

## Transfer of Rotational Energy in Molecular Collisions II. Exchange of Energy in Collisions Between Unexcited HgH and N<sub>2</sub> Molecules

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## Transfer of Rotational Energy in Molecular Collisions

### II. Exchange of Energy in Collisions Between Unexcited HgH and N<sub>2</sub> Molecules

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(Received August 13, 1937)

It has been found that the intensity distribution in the HgH 4017 band excited by sensitized fluorescence in the mixture Hg+H<sub>2</sub>+N<sub>2</sub> is influenced by the intensity of the primary light which excites the fluorescence. This observation may be interpreted as evidence of a very slow exchange of vibrational energy in collisions between N<sub>2</sub> and HgH molecules in their normal electronic states. Two other possible causes of the phenomenon—self-reversal and reactions involving high energy Hg atoms formed by stepwise excitation—are ruled out by additional experiments.

#### I. INTRODUCTION

IN the past few years a great deal of information concerning intermolecular transfers of energy has been derived from experiments on the dispersion of high frequency sound in gases. Of particular interest is the discovery that in a few cases the cross section for exchange of energy between vibration and translation is tens of thousands of times smaller than the gas-kinetic cross section. However, no case has been discovered in which the exchange of rotational energy is slow enough to cause dispersion of sound at even the highest frequencies used in the experiments.

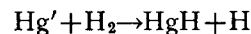
Another approach to the problem of transfers of energy in collisions is the study of intensity distributions in band spectra, which give detailed information about the distribution of molecules among rotational and vibrational levels. It is often found that the intensity distribution shows a pressure dependence, and the effect of collisions may be studied by following the intensity distribution as a function of the pressure of the emitting gas or of an added foreign gas. If, as is usual, it is the emission spectrum on which the observations are made, the collisions which are most effective in modifying the intensity distribution are those that occur during the brief interval ( $\sim 10^{-8}$  sec.) during which the molecule occupies an excited electronic state.<sup>1</sup>

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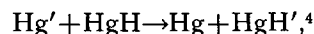
<sup>1</sup> For a bibliography and critical discussion of the general field of transfers of energy in collisions the reader is referred to a review by Oldenberg and Frost, *Chem. Rev.* **20**, 99 (1937).

Experiments of this type, in which the spectrum studied was that of HgH excited by sensitized fluorescence and the foreign gases were water vapor and nitrogen, have been described in a previous paper.<sup>2</sup> It was found that both H<sub>2</sub>O and N<sub>2</sub> are effective in altering the rotational distribution of the excited HgH molecule. Because of the fact that the dependence of intensity distribution on pressure is caused primarily by collisions which occur while the HgH is in an excited state, it is difficult to obtain from the pressure variations any information about the exchanges of energy which occur when the molecule is in the normal electronic state. The following considerations suggested that for this purpose it would be worth while to carry out further experiments on the sensitized fluorescence in which the intensity distribution in the HgH spectrum is studied as a function of the intensity of the primary Hg 2537 radiation which excites the fluorescence.

The HgH bands appear when the mixture (1/1000 mm Hg vapor + a few 1/1000's mm H<sub>2</sub> + a few mm N<sub>2</sub>) is irradiated with the unreversed 2537 resonance line of Hg.<sup>3</sup> The HgH molecules are formed in the reaction



and are excited by a collision of the second kind



(Hg' denotes a metastable ( $6^3P_0$ ) Hg atom).

<sup>2</sup> F. F. Rieke, *J. Chem. Phys.* **4**, 513 (1936).

<sup>3</sup> E. Gaviola and R. W. Wood, *Phil. Mag.* **6**, 1191 (1928).

<sup>4</sup> H. Beutler and E. Rabinowitch, *Zeits. f. physik. Chemie* **B8**, 403 (1930).

The intensity distribution in the spectrum shows that a considerable proportion of the excited HgH molecules have rotational energy greatly in excess of the thermal value. Because of the selection rule for the rotational quantum number, the rotational energy is not changed appreciably by the emission process which restores the molecule to the normal electronic state. The spectrum (reference 2, Fig. 7) shows also that many excited molecules reach the normal electronic state by a transition to the vibrational level  $v=1$ .

Let us now assume that there is an appreciable probability that a molecule which has an excess internal energy (of rotation or vibration) immediately after the radiation process may retain the energy until it is re-excited by an encounter with a metastable Hg atom. It is reasonable to assume that the energy level to which such a molecule is excited in a collision of the second kind is different than for a molecule which has only the thermal energy. Whether or not the conditions are favorable for such a retention of internal energy should then have an influence on the intensity distribution in the emission spectrum.

The probability  $P$  that the excess internal energy be lost in the interval between the radiation process and the following excitation process is determined by the ratio  $R = \sigma_1^2[N_2]/\sigma_2^2[\text{Hg}']$  where  $\sigma_1^2$  is the cross section for loss of energy in a collision with an  $N_2$  molecule,  $\sigma_2^2$  the cross section for a collision of the second kind with metastable mercury, and  $[N_2]$  and  $[\text{Hg}']$  are partial pressures. If all other conditions remain constant,  $[\text{Hg}']$  is directly proportional to  $I$ , the intensity of the primary radiation; in this case  $P$  is a function of  $I$  only. Consequently the intensity distribution in the fluorescence spectrum should depend on the intensity of primary radiation; but for the effect to be appreciable it is necessary that  $R$  be of the order of magnitude of 1. This can happen only in case  $\sigma_1^2/\sigma_2^2$  is of the order of magnitude of  $10^{-5}$ , for even under the best conditions  $[\text{Hg}']$  is of the order of  $10^{-5}$  mm,<sup>5</sup> while  $[N_2]$  is a few mm.<sup>6</sup>

<sup>5</sup> H. Beutler and E. Rabinowitch, *Zeits. f. physik. Chemie* **B6**, 233 (1929).

<sup>6</sup> The argument of these two paragraphs was suggested by, and is somewhat similar to, parts of reference 4.

Although the ratio  $[N_2]/[\text{Hg}']$  can also be influenced by varying the pressure of  $N_2$ , the relation is not simple; furthermore the average number of collisions during the lifetime of the excited state of HgH is also dependent on the pressure of  $N_2$ . Consequently experiments in which only the exciting intensity is varied are most suitable for studying the exchange of energy in collisions between the unexcited HgH and  $N_2$  molecules.

## II. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

### (1) Persistence of internal energy between consecutive excitation processes

Photographs of the HgH bands excited by sensitized fluorescence were taken, following the procedure described previously.<sup>2</sup> Then wire gauzes were inserted between the Hg arcs and the fluorescence tube, in order to reduce the illumination of the latter by a known ratio, and additional exposures were taken. Two pairs of wire gauzes were used; one pair had a transmission of about  $\frac{1}{2}$ ; the other,  $\frac{1}{5}$ . The first experiment was performed with  $H_2$  and  $N_2$  in the fluorescence tube. Photometry of the photographic plate resulted in a definite indication that the intensity of the high rotation lines, relative to the low rotation lines, in the 4017 band<sup>7</sup> decreased with the intensity of the primary radiation.

The exposure times necessary for obtaining comparable spectra varied approximately as the inverse square of the exciting intensity, as had been observed by Gaviola and Wood.<sup>3</sup> Independent trials had been made to determine the relation between exposure time and the proper-

Beutler and Rabinowitch were concerned with the possibility that abnormal rotation resulting from the chemical reaction in which the HgH is formed (reaction of metastable mercury with  $H_2$  and with  $H_2O$ ) might persist until a subsequent excitation process and thus influence the emission spectrum. However, the experiments described in reference 2 prove that the abnormal rotation contributed by the formation process is negligible compared to that which results from the excitation process and collisions which occur during the lifetime of the excited state. The present paper is concerned with a persistence from one excitation process to the next; the number of collisions which intervene is estimated from the considerations advanced by Beutler and Rabinowitch.

<sup>7</sup> This is the only band which is sufficiently intense and free from overlapping to permit quantitative measurements with low dispersion apparatus.

ties of the photographic plates which were used.

Nevertheless, since the difference in intensity distribution observed in the first experiment was not very large, the experiment was repeated in such a way as to eliminate the possibility of any error arising from uncertainty in the correction for different exposure times. For one of the exposures made with the full intensity of primary light, a wire gauze was placed over the lens used to project the fluorescence radiation onto the slit of the spectrograph and a long exposure made. Comparison could then be made between spectra of similar densities for which the exposure times were equal. The result of the previous experiment was confirmed. The observations are given in detail in Table I; values of  $t/h$  given in the table indicate the intensity of the tail (high rotation lines) relative to the head (low rotation lines).

The HgH bands can also be excited if the fluorescence tube contains a few mm of water vapor instead of the  $H_2+N_2$  mixture, but the relative intensity of the high rotation lines is much less.<sup>3</sup> The intensity distribution in the 4017 band excited with 3.6 mm of water vapor in the fluorescence tube did now show any variation with the intensity of the primary radiation.

The observation of a dependence of the intensity distribution on the intensity of the primary radiation for the 4017 band excited in  $H_2+N_2$  is consistent with the assumption that the exchange of either vibrational or rotational energy in collisions between normal HgH and  $N_2$  molecules is very slow. But before the agreement may be taken as evidence of the persistence of energy in collisions, some alternative interpretations must be taken into account.

## (2) Discussion of alternative explanations

One possibility is that the observed dependence of intensity distribution on the exciting intensity might be caused by strong self-reversal of the 4017 band (the "resonance band" of HgH) within the fluorescence tube. Oldenberg's experiments with OH show that even though the emission spectrum shows abnormal rotation, the absorption is confined to the low rotation lines.<sup>8</sup> If similar conditions held in the fluorescence tube,

<sup>8</sup> O. Oldenberg, *Phys. Rev.* **46**, 210 (1934).

TABLE I. Observed intensity distributions in the 4017 band of HgH.

$pH_2$	$pN_2$	EXCITING INTENSITY	INTENSITY DISTRIBUTION ( $t/h$ )
0.007 mm	2.8 mm	1.0	0.43
		0.5	0.27
		0.2	0.22
.007	6.0	1.0	0.76
		0.2	0.42

self-reversal would influence the intensity of the band head only. Reducing the intensity of the primary radiation decreases the concentration of HgH, consequently at low intensities the band head should appear with its full intensity; in other words, the intensity of the tail relative to the head should decrease when the intensity of the primary radiation is decreased. This is just the effect observed.

In order to test for this source of error, the following experiment was performed. In the fluorescence tube used for the preceding experiments, the depth of the region in which the fluorescence is excited is only three cm., but there is an additional path of eight cm to the exit window. An appreciable concentration of HgH should imply a rather long life and therefore diffusion into this space. This argument suggested the construction of a fluorescence tube in which the fluorescence could be observed from either end of the tube; in one direction the maximum absorbing path was two cm; in the opposite direction a path of fifteen cm was possible. It seems reasonable that if there is any appreciable absorption, it would be greater for spectra taken through the more distant window. However, spectra taken from either end under otherwise identical conditions were very similar. Therefore it may be concluded that the amount of self-reversal is negligible, and that all of the observed intensity distributions are determined by the population ratios of the various rotational levels.

The possibility remained that in the case of intense illumination molecules with abnormal rotation might be excited largely as a result of the presence of Hg atoms in the  $6^3P_2$  or higher states. Since the filter does not transmit the 1849 line, any atoms of excitation higher than

the  $^3P_1$  state can occur only as a result of step-wise excitation, and their concentration must vary as a higher power of the exciting intensity. Since the ratio  $6^3P_2/6^3P_0$ , for instance, increases with the intensity of exciting radiation<sup>9</sup> (of constant energy distribution), the effect of exciting intensity on the intensity distribution in the HgH bands might be explained by the variation in the above ratio. But in that case a corresponding change in intensity distribution should occur when the ratio is varied by changing only the intensity of the higher series Hg lines in the primary radiation. Consequently the following experiment was made.

One exposure, with 0.01 mm H<sub>2</sub>+5 mm N<sub>2</sub>, was made with the fluorescence tube illuminated by one of the water-cooled, magnetically-deflected mercury arcs. A second exposure was made with the fluorescence tube illuminated by both the low temperature arc and another arc run at a high pressure. The 2537 line emitted by the high pressure arc is strongly reversed, and is not absorbed by the cool Hg vapor in the fluorescence tube, but the higher series lines are only slightly reversed in the arc, and can be absorbed by the excited Hg atoms in the fluorescence tube. The rate of excitation of  $6^3P_1$  Hg atoms, and therefore of  $6^3P_0$  atoms, was approximately the same for both exposures, but the rate of excitation of higher states was many times greater for the second exposure. Nevertheless, there was no indication of a difference in the intensity distribution in the HgH 4017 band. This result proves that the high rotation lines observed in the sensitized fluorescence experiments cannot be attributed to any process involving Hg atoms in the  $6^3P_2$  or higher states. The foregoing conclusion is also supported by the observation that with H<sub>2</sub>O (instead of H<sub>2</sub>+N<sub>2</sub>) in the fluorescence tube, the intensity distribution in the 4017 band is independent of the exciting intensity.

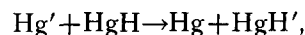
### (3) Conclusions

Since both of the alternative hypotheses are inconsistent with the additional experimental evidence, we conclude that the first explanation of the relation between intensity distribution and exciting intensity, based on the persistence of

internal energy in collisions, is correct. We may now attempt to decide whether it is a persistence of rotational or of vibrational energy which occurs.

In a preliminary report<sup>10</sup> it was suggested that the experiments indicate that it is the rotation which persists, since it is the distribution among rotational quanta which was observed to depend on the primary intensity. This conclusion is open to the following objections. Firstly, evidence obtained from the dispersion of sound experiments uniformly indicate a good exchange of energy between rotation and translation. Secondly, by analogy with transfers of vibrational energy, a persistence is to be expected only in case the quanta involved are large compared to  $kT$ ;<sup>11</sup> but the rotational quanta of HgH are at most (for  $J=30\frac{1}{2}$ ) only equal to  $kT$ .

In subsequent discussions, Professor J. Franck has pointed out that the observations may be interpreted to be a consequence of the persistence of vibration, rather than of rotation. It is necessary to assume only that in the collision of the second kind,



the probability that the HgH be excited to a high vibrational level ( $v=4$  or  $5$ ) is greatly enhanced if the molecule is originally in the first, rather than the zero, vibrational level. This assumption is supported by the Franck-Condon principle applied to the potential curves of HgH derived by Rydberg.<sup>12</sup> In this case, the increased rotation observed with high exciting intensities is to be explained as an indirect result of an enhanced proportion of molecules excited to the levels  $v=4$  or  $v=5$  of the  $^2\Pi$  state, for it has been shown previously that molecules in these levels are transferred by collisions with N<sub>2</sub> molecules to the high rotation levels of the  $v=0$  level.

The foregoing, which appears to be the most plausible interpretation of the experiments, leads to the conclusion that collisions with N<sub>2</sub> have a very small effective cross section for the removal of the last quantum of vibration from the HgH molecule in the normal electronic state, although only a very rough estimate of the actual cross

<sup>10</sup> F. F. Rieke, *Phys. Rev.* **47**, 788(A) (1935).

<sup>11</sup> Reference 1, p. 118.

<sup>12</sup> R. Rydberg, *Zeits. f. Physik* **80**, 514 (1933).

<sup>9</sup> E. Gaviola, *Phil. Mag.* **6**, 1154 (1928).

section can be made. As shown in Section I of this paper, an effect of the kind observed should occur only in case the cross section for loss of the final quantum of vibration is of the order of magnitude of  $10^{-5}$  times the cross section for the collision of the second kind with metastable Hg. The latter cross section may be comparable to

the gas kinetic cross section, or even somewhat larger, but it is very unlikely that it is larger by a factor as great as  $10^2$ . This rough argument indicates that the cross section in question is of the same order of magnitude as some of the smaller cross sections found for similar processes by the dispersion of sound method.

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## The Effect of Concentration on the Production of the Latent Photographic Image by Hydrogen Peroxide

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Much of the density previously reported as produced by short immersions of photographic plates in aqueous solutions of hydrogen peroxide was found to have been produced during the washing interval between exposure and development. Data are presented concerning the production of the latent image by various concentrations of hydrogen peroxide. Analysis of this data suggests that, initially, the net reaction is of the second order. An optimum concentration for the production of maximum density was indicated.

MANY substances have been reported as producing latent images when placed near or in contact with photographic emulsions. Radioactivity, phosphorescence and thermal fogging furnish satisfactory explanations in many cases. In many others, the action is due to the presence or formation of at least traces of hydrogen peroxide.<sup>1</sup> For this reason and because of its own intrinsic interest, especially its bearing on the problem of the mechanism of latent image formation, the fogging action of hydrogen peroxide has been the subject of much investigation.

In practically all the early work,<sup>2-4</sup> photographic plates were exposed to hydrogen peroxide vapor. In previously reported work where plates were immersed in aqueous solutions of hydrogen peroxide,<sup>5, 6</sup> they were washed for 30 minutes before development. We find that much of the density observed was produced during this washing period. Among other studies employing

this technique, Sheppard and Wightman<sup>5</sup> made some tests with the same time of immersion for different concentrations and concluded that the effect of increasing concentration was similar to that of increasing light intensity. Further investigation along somewhat similar lines, but substituting a 1-2 second rinse for the 30 minute washing interval, has been carried out in this laboratory. Plates so briefly rinsed inevitably carry along some hydrogen peroxide into the developer. However, in agreement with observations of Wightman, Trivelli and Sheppard,<sup>7</sup> tests showed that negligibly little additional density was produced by the presence of small quantities of hydrogen peroxide in the developer.

The first group of tests was performed with ten concentrations ranging by geometrical progression from 3 percent to 3/512 percent and immersions, also in geometrical progression, from 1 second to 128 seconds. Portions of Eastman "33" plates were immersed for measured intervals in hydrogen peroxide of a given concentration, rinsed 1-2 seconds in water, developed 5 minutes in a pyro-soda formula, rinsed in 1 percent

<sup>1</sup> Keenan, *Chem. Rev.* **3**, 95 (1926).

<sup>2</sup> Russell, *Proc. Roy. Soc. London* **64**, 409 (1899).

<sup>3</sup> Dony-Henault, O. and A., *Bull. Soc. Chim. Belg.* **22**, 224 (1908).

<sup>4</sup> Dombrowsky, *Inaug. Dissert.*, Leipzig (1908).

<sup>5</sup> Sheppard and Wightman, *J. Frank. Inst.* **195**, 337 (1923).

<sup>6</sup> Jones and Blair, *J. Frank. Inst.* **218**, 29 (1934).

<sup>7</sup> Wightman, Trivelli and Sheppard, *J. Frank. Inst.* **200**, 335 (1925).