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Elementary Processes in the Sensitized Fluorescence of OH Molecules

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The processes involved in the sensitized fluorescence excitation of the OH molecules have been investigated by photometric measurements of the intensities of lines of the (0,0), (1,0) and (1,1) OH bands. Collisions between metastable $^3P_0$ mercury atoms and water molecules produce unexcited OH molecules which are then excited by further collisions with $^3P_0$ mercury atoms to levels whose energies are equal to or less than the energy of the $^3P_0$ mercury atoms. Abnormal rotational energy is produced in the excitation of the OH molecules. Collisions between nitrogen and OH molecules transfer vibrational energy of the OH molecules to rotational energy and also reduce the rotational energy of the OH molecules somewhat toward thermal values. Collisions between helium and OH molecules are very much less effective in transferring energy than nitrogen collisions.

INTRODUCTION

THE effect of elementary processes such as collisions on the rotation of molecules gives information about the transfer of energy between molecules. Some molecules exhibit abnormal rotational energy characteristic of a temperature of several thousand degrees even when the molecules themselves are expected to have kinetic energy corresponding to room temperature. These molecules may lose energy through collisions. Gaviola and Wood[1] first observed an abnormal rotational energy in the fluorescence spectrum of HgH. Rieke[2] has made a study of the molecular processes involved in the production of the excess rotational energy of the HgH molecule and the effects of collisions with foreign gases on the rotation. An example of abnormal rotation reduced by collisions, although less conspicuous than the HgH case, is in the band spectrum of hydrogen excited by electron impact. Addition of a small amount of helium to the hydrogen as discovered by Richardson[3] and further investigated by Roy[4] gives abnormal rotational energy to the hydrogen molecules which disappears with an increase in the helium pressure.

The spectrum of the OH molecule shows abnormal rotational energy when it is excited in discharge tubes.[5] Bonhoeffer and Pearson[6] stated that the source of such energy arises from the process of simultaneous dissociation of H_2O and excitation of OH by electron impact. Oldenberg[7] showed experimentally by a comparison of the absorption spectrum of normal rotation with the abnormal emission spectrum that the abnormally rotating molecules do not originate from the OH molecules normally present in the discharge, but from the simultaneous dissociation and excitation process. After radiation the molecules lose their excess rotational energy through collisions.

Since the process of excitation in electric discharges is complicated, a further key to the explanation of the abnormal rotation of the OH molecules might be found in a study of the spectrum excited under more simple conditions. Flame and arc excitation (thermal types of excitation) show distributions of rotational energy representing thermal equilibrium as expected,[5] but sensitized fluorescence excitation exhibits the characteristic abnormal rotation of the discharge tube spectrum. In fluorescence experiments the elementary processes can be traced in great detail. The following investigation of the rotational energy distribution in the sensitized fluorescence spectrum of OH, therefore, was undertaken in an attempt to explain the source of the excess rotational energy of the OH molecule, and to determine some information about the exchange of energy between OH molecules and foreign gas molecules in collisions.

EXPERIMENTAL

A quartz fluorescence tube was used similar in shape and dimensions to that used by Rieke[2] in

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* Experimental work carried out at the Department of Physics, University of California, Berkeley, California.

[1] E. Gaviola and R. W. Wood, Phil. Mag. **6**, 1191 (1928).

[2] F. F. Rieke, J. Chem. Phys. **4**, 513 (1936).

[3] O. W. Richardson, Proc. Roy. Soc. London **111**, 720 (1926).

[4] A. S. Roy, Proc. Nat. Acad. Sci. **19**, 441 (1933).

[5] E. R. Lyman, Phys. Rev. **53**, 379 (1938).

[6] K. F. Bonhoeffer and T. G. Pearson, Zeits. f. physik. Chemie **14**, 1 (1931).

[7] O. Oldenberg, Phys. Rev. **46**, 210 (1934).

his work with HgH. The tube was flattened in the central portion to reduce the absorbing layer of mercury vapor in the fluorescent region. Two vertical quartz mercury arcs were placed one on either side of the flattened portion of the fluorescence tube which was held horizontally. The mercury arcs were watercooled, were each in a magnetic field, and were run at low currents between 1 and 2 amperes. These precautions guarded against self-absorption of the resonance line λ2537. An image of the cross section of the fluorescent region was focused on the slit of the spectrograph by a quartz lens.

The source of mercury vapor was a drop of mercury placed in the tail end of the fluorescence tube. In some experiments water vapor was admitted through a double stopcock arrangement to obtain the desired pressure, and in others continually flowed through the tube. In the nonflowing vapor experiments sufficient hydrogen to quench the fluorescence did not seem to be produced by the dissociation of the water during the time necessary for exposures.

Three groups of photographs were obtained with mixtures of mercury, water vapor and nitrogen; mercury and water vapor; and mercury, water vapor and helium. The spectrograph used was the 21-foot 30,000-line/inch aluminum grating in the Paschen mounting. Photographs of the (0,0), (1,0), and (1,1) bands were taken in the first order. Exposures varying from 1 to 2 hours were necessary with Eastman 40 plates. The plates were developed in Rodinal. The method of calibrating and measuring the intensities of the lines on the plate was described in a previous publication.[5] The lines of the (0,0), and (1,1) bands were identified from data of Heurlinger,[8] and of the (1,0) band from data of Watson.[9]

RESULTS

The relative intensities of the measured lines of the Q_1 branch of the (0,0) band are plotted against the corresponding rotational quantum numbers, J', (Fig. 1). The gas in the fluorescence tube was 3.5 mm of water vapor and 10 cm of nitrogen. The shape of the distribution curve, typical of all OH fluorescence distribution curves obtained, is not thermal since there is an excess of rotational energy among the upper rotational states and a sudden drop-off of intensities starting at $J'=17\frac{1}{2}$. The Q_1 branch is used as an example of all the branches in the (0,0) band because it is the branch least perturbed by overlapping lines. Graphs for the other principal branches in the band showed the same excess rotational energy in the upper rotational levels with sharp decreases in intensities beginning with lines arising from the level $J'=17\frac{1}{2}$. In the (1,0) band a similar drop-off of intensities was found for lines originating above the rotational level $J'=11\frac{1}{2}$. Regardless of the mixtures of gases in the fluorescence tube, the spectrum always showed the sudden decrease of intensity toward zero above the levels $J'=17\frac{1}{2}$ for the (0,0) band and $J'=11\frac{1}{2}$ for the (1,0) band.

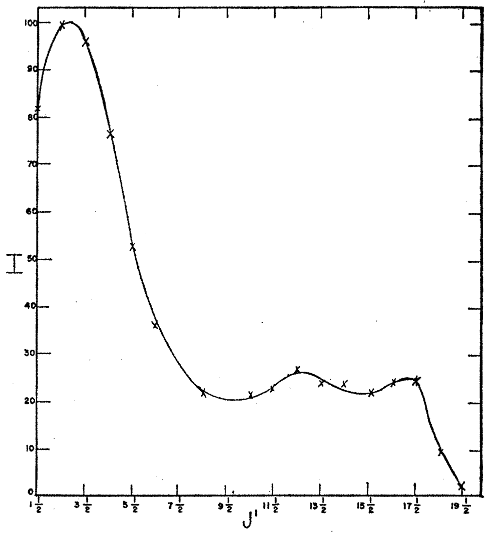

FIG. 1. Intensities of lines of the Q_1 branch of the λ3064 band from the sensitized fluorescence spectrum as a function of the rotational quantum number. 3.5 mm water vapor and 10 cm nitrogen in the fluorescence tube.

Assuming thermal equilibrium among the molecules, there exists a linear relationship according to the Maxwell-Boltzmann theory between the logarithms of I/i and the corresponding rotational term values, $T(K')$, where I is the measured intensity of each line, and i the theoretical intensity factor. The theoretical intensity factors were calculated from Earls'[10]

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[8] T. Heurlinger, Dissertation (Lund, 1918).

[9] W. W. Watson, Astrophys. J. **60**, 145 (1924).

[10] L. T. Earls, Phys. Rev. **48**, 423 (1935).

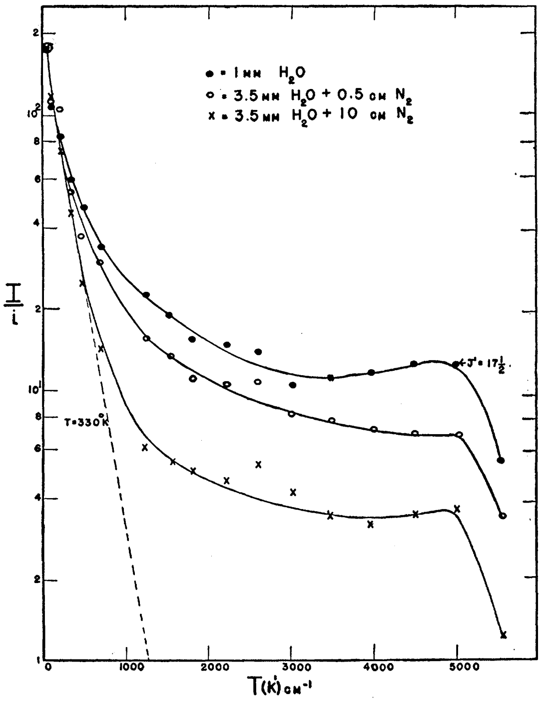

FIG. 2. Rotational term values as a function of log I/i for water vapor-nitrogen mixtures.

adaptations of the Hill and Van Vleck[11] formulas for the $^2\Sigma$, $^2\Pi$ transitions and the term values for the (0,0) band were calculated from data of Heurlinger.[8] Graphs of log I/i vs. $T(K')$ for the (0,0) band illustrate clearly the sudden decrease of intensities above $J' = 17\frac{1}{2}$. Fig. 2 shows such graphs for three different conditions in the fluorescence tube. The curved line through the points indicates that no thermal equilibrium exists among the molecules. In the case of a small amount of water vapor alone, there is a large amount of excess rotational energy among the high levels. Addition of a small amount of nitrogen reduces the excess rotational energy somewhat, and addition of a greater pressure of nitrogen reduces the excess even more towards thermal values. A straight line drawn through the first few points in the latter case has a slope from which a temperature of 330°K may be calculated. This is of the order of room temperature. Addition of small amounts of helium in the fluorescence tube showed no effect on the reduction of rotational energy comparable to the effect of the addition of nitrogen.

There is a slight enhancement of the lines just before the sharp decrease in intensities. The lines arising from around the level $J'_{(0,0)} = 12\frac{1}{2}$ are also enhanced, especially in the case with the greater amount of nitrogen in the fluorescence tube. Both cases of enhancement of intensities are noticeable in other branches besides the Q_1 branch.

If the intensity of the strongest line of the (0,0) band is called 100, and the intensities of corresponding strong lines in the (1,0) and (1,1) bands are compared to this line, an approximate idea of the relative intensities of the bands in relation to one another can be obtained, i.e. a measure of the respective amounts of vibrational energy may be obtained. Table I gives these data. It is noted that the intensities of the (1,1) and the (1,0) bands are weak compared to the (0,0) band when there is an increase in the amount of nitrogen present. There is a large amount of vibrational energy in the (1,0) and the (1,1) bands when a small amount of water alone is in the fluorescence tube. Helium seems to be less effective than nitrogen in reducing vibrational energy.

INTERPRETATION OF RESULTS

In the process of sensitized fluorescence, the $^3P_1$ mercury atoms formed by the absorption of the resonance radiation λ2537 are very effectively transferred to the metastable $^3P_0$ state by collisions with water or nitrogen.[1] According to Beutler and Rabinowitch,[12] the OH molecules are formed in the following manner:

$$\mathrm{Hg}(6^3P_0) + \mathrm{H_2O} \rightarrow \mathrm{HgH} + \mathrm{OH} - 0.1\ \mathrm{v}. \quad (1)$$

TABLE I. *Intensities of strongest lines. Strongest line of (0,0) = 100.*

	3.5 MM H_2O +10 CM N_2	3.5 MM H_2O +5 CM N_2	3.5 MM H_2O +1.5 CM N_2	3.5 MM H_2O +0.5 CM N_2	3.5 MM H_2O +1 CM He	1 MM H_2O
(1,0) λ2811	4	4	8	8	19	45
(1,1) λ3122	4	6	8	13	24	50

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[11] E. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

[12] H. Beutler and E. Rabinowitch, Zeits. f. physik. Chemie **B8**, 231 (1930).

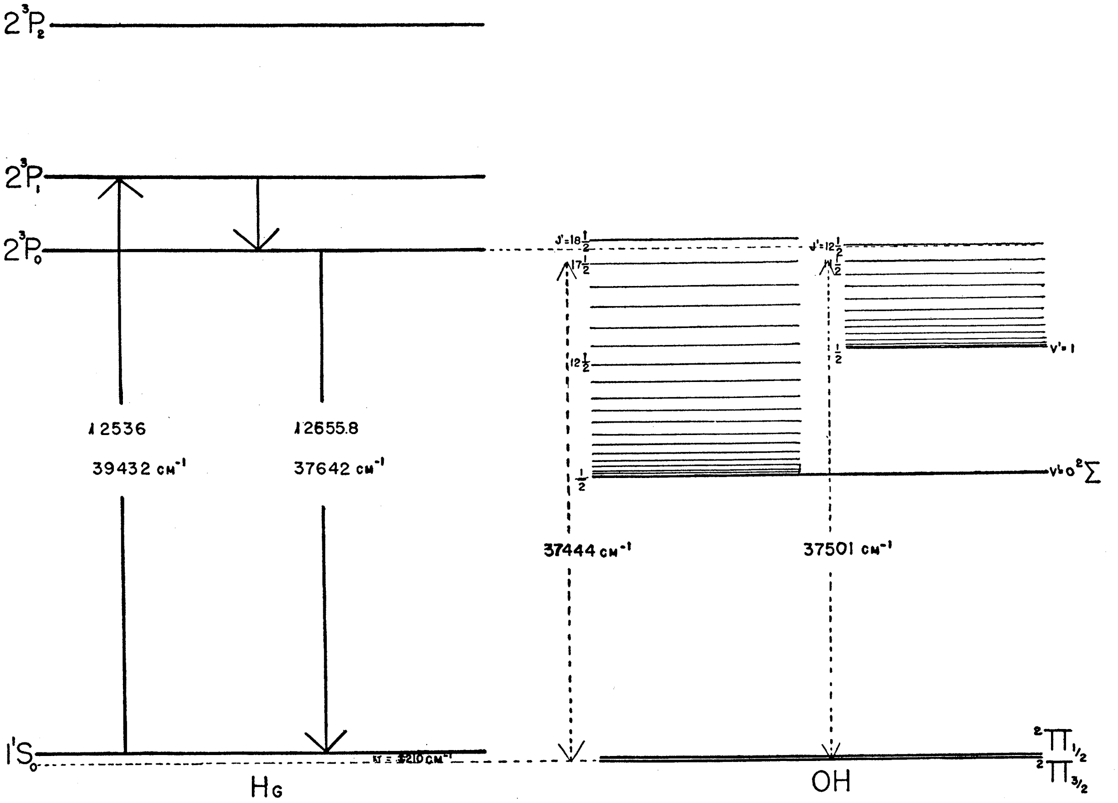

FIG. 3. Vibrational and rotational levels of the OH molecule, and the lower energy levels of the Hg atom.

Since there is a deficiency of energy in (1) and yet OH molecules are known to be formed, the excess energy must be made up from thermal energy of the reacting molecules. The OH molecules, therefore, must be formed in the ground state, $^2\Pi_{3/2,\,1/2}$, with little if any excess rotation at this point. Since experimental evidence shows that excited OH molecules in sensitized fluorescence do exhibit abnormal rotational energy, the excess rotation must be acquired, as in the case of HgH[2], in the excitation process of the OH molecule:

$$Hg(6^3P_0)+OH\rightarrow Hg(6'S_0)+OH' \qquad (2)$$

or in further collisions during the lifetime of the excited molecule.

The sudden decrease in intensities previously described indicates that few transitions from levels above $J'=17\frac{1}{2}$ for the (0,0) band and $J'=11\frac{1}{2}$ for the (1,0) band are possible, i.e. few molecules can be excited above $J'_{(0,0)}=17\frac{1}{2}$ or $J'_{(1,0)}=11\frac{1}{2}$. The energy corresponding to the level $J'_{(0,0)}=17\frac{1}{2}$ is 37,444 cm⁻¹ and to $J'_{(1,0)}=11\frac{1}{2}$, 37,501 cm⁻¹. The energy of the $^3P_0$ mercury atoms is 37,642 cm⁻¹. To the latter value must be added the thermal energy, kT, which is 210 cm⁻¹ at 300°K, i.e., $Hg(^3P_0)$ lies at 37,852 cm⁻¹. Fig. 3 is an energy level diagram for the OH molecule and the mercury atom. The levels $J'_{(0,0)}=17\frac{1}{2}$ and $J'_{(1,0)}=11\frac{1}{2}$ lie below the $^3P_0$ mercury level and $J'_{(0,0)}=18\frac{1}{2}$ and $J'_{(1,0)}=12\frac{1}{2}$ lie above it. The maximum amount of energy that can be given to the OH molecule when it is excited by collisions with $^3P_0$ mercury atoms is, therefore, the energy of the $^3P_0$ mercury atoms. The fact that a few transitions (see Fig. 2) from levels above $J'_{(0,0)}=17\frac{1}{2}$ do occur can be explained by the presence of a few molecules raised to those states by thermal energy alone. The apparent violation of the law of conservation of angular momentum evidenced in the enhancement of the levels $J'_{(0,0)}=16\frac{1}{2}$, $17\frac{1}{2}$ may be explained as due to the large cross section for energy transfer between molecules in states with nearly the same energy as the $^3P_0$ mercury level.

When nitrogen is present, collisions of the second kind can take place between nitrogen and the excited OH molecules. The energy in excess of electronic energy is redistributed over the degrees of freedom of the OH molecule, and vibrational energy is, therefore, transferred to rotational energy. The reduction of intensity of the (1,0) and (1,1) bands with respect to the intensity of the (0,0) band with increasing pressures of nitrogen (Table I) indicates a reduction of vibrational energy. In Fig. 2 a reduction of rotational energy toward thermal values exists with increasing pressures of nitrogen present in the fluorescence tube. Collisions with nitrogen can remove molecules from higher to lower v' and J' states. The nitrogen molecules can take away rotational energy from the OH molecules. The excess rotational energy in the upper states is not reduced a very great amount, however, by collisions with the nitrogen. There are probably two processes occurring simultaneously during these collisions, a transfer of molecules from high to low rotational states of the $v'=0$ level and at the same time a transfer of molecules from higher vibrational states to high rotational states of the zero vibrational level so that excess rotational energy still exists among the upper states.

A possible explanation of the enhancement of lines arising from the level $J'_{(0,0)}=12\frac{1}{2}$ or from nearby levels of the zero vibrational state arises from the hypothesis of the transfer of molecules in collisions with nitrogen from the higher vibrational states to the high rotational levels of the zero vibrational state. The level $J'_{(0,0)}=12\frac{1}{2}$ lies approximately at the same place in the energy level diagram (Fig. 3) as $v'=1$. From these experiments there is evidence of a loss of excess rotation by collisions during the lifetime of the excited state. Such transfers of energy occur most efficiently for small energy changes. One would expect, therefore, an accumulation of molecules in the low rotational states of the first vibrational level, $v'=1$. Hence transfers of the energy of one vibrational quantum into rotation should be more probable than transfers of nearby amounts. The result of these transfers is the enhancement of the lines originating from the $v'=0$, $J'=12\frac{1}{2}$ level. The more collisions possible during the lifetime of the excited molecules, the greater is the enhancement to be expected. Such an effect is observed as the pressure of nitrogen in the fluorescence tube is increased (Fig. 2).

CONCLUSIONS

The correspondence of the energy of the metastable $^3P_0$ mercury atoms and the energies of the rotational states above which the OH molecules are not excited in sensitized fluorescence indicates that the OH molecules obtain their excitation energy from collisions with the $^3P_0$ mercury atoms.

The relatively small effect of collisions with foreign gases, even with nitrogen, on the distribution of energy among the excited OH molecules shows that the abnormal rotational energy of the excited OH molecules is acquired in the excitation process of the OH molecule. There is definite evidence, however, that there is a transfer of vibrational energy into rotational energy as well as some reduction of rotational energy as a result of collisions between nitrogen and excited OH molecules. Collisions between helium and OH molecules are very much less effective than nitrogen collisions.

The present experiments have no bearing on the results of the work on the discharge tube excitation of the OH molecules. The origin of the abnormal rotation in the OH spectrum excited in electric discharges is a different process from that in sensitized fluorescence.[6, 7]

In conclusion the author wishes to express her gratitude to Professor F. A. Jenkins for his interest and suggestions during the experimental part of this research, and to Professor G. M. Almy for many helpful discussions concerning the interpretation of the results.