero-ammonia	770	1158	2421
Water	1615	3670	3795
Heavy water	1216	2670	2782

<sup>9</sup> Morse and Stueckelberg, Ann. d. Physik [5] 9, 579 (1931).



from one of 4. It is difficult also to assess the importance of the overtones of the first fundamental frequency. These may in certain cases lie very close to the energy of the  $^3P_1 \rightarrow ^3P_0$  mercury transition, but since the relative probabilities of transition to an overtone level as compared with that to a fundamental are unknown, and since their statistical weight is only 1 as compared with 4, it may be that these factors may counterbalance the effect of closer resonance.

Similar considerations will apply in the case of water vapor. Fig. 4 (b) shows the three fundamental frequencies in the case of water in which the hydrogens have been successively replaced. In this case it is the lower vibrational level which is always responsible for the quenching process, the upper level never being depressed sufficiently to become effective. Reference to Fig. 5 will show that the quenching cross section of  $D_2O$  lies very well on the resonance curve at its appropriate energy level. Fig. 4 (c) and (d) show diagrammatically the modes of vibration of ammonia and water corresponding to the different energy levels, and since in the case of ordinary and heavy water the quenching process is concerned with the same frequency of the water molecule, the vibrations of this molecule after quenching will be of the same kind in both cases. Not so, however, in the case of the ammonias where deuterio-ammonia after quenching is vibrating in a different way from ordinary ammonia under the same conditions.

An examination of the possible energy changes involved in transitions between vibrational levels other than from the ground state reveals, that some of these changes lie very close to 0.218 volt, and it would be of interest, therefore, in this connection to study the quenching efficiency of such molecules at higher temperatures when a

larger number of molecules would be in vibrational levels other than the ground level, and when transitions involving closer resonance would be increasingly possible.

It is impossible to decide from such experiments as these whether the quenching process in the case of ammonia is one involving a change to the metastable state of the mercury or whether the whole of the 4.86 volts of the excitation energy of mercury is taken up by the ammonia molecule. That some such process involving more energy than 0.218 volt is involved is shown by the photosensitized decomposition of ammonia. There is a singlet excited state of ammonia known at a level 5.75 volts above the ground level but because of the large difference in energy, and also because conservation of total spin momentum would not be obeyed, this may be a very improbable process. There may, however, be a triplet state of ammonia between the ground state of ammonia and the excited singlet state, which may be responsible for quenching excited mercury to the ground state. The differences observed in the quenching efficiencies of ammonia and deuterio-ammonia would then have to be attributed to the differences in excitation energy of the two molecules due to the differences in zero point energy in the ground and triplet states, and since the position of the triplet state is imperfectly known, it is impossible to assess the energy which would be required in the two cases.

The author is extremely grateful to Professor Hugh S. Taylor for the facilities afforded in these laboratories and also for the helpful interest which he has taken in this work, and to Dr. W. S. Benedict for many helpful discussions and for placing at the author's disposal the results of his spectroscopic analysis of the deuterio-ammonias.