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## The Persistence of Molecular Vibration in Collisions

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The dispersion of sound is theoretically interpreted by the idea that the exchange of energy in collisions between molecular *translation* and *rotation* on one side and *vibration* on the other side is much slower than, for example, between the various translational degrees of freedom. It seemed desirable to find a direct optical method of observing this hypothetical effect. Apparatus has been developed in this laboratory for the purpose of investigating molecules present in very small concentration, like radicals, by their absorption spectra; with this method, relative concentrations of molecules are determined by comparing intensities of certain rotational lines. This test was applied to the

higher vibrational levels of the  $I_2$  molecule. Their concentration was artificially increased beyond the small amount present in thermal equilibrium by an electric discharge of brief duration. By varying the phase between an electric switch and optical shutter, snapshots of the absorption spectrum could be taken at different intervals after the discharge was interrupted. The result was that iodine molecules raised from the ground level to the first excited vibrational level are able to persist in this level through several thousand collisions with other iodine molecules before losing their vibration.

### I. PROBLEM

THE dispersion of sound was discovered in 1925 by G. W. Pierce, who was working in the supersonic range. Since then it has been observed in various gases but only for molecules which at the temperature of the experiment have some vibrational energy levels excited. The velocity within the audible range does not depend upon the frequency; it is predicted by Einstein's theory of specific heats for gases with translational, rotational and some vibrational energy, like chlorine at room temperature. As the frequency of the sound is increased, a critical range is entered in which the velocity also increases. Above this critical range it is again constant and has the same value as that predicted by specific heat theory for gases with no excited vibration, such as hydrogen at room temperature. So the main result of the experiment may be described as follows: above a certain frequency range the molecular vibration apparently loses its share in the specific heat.

This effect is explained by Herzfeld and Rice<sup>1</sup> on the hypothesis that the molecular *vibration* requires a large number of collisions—more than *translation* or *rotation*—for reaching the value of

thermal equilibrium after a sudden temperature change. The transmission of high frequency sound waves through a gas is accompanied by rapid changes of temperature, and with increasing frequency a range is reached at which the transfer of thermal energy of translation and rotation to energy of vibration fails to follow the rapid temperature changes. Instead, the energy of vibration assumes an average value determined by the average temperature. When this frequency is reached, the vibration no longer affects the velocity of the sound transmission, which consequently approaches the same value as that predicted for gases in which no vibration is excited. In recent years, on the basis of this theory, a great deal of work has been done, in particular by Knudsen and Kneser and by Eucken and his collaborators,<sup>2</sup> determining the persistence of molecular vibration by measurements of dispersion of sound.

It is desirable to find a more direct test for such a persistence of vibrations in collisions. Some spectroscopic experiments<sup>3</sup> on fluorescence radiation indicate such a persistence. All fluorescence experiments, however, deal with vibrating molecules *in an excited electronic level* colliding during their lifetimes with nonexcited molecules, whereas in dispersion of sound obviously no electronic excitation takes place. Therefore both types of experiment, acoustic and

\* Now with The R.C.A. Institutes, Inc., Chicago. The experimental work reported here was done during the year 1936-37. As the investigation was interrupted before completion by the author going to Chicago, only a preliminary report is presented here.

<sup>1</sup> K. F. Herzfeld and F. O. Rice, *Phys. Rev.* **31**, 691 (1928).

<sup>2</sup> See the survey by O. Oldenberg and A. A. Frost, *Chem. Rev.* **20**, 99 (1937).

spectroscopic, do not directly compare. The case of greater practical importance is the normal electronic level. The reason is that its vibration is recorded in many chemical reactions as "energy of activation." Therefore its persistence in collisions is an important problem in chemical kinetics. It seems desirable to devise a spectroscopic experiment in which such a persistence of vibration of molecules *in their normal electronic level* is more directly observed. This seems feasible with a technique developed at this laboratory for a similar purpose, that is a test for free radicals which may be present in reacting gases in very small concentrations (0.003 mm).<sup>3</sup> They are observed by their absorption spectrum. The only difference is that in the present problem we are dealing with unstable molecules which rapidly disappear, not by their chemical reactivity—like radicals—but by deactivation in collisions.

A similar investigation for *rotation* of molecules was, incidentally, carried out by Frost and Oldenberg<sup>3</sup> in their investigation of the lifetime of free OH. No persistence of rotational energy in collisions could be observed by absorption spectra. For *vibration*, however, various arguments<sup>2</sup> point to a far more pronounced persistence.

The problem, therefore, is first to produce in a diatomic gas highly vibrating molecules by some kind of a brief shock and next trace their gradual disappearance by the fading with time of their absorption spectrum.

## II. EXPERIMENT

Since by dispersion of sound chlorine gas was found to manifest a very great persistence of vibration (34,000 collisions at room temperature)<sup>4</sup> it seems advisable to do the spectroscopic investigation with the halogen that has the strongest absorption spectrum, that is, iodine. Its vapor pressure may be controlled by the temperature of a trap. It has the disadvantage, though, of being highly active and requiring extreme measures to prevent the formation of impurities.

<sup>3</sup> O. Oldenberg, J. Chem. Phys. **3**, 266 (1935). A. A. Frost and O. Oldenberg, J. Chem. Phys. **4**, 782 (1936). O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938).

<sup>4</sup> A. Eucken, Oesterr. Chem. Ztg. **20**, 1 (1935).

The molecular absorption bands in the visible have been measured and classified by Mecke.<sup>5</sup> They consist of bands resulting from transitions originating in different vibrational levels in the lower electronic energy state. Each band has a complex rotational structure in which the distribution of intensities is determined by the temperature, and may be calculated from kinetic theory. Except for a small correction,<sup>6</sup> the absorption coefficient representing a rotational line is proportional, by Beer's Law, to the population of the energy level from which the line originated. Hence the rotational structure of a band gives us a set of absorption lines of which the ratio of intensities of any two lines is the same as the ratio of populations in the rotational energy levels giving rise to the two lines.

Two photographic plates taken of the absorption spectrum under different conditions are inserted in a comparator<sup>7</sup> which permits them to be observed side by side through a microscope. If in the first plate two rotational absorption lines in a certain vibration-rotation band represent transitions from rotational levels of which the populations are calculated to be as seven to five, say, and the later plate shows that the second line has increased in intensity and now compares with the first line of the first plate, then the population of the vibrational energy level giving rise to the band has increased in the ratio of seven to five, or 40 percent. Thus it is not necessary to measure the absolute intensities of the two absorption spectra as the rotational lines give us a set of graduated concentration marks.

The change of concentrations in the iodine vibrational energy levels was accomplished by an electric discharge of brief duration. By electron impact molecules are produced with electronic excitation and preferably high vibration as explained by the Franck-Condon rule. They radiate after a negligible lifetime, going back into the normal electronic state with normal rotation, but most of them with a considerable amount of vibration. (A very similar

<sup>5</sup> R. Mecke, Ann. d. Physik **71**, 108 (1923).

<sup>6</sup> Hill and Van Vleck, Phys. Rev. **32**, 250 (1928).

<sup>7</sup> A. A. Frost, D. W. Mann and O. Oldenberg, J. Opt. Soc. Am. **27**, 147 (1937).

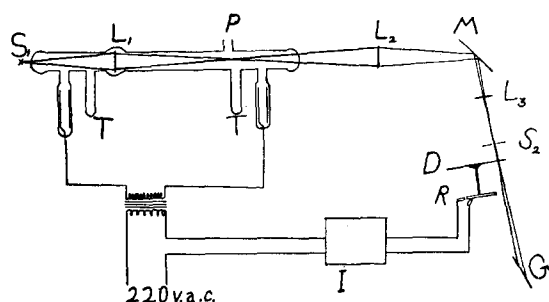


FIG. 1. Sketch of Apparatus.  $S_1$ , light source;  $L_1$  and  $L_2$ , spherical glass lenses;  $P$ , tube to pump;  $T$ , iodine traps;  $M$ , plane mirror;  $L_3$ , cylindrical lens;  $S_2$ , slit of spectrograph;  $D$ , sector disk;  $R$ , revolving switch;  $I$ , thyatron interrupter;  $G$ , grating.

sequence of processes is excitation by light and the subsequent fluorescence radiation which shows by its spectrum the production of highly vibrating molecules in the normal electronic state). The increase in relative concentration of molecules in the first vibrational level with respect to the ground level was observed spectroscopically by the method previously described. This was done during the operation of the discharge and, furthermore, after interrupting the discharge, by snapshots at various time intervals selected by an optical shutter, in order to find the gradual loss of vibration through collisions. In order to produce an adequate density on the photographic plate this sequence of discharge and snapshot was periodically repeated.

Contamination by iodine of the mercury in the diffusion pump was guarded against by a trap surrounded by carbon dioxide snow and acetone. A spiralled copper sheet between the first trap and the pump provided additional protection from the iodine. The oil pump was protected from water vapor by activated alumina.

The vapor pressure was measured with a Coolidge bifilar quartz fiber manometer,<sup>8</sup> for which the writer is obliged to Professor A. S. Coolidge, who very kindly made available his original instrument. This proved highly satisfactory when used in the basement of the Research Laboratory, which is comparatively free from vibrations. Since it consisted only of Pyrex and quartz, it introduced no new impurities into the system from contamination by the iodine.

<sup>8</sup> Albert Sprague Coolidge, *J. Am. Chem. Soc.* **45**, 7 (1923).

It was necessary to work with a vapor pressure low enough so the number of collisions through which the vibration might persist would be spread over as long an interval as possible to facilitate observation, yet high enough to give a good absorption spectrum and a stable electric discharge through the tube. A pressure of three hundredths of a millimeter proved to be quite satisfactory. At this pressure the mean free path is about 0.6 mm, small enough so that the great majority of all collisions takes place between molecules, not with the wall. This vapor pressure was obtained by condensing the iodine into two traps maintained at a temperature of zero degrees Centigrade by surrounding them with crushed ice. The two traps were necessary, for clean-up in the discharge in iodine was so rapid that the iodine was removed faster than it could be replaced by evaporation from one trap.

The discharge and absorption tube (Fig. 1) had to be very long in order to provide light absorption in spite of the low vapor pressure; it was a Pyrex tube three meters long and five centimeters in diameter. The windows were bulbs made as thin as possible, but which nevertheless did introduce some astigmatism. To neutralize this an equal amount of opposite sign was developed by adjusting the external lens to a slight angle. Because of the unusual length of the apparatus it was impossible to mount the tube directly in front of the slit, so a plane mirror was used to reflect the light.

The internal lens was supported by three strips of glass cane about five centimeters long sealed to a short piece of tubing telescoped inside the main tube. A slight bulge in the tube permitted the discharge to pass around the lens. The electrodes were molybdenum cylinders about ten centimeters long and three centimeters in diameter. They were supported from the tungsten-Pyrex seal by heavy tungsten wire to prevent touching and fracturing the glass when heated in the baking out process by high frequency induction currents. Only tungsten and molybdenum were used in order to minimize the formation of impurities by the ionized iodine.<sup>9</sup> In order to protect the discharge tube from vapors that may be formed by the effect of

<sup>9</sup> Fruth, *Phys. Rev.* **31**, 615 (1928).

iodine on the stopcock grease, a magnetically operated glass valve separated the discharge tube from an ordinary glass stopcock lubricated with low vapor pressure Apiezon grease, which is practically immune from attack by iodine. Between the valve and the stopcock was connected a trap surrounded by carbon dioxide snow, which served to condense any iodine escaping through the glass valve.

The molybdenum electrodes were cleaned of gases and vapors by heating to incandescence with the Cruft Laboratory 2-kw High Frequency Bombarder. It was necessary to approach this high temperature in a number of successive steps, carefully pumping out all impurities released each time, so they would not attack the heated molybdenum and cause it to split along the edge. Unless the molybdenum was heated to this high temperature, a brownish impurity was formed rapidly by the iodine during the discharge.

The tube was degassed by successive discharges in helium followed by pumping of the helium and the impurities released during the discharge. The process was repeated until the helium spectrum remained unchanged after a lengthy discharge. Relatively pure helium was available and this was further purified by passing slowly through a carbon trap surrounded by liquid air, the carbon first having been treated to a long pumping while maintained at a temperature as high as the Pyrex would stand. When the tube had been thoroughly degassed, C.P. iodine was fractionated over from a side tube.

A synchronous motor was geared down to a shaft on which rotated a brass and Bakelite sector disk. This served as a switch operating a Thyatron (FG29) in the primary circuit of the discharge transformer. An optical sector cardboard disk rotated on the same axis with the switch. The apparatus was mounted inside the grating room with the cardboard disk just behind the slit. By varying the phase between electrical and optical sectors, snapshots could be taken of the iodine absorption spectrum at different time intervals after interrupting the discharge.

The spectra were photographed in the second order of a twenty-one-foot Rowland grating. A five hundred-watt Mazda projection lamp served as light source for the absorption spec-

trum. Pre-exposed Eastman Type 144D plates were used, as this emulsion when sensitized for the red has a sensitivity corresponding to Type III with a contrast corresponding to Type IV. The exposure time was considerably reduced by a cylindrical lens which concentrated on the slit light that otherwise would have been lost. A slit width of 25 microns was used.

The rotating disk had two 22.5° openings separated by 180°. It was operated from an 1800-r.p.m. synchronous motor, geared down by a ratio of sixteen to one. Exposures of the order of an hour, including intermissions, were necessary. This corresponded to a continuous exposure of 7.5 minutes. The final image was the cumulative result of about 13,500 snapshots of 0.033 seconds each.

A photographic plate of the normal iodine absorption spectrum was split lengthwise and the two halves placed in the comparator. This instrument was specially built for the purpose of selecting from two spectra absorption lines of equal intensity. Two equal rotational lines, one belonging to a transition originating in the ground vibrational level and one belonging to a transition originating in the first excited vibrational level, were selected. They served as reference lines for thermal distribution. Any divergence from thermal distribution caused a relative change in absorption by the vibrational levels responsible for these two lines, and they no longer matched.

### III. RESULT

The plates taken while the discharge was passing through the absorption tube showed, when split and observed in the comparator, that these two lines were no longer of equal intensity, the one originating in the first excited vibrational level now being the stronger. The shift in relative intensities was not large, but it was quite clear and definite. This showed directly an increase in relative population of the first excited vibrational level with respect to the ground level caused by the discharge.

Repetition of the experiment more than a score of times showed that optimum values for the discharge were about 12,000 volts at 100 milliamperes. Much increase in the current

caused excessive dissociation which made comparison of the spectra difficult, while smaller currents gave less excitation and therefore reduced the shift of relative intensities.

Snapshots of the absorption spectrum taken at different intervals after the discharge was interrupted showed that the increase perceptibly persisted for at least a thirtieth of a second. Under the conditions of the experiment, this corresponded to seven thousand collisions between iodine molecules. This gave a direct spectroscopic confirmation of the hypothesis of the persistence of vibration in collisions proposed by Herzfeld and Rice in their theory of the dispersion of sound.

The method described here offers the advantage of giving the *most direct evidence* for the persistence of vibration in collisions. However,

it does not lend itself to a *quantitative* treatment as well as the dispersion of sound method. The reason is that each vibrational level above the normal level not only *loses* concentration by the general slow approach to the thermal distribution, but at the same time it registers a certain *gain* coming from higher vibrations. We observe a difference of two effects that cannot easily be treated quantitatively.

In conclusion, the author takes great pleasure in expressing his gratitude and appreciation to Professor O. Oldenberg, who proposed and guided this investigation, for his cooperation and encouragement. He wishes also to acknowledge his indebtedness to Professor E. Leon Chaffee and to Dr. W. M. Preston for their helpful suggestions, and to Mr. H. L. Leighton for his excellent glass blowing.

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## The Equilibrium Dissociation and Thermodynamic Constants of Nitrosyl Chloride. Comparison with Spectroscopic Data

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Careful measurements of the equilibrium dissociation of nitrosyl chloride into nitric oxide and chlorine have been made in the temperature range 100–220°. Pressure-temperature measurements at 0°–100° on mixtures of nitrosyl chloride and nitric oxide were made and from them the second virial coefficients of nitrosyl chloride gas were calculated. These vary from  $-389 \text{ cm}^3/\text{mole}$  at 0° to  $-196 \text{ cm}^3/\text{mole}$  at 100°. The virial coefficients were used to correct the measured equilibrium constants to those for perfect gases. Equations for free energy, entropy and heat content changes accompanying the dissociation were derived as functions of the temperature. The experimentally found entropy changes for the reaction were found to be less than those calculated from spectroscopic data by  $3.61 \pm 0.3 \text{ cal./deg.}$  To attain agreement, the spectroscopic entropy of nitrosyl chloride must be increased by  $1.8 \text{ cal./deg.}$ , and this was attained by assuming that an observed infra-red frequency at  $923 \text{ cm}^{-1}$  is a combination,  $633 + 290 \text{ cm}^{-1}$ . For the reaction  $2\text{NOCl(g)} = 2\text{NO(g)} + \text{Cl}_2(\text{g})$ ,  $\Delta F^\circ_{298} = 9,720 \pm 60 \text{ cal.}$ ,  $\Delta S^\circ_{298} = 28.0 \pm 0.5 \text{ cal./deg.}$ ,  $\Delta H^\circ_{298} = 18,060 \pm 200 \text{ cal.}$ ,  $S^\circ_{298}(\text{NOCl}) = 63.0 \pm 0.3 \text{ cal./deg.}$

### INTRODUCTION

THE dissociation of nitrosyl chloride,  $\text{NOCl}$ , into nitric oxide and chlorine under equilibrium conditions has been studied by several investigators, but only the work of Dixon<sup>1</sup> lays claim to any accuracy. Dixon's results are subject to some uncertainties in the temperature scale

( $\pm 2^\circ$ ), the measurements, and the effect of gas imperfections, so that comparisons with the thermodynamic quantities calculated from molecular and spectroscopic data, while suggestive, are not altogether satisfying. Recently, and after the present investigation was nearly completed, Jahn,<sup>2</sup> employing the electron diffraction results

<sup>1</sup> Dixon, Zeits. f. physik. Chemie Bodenstein Festband, 679 (1931).

<sup>2</sup> Jahn, J. Chem. Phys. 6, 335 (1938).