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INCOHERENT SCATTERED RADIATION IN DIATOMIC MOLECULES

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ABSTRACT

Raman spectra excited in diatomic gases by the line λ2536 of mercury have been photographed with a quartz spectrograph. An apparatus for using gases at pressures from ten to fifteen atmospheres has been built, with great improvement as compared with the use of gases at atmospheric pressure. Results obtained with H_2, N_2, O_2, NO are reported. A particularly complete investigation has been made of the hydrogen spectrum, leading to an accurate determination of the constants of the molecule in the normal electronic state. The numerical values are (in cm^{-1}) $B_0=h/8\pi^2I_0c=59.40$; $\omega_{0/1}=4162.1$. For N_2, the corresponding values resulted to be: $B_0=1.992$; $\omega_{0/1}=2330.7$. For O_2: $B_0=1.436$; $\omega_{0/1}=1554.7$. All these molecules are in Σ states, and the Raman spectra consist of Q-, double R-, and double P- form branches, as deduced from the Kramers-Heisenberg formula by the author and by Hill and Kemble. Nitric oxide is the only molecule so far investigated which is in a $^2\Pi$ state. The transition between the two terms of the doublet has been observed in the scattered radiation.

THE structure of the Raman spectrum for a diatomic molecule has been deduced from the quantum mechanical theory of dispersion by the author[1] and by Hill and Kemble.[2] It is easy to show, by means of the Kramers-Heisenberg formula, that rotational and vibrational transitions are to be expected in the scattering process for non-polar molecules also; and that, if the molecule is in a Σ state, only transitions satisfying the selection rule $\Delta j=0, \pm 2$ can take place, thus giving rise to Q-, double R-, and double P-branches. Hill and Kemble have worked out the theory more completely, to include a qualitative treatment of intensities and polarization.

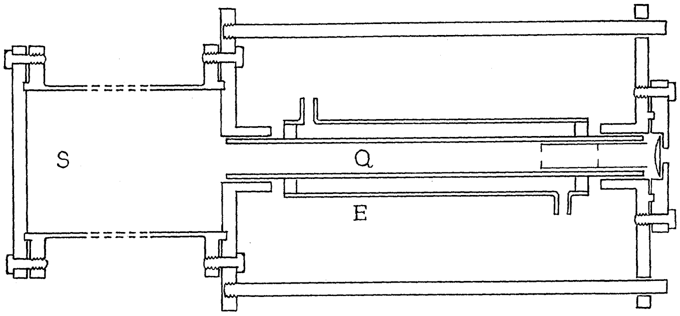

Fig. 1. High pressure tube.

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[1] F. Rasetti, Proc. Nat. Acad. Sci., **15**, 234 and 515 (1929); Nature **123**, 757 (1929).

[2] E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Sci., **15**, 387 (1929).

The author has already reported on the results of some experiments[1] in which the double R- and double P-form branches of the pure rotational bands, and unresolved Q-form branches of vibrational bands were recorded. Similar spectra have been obtained by Wood[3] in HCl.

The experimental arrangement has been considerably improved, bringing out new results. In order to avoid extremely long exposures, the intensity of the scattered radiation has been increased by the use of gases at pressures from ten to fifteen atmospheres. The apparatus was similar to the one which has been described,[1] except that it was built in such a way to stand the above-mentioned pressure. It will be sufficiently explained by Fig. 1. The illuminated part of the tube was made of thick-walled quartz Q, 2.2 cm internal diameter, and about 20 cm long. This quartz tube was fastened to a large steel tube S by means of sealing-wax. The external quartz tube E was filled with a solution of acetic acid in water, in order to absorb the λ1849 radiation, which otherwise would have caused troublesome photochemical reactions in many gases (for example, the formation of ozone in oxygen).

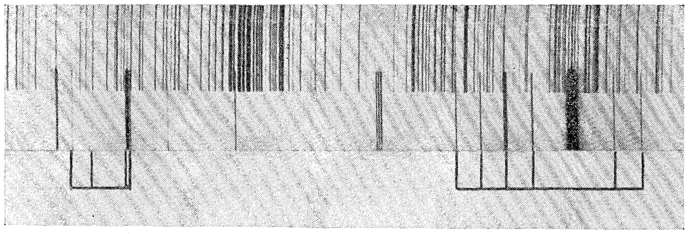

Fig. 2. Raman spectrum of H_2, showing rotational and vibrational-rotational lines.

The primary source of light was a commercial mercury arc, 12 cm long. Water-cooling and deflecting the discharge by means of a strong magnet were employed as usual.

With the described apparatus, strong Raman spectra were recorded in exposures from 10 to 40 hours. The same Hilger quartz spectrograph as in the previous work was used.

HYDROGEN

Spectrograms taken with H_2 at 12 atmospheres showed four positive and two negative rotational lines, and four lines in the Q branch, four in the positive branch, and two in the negative branch in the 0→1 vibrational band. Fig. 2 shows the appearance of the whole spectrum; Fig. 3 shows, much enlarged, the Q-form branch of the 0→1 band, resolved into four lines.

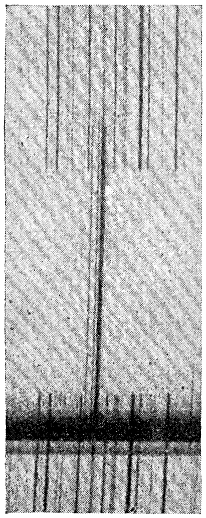

Fig. 3. Q-branch of the $0 \rightarrow 1$ band in H_2.

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[3] R. W. Wood, Phil. Mag. **7**, 744 (1929).

Frequencies were measured by comparison with the iron spectrum. In measuring plates, I noticed that the position of the λ2536 line, as deduced from the symmetry of positive and negative rotational lines, was not exactly as given in the tables, that is 39412.6 cm^{-1}, but was shifted, and uniformly in all the plates, the observed value being 39411.1 cm^{-1}. I have considered it more correct to adopt this last value for the frequency of the exciting line in calculating Raman shifts.

The error in the measurement of the frequencies is believed to be always smaller than one frequency unit (except perhaps for a few weak lines). This follows both from the consistency of values from different plates, and from the agreement with the calculated values.

The energy E_{nj} of the nth vibrational and jth rotational state can be represented in first approximation by a formula of the following form:[4]

$$E_{nj}/hc+\text{const.}=\omega'_{0/n}+B_0'\left[1-\alpha(n+\tfrac{1}{2})\right](j+\tfrac{1}{2})^2-4(B_0'^3/\omega_0^2)(j+\tfrac{1}{2})^4$$

where B_0' is the value of $h/8\pi^2Ic$ for *zero* vibration, ω_0 the vibration frequency for zero amplitude, and α is a constant which measures the coupling between vibration and rotation. The frequency $\omega_{0/1}$ of the transition from the zero to the first vibrational state, and the moment of inertia, I_0, in the zero vibrational state and for zero rotation are evidently connected to the above used symbols by the relations:

$$\omega_{0/1}=\omega'_{0/1}-\alpha B_0'/4$$
$$B_0=h/8\pi^2I_0c=B_0'(1-\alpha/2)$$

Table I gives the calculated and observed values for 16 transitions (in cm^{-1}), using for the constants the values $\omega'_{0/1}=4162.8$, $B_0'=60.862$, $\alpha=0.0481$.

TABLE I. *Calculated and observed values for* 16 *transitions in the hydrogen molecule.*

n	j	ν calc.	ν obs.	difference
0→0	3→1	−587.3	−587.3	0
	2→0	−354.6	−354.5	−0.1
	0→2	354.6	354.1	−0.5
	1→3	587.3	587.5	+0.2
	2→4	814.4	814.4	0
	3→5	1033.9	1034.6	+0.7
0→1	0→0	4162.1	4162.1	0
	1→1	4156.2	4156.0	−0.2
	2→2	4144.5	4144.8	+0.3
	3→3	4126.9	4126.9	0
	0→2	4499.1	4498.4	−0.7
	1→3	4714.2	4713.3	−0.9
	2→4	4917.9	4917.8	−0.1
	3→5	5108.0	5109.8	+1.9
	2→0	3807.5	3807.4	−0.1
	3→1	3568.9	3568.9	0

From the difference between the observed and calculated values, I believe that we may assign the following limits of accuracy to the constants of the hydrogen molecule:

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[4] A. Sommerfeld, Atombau, Wellenmechanischer Ergänzungsband, p. 29.

$$B_0=59.40\pm0.03$$
$$\omega_{0/1}=4162.1\pm0.3$$

The intensities of the lines, so far as a qualitative inspection can tell, agree with those predicted by Hill and Kemble, including the fact that the Q-form branch of the vibrational band is more intense than the other branches, even when resolved into its components as is the case here. As to the ratios of the intensities of the lines in the same branch, we have to consider several factors, that is, the *a priori* statistical weights of the rotational states, the transition probabilities to rotational states of other electronic levels, and the Boltzmann distribution. The increasing statistical weight with increasing j partly compensates the Boltzmann factor and favors the higher rotational lines; then the fact that the odd rotational levels have three times the statistical weight of the even levels has to be taken into account. All this explains the observed distribution of the intensity. The 1→1 line is the most intense in the Q branch, the 1→3 line in the positive branches. These data on the normal state of the H_2 molecule are in very close agreement with those deduced by Hori[5] from the absorption bands in the far ultra-violet, $\omega_{0/1}=4162.8$; $B_0=59.2$. Hori's value 4415 for ω_0 has been used in the correction term containing $(j+\frac{1}{2})^4$.

NITROGEN AND OXYGEN

No new features have been found in the Raman spectra of these molecules, but better plates (one of which is reproduced in Fig. 4) have been obtained. I give only the most probable values of the constants and of their uncertainty, as deduced from the consistency of the determinations from different plates:

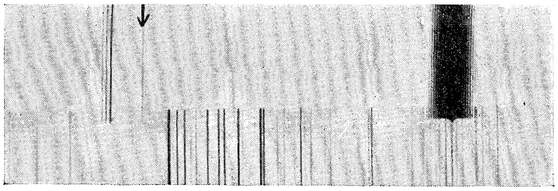

Fig. 4. Raman spectrum of O_2

$$N_2:\ \omega_{0/1}=2330.7\pm2$$
$$B_0=1.992\ \pm0.005$$
$$O_2:\ \omega_{0/1}=1554.7\pm1$$
$$B_0=1.436\ \pm0.005$$

NITRIC OXIDE

This molecule differs from all the others so far investigated in the Raman effect, being in a $^2\Pi$ state, with a separation of about 121 cm^{-1}. An inspection of the scheme of the $^2\Pi\rightarrow{}^2\Sigma$ absorption system[6] shows that here we have to

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[5] T. Hori, Zeits. f. Physik **44,** 834 (1927).

[6] R. S. Mulliken, Phys. Rev. **32,** 388 (1928).

expect transitions with $\Delta j=0, \pm 1, \pm 2$ which give a pattern of rotational lines too close to be resolved with the present apparatus. Therefore, we must expect continuous darkening of the plate near the exciting line. However, at a distance of 121 cm^{-1} from the exciting line, the intensity must increase suddenly, because we have, besides the transitions between rotational states of the lowest $^2\Pi_{\frac{1}{2}}$ level, also the transitions from those of the $^2\Pi_{\frac{1}{2}}$ to those of the $^2\Pi_{1\frac{1}{2}}$ level.

Nitric oxide was prepared by the action of acetic acid on a mixture of potassium nitrite and potassium ferrocyanide. It was used at atmospheric pressure and a very long exposure was necessary to obtain the spectrogram shown in Fig. 5. The darkening at the expected distance from the exciting line is clearly visible.

The measured shift is 119 ± 5, in agreement with the value deduced from the absorption bands.

In conclusion, I wish to express my thanks to Professor R. A. Millikan for the facilities of the Norman Bridge Laboratory placed at my disposal; and to the International Education Board, to whose grant of fellowship my vist to America was due.

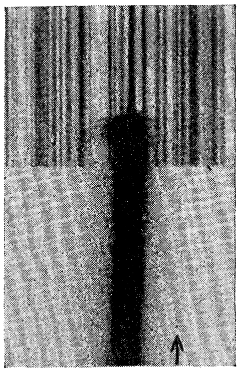
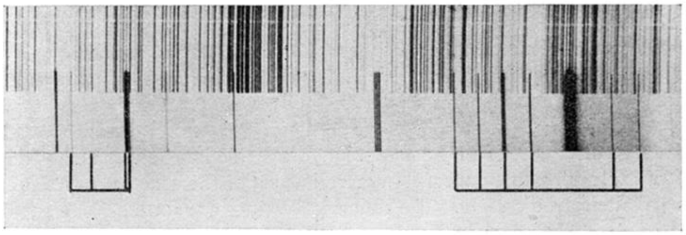


Fig. 5. Transition between the two terms of the $^2\Pi$ doublet in NO.



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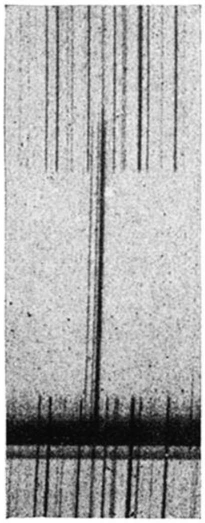

Fig. 3. Q-branch of the $0 \longrightarrow 1$ band in H_2.

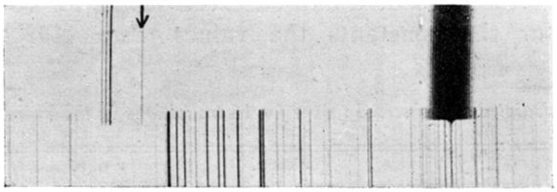

Fig. 4. Raman spectrum of O_2

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