

ON THE RAMAN EFFECT IN DIATOMIC GASES. II

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In a recent paper¹ the writer has pointed out how the phenomena observed in the incoherent scattering of light by molecules can be easily accounted for with the quantum theory of dispersion. Kemble and Hill,² Langer³ and Dieke⁴ have independently developed similar considerations. The experimental results obtained by the writers, McLennan and McLeod,⁵ and Wood⁶ all support these theoretical conclusions.

In the present paper I want to report some experiments which I have been carrying on recently, and which show the relationship between Raman transitions and band spectrum structure much more clearly than before. A preliminary communication of these results has already been given in a letter to *Nature*,¹ but they were incomplete, and besides some inaccurate statements were made concerning the N₂ spectrum. Recently Wood⁶ seems to have obtained similar results on HCl, in which the separation of rotational levels is large enough to be resolved with the low dispersion employed.

The essential improvement in the experimental arrangement consists in the use of the $\lambda 2536$ mercury line as exciting light. The scattering is much stronger in that spectral region than in the visible, so that the Raman lines could be photographed with fairly large dispersion in a Hilger quartz spectrograph.

The primary source of light consisted of an especially built quartz lamp, about 25 cm. long and 2.5 cm. in diameter. The electrodes were water-cooled to keep the mercury vapor pressure low. In order to prevent too much reabsorption of the $\lambda 2536$ radiation in the lamp itself, the discharge was bent toward the wall facing the tube with the scattering gas, by means of a properly designed electromagnet.

The lamp was used with a current intensity of 7 amp. The gases were contained in the tube at atmospheric pressure, and exposures of 60 to 120 hours were needed to get spectrograms of the scattered radiation.

The dispersion in the region of the $\lambda 2536$ line was 129.7 frequency units per mm.

An iron arc spectrum was used as a standard. Working with a very narrow slit, perfectly sharp Raman lines were obtained, and their frequencies could be measured within a few tenths of a frequency unit.

The main result of these experiments has been to obtain well-resolved Raman lines corresponding to rotational transitions.

In the former paper, only the general consequences of the application

of the Kramers-Heisenberg formula to electronic and vibrational transitions in molecules were considered. Now we need to take into account also rotational states and electronic fine structure of molecular levels.

For our case, some general selection rules developed by Heisenberg,⁷ Hund,⁸ and Kronig⁹ for molecular spectra are particularly useful.

Kronig deduces from the properties of symmetry of the eigenfunctions of diatomic molecules the general selection principle, that between any three terms in a molecular spectrum no more than two combinations can occur. Now, if we consider that for observing a transition $i \rightarrow k$ in the Raman effect there must be at least a third state s such that the transitions $i \rightarrow s$, $k \rightarrow s$ occur in emission and absorption, we deduce from Kronig's rule the following general principle: only transitions between non-combining terms take place in the scattering process.

Of course, in the applications one has to be sure that the terms considered are really single; for instance, P terms are generally unresolved σ -type doublets, and each of the two components, which have different combination properties, has to be considered separately.

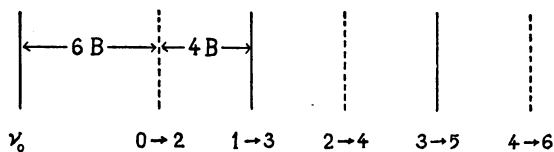


FIGURE 1

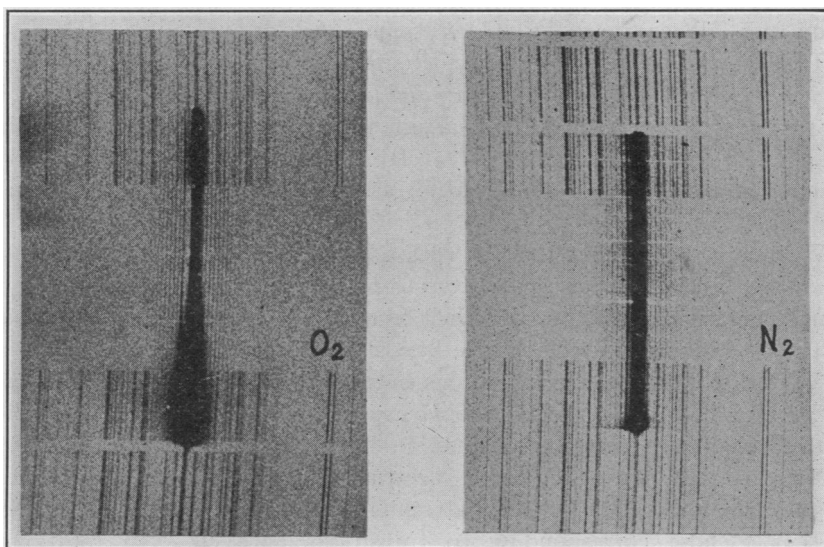
In the case of a symmetrical molecule, it has been shown by Heisenberg and Hund that the whole system of terms splits into two classes, according to the property of the total eigenfunction of being symmetrical or anti-symmetrical in the coordinates of the nuclei. If the nuclei have no spin, only one of the two classes exists (the antisymmetrical class if the nuclei satisfy the Fermi-Pauli statistics, the symmetrical class if they satisfy the Einstein-Bose statistics). This is what happens, for instance, in O_2 and He_2 .

The presence of a nuclear spin with different possibilities of orientation can make completely symmetrical or completely antisymmetrical the whole system of terms which was partly symmetrical and partly anti-symmetrical before the introduction of the spin coordinates. Then both classes of terms exist, but they are practically non-combining, because of the extremely weak coupling between the nuclear spins. This behavior, similar to the splitting of the He terms in para- and ortho-terms, has been observed in N_2 and H_2 .

The molecules so far investigated in the Raman effect are all in S states; therefore we will consider this case in detail from the theoretical standpoint. Mulliken's¹⁰ notations will be used.

It has been shown by Hund⁸ that in the case of S levels in a symmetrical molecule the successive rotational states belong alternatively to the two non-combining classes. If they have a fine structure (2S , 3S terms), all components having a common j_k and different values of j belong to the same class.

Now let us admit (as it will be justified later for the molecules actually investigated) that in the electronic bands to which the incoherent scattering is essentially due, besides the general selection rule $\Delta j = 0, \pm 1$ also $\Delta j_k = 0, \pm 1$ holds (which is true if the coupling between electronic orbital angular momentum, electronic spin and rotation is as in Hund's



Rotational Raman spectra in nitrogen and oxygen, showing the alternating intensities in N_2 , due to the nuclear spin.

case b^8). Then the transitions occurring in the scattering process must satisfy the condition $\Delta j_k = 0, \pm 2$. Considering pure rotational transitions, and neglecting the fine structure, the Raman shift is then given by

$$\pm \Delta\nu = F(j_k + 2) - F(j_k) = B(4j_k + 6),$$

where for a molecule with no nuclear spin j_k assumes either only odd or only even integral values; in the case of a nuclear spin, both.

The structure of this Raman spectrum is shown clearly in figure 1, where the full lines correspond to odd values of j_k , the dotted lines to even values.

After these considerations it is easy to understand the experimental results which I have obtained on O_2 , N_2 and H_2 .

Oxygen gives a pattern of equally spaced lines (six or seven of them are well measurable on each side of the exciting line; then they become very weak with increasing distance from the unmodified frequency, as it is to be expected from the Boltzmann factor.

The first one or two lines on each side cannot be measured as they overlap with the over-exposed image of the $\lambda 2536$ line; but from the position of the other lines it is possible to show definitely that they constitute a pattern like that represented by the full lines in figure 1. That is, the distance of the nearest Raman line from the exciting line is $10/8$ times the other equal intervals (and not $6/8$ times as given by the pattern of the dotted lines, or $12/8$ as given by the complete pattern of both systems.) From this follows that only odd rotational levels are present.

This agrees with Ossenbrüggen's¹¹ analysis of the Schumann-Runge, $^3S \rightarrow ^3S$ absorption band system; and also the quantitative agreement is as good as it can be expected. From the measurements I get for the constant B (which is given by $1/8$ of the distance between consecutive Raman lines) the value 1.430 cm.^{-1} , as compared with Ossenbrüggen's value 1.439 .

We may observe that the absorption bands which we must expect to take an essential part in the scattering process are the Schumann-Runge bands, as they are intense, and their frequency is not very far from that of the exciting light used. These bands satisfy the selection rule $\Delta j_k = 0, \neq 1$ as it must be for transitions between S states, which always fall under Hund's case b . So we should expect the rule $\Delta j_k = \neq 2$ to hold in this case in the scattering process.¹²

Nitrogen presents in the Raman spectrum the characteristic phenomenon of alternating intensities. The pattern is like in figure 1 with all the lines present. Those corresponding to transitions between even rotational states (dotted lines in the figure) are strong, the lines of the other system are weak.

This also fits with our knowledge of the N_2 spectrum. The normal state is a 1S level,¹³ so that here $j = j_k$, and the selection rule $\Delta j = 0, \neq 1$ allows only transitions with $\Delta j_k = \neq 2$ in the scattering process. Even and odd rotational states belong to two different non-combining classes, so that transition between consecutive levels are excluded.

The numerical value of B results to be $1.975 \pm 0.01 \text{ cm.}^{-1}$. From this, the (hitherto unknown) moment of inertia of the nitrogen molecule in the normal state is found to be

$$I_0 = 14.0 \pm 0.1 \cdot 10^{-40}.$$

The considerations developed for N_2 hold also for H_2 , which has also a nuclear spin and a normal 1S level. I have been able to obtain in the Raman rotational spectrum only the transition $1 \rightarrow 3$, which gives a line

displaced of 583 cm.^{-1} from the exciting line. McLennan⁵ has obtained also the weaker $0 \rightarrow 2$ transition in liquid hydrogen. This shows, in conformity with Hori's¹⁴ analysis of the absorption bands, that odd rotational states have a higher statistical weight in H_2 .

Perhaps it is significant for the properties of the nuclei that N_2 and H_2 , which have a similar electronic structure (1S states), behave in opposite ways as to the relative weight of odd and even rotational states.

Most of what has been said about purely rotational transitions applies also to vibrational-rotational Raman spectra. In this case, for the molecules of the considered type, the Raman shift must be given, in first approximation, by

$$\begin{aligned}\Delta\nu_1 &= \nu_0 + F(j_k) - F(j_k) = \nu_0 \\ \Delta\nu_2 &= \nu_0 + F(j_k + 2) - F(j_k) = \nu_0 + B(4j_k + 6) \\ \Delta\nu_3 &= \nu_0 + F(j_k) - F(j_k + 2) = \nu_0 - B(4j_k + 6),\end{aligned}$$

where ν_0 is the difference between the vibrational energies. We should have a Q -form branch, reduced to a single line, and PP - and RR -form branches. The coupling between rotation and vibration should separate the lines of the Q -form branch, and alter the spacing in the other branches.

So far only the unresolved Q -form branch has been observed. With the resolution available in the present experiments it actually shows an appreciable width. It is not surprising that the other branches should be missing, when we take into account that the Q -form branch is composed of something like ten or fifteen overlapping lines, and has on the plates just intensity enough to be observed. A line ten times weaker would certainly escape notice. Nevertheless I hope that further experiments will bring out the complete vibrational-rotational Raman bands.

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⁸ F. Hund, *Ibid.*, **40**, 742, 1927; **42**, 93, 1927.

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¹² Otherwise also $\Delta j_k = \pm 4$ and $\Delta j_k = \pm 6$ could be possible.

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