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THE RAMAN EFFECT IN HCL GAS

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Abstract

Improvements in the experimental conditions made it possible to get much better pictures of the Raman effect of HCl-gas than before. The results are in perfect agreement with what is predicted by the dispersion theory.

The first report of the Raman effect in the case of a gas at atmospheric pressure was published by R. W. Wood in Nature, February 2, 1929, where it was shown that hydrochloric acid gas contained in a long glass tube mounted in contact with a Cooper-Hewitt glass mercury arc, the whole surrounded by a reflecting cylinder of highly polished sheet aluminum, gave a Raman line excited by the Hg 4046 line, the frequency difference corresponding to an infrared line in the position of the "missing line" of the absorption band at 3μ. In the following number of Nature, Rasetti announced the discovery of the Raman lines of CO and CO_2 also at atmospheric pressure.

The experiments in HCl were more fully described in the Phil. Mag. for April 1929 and it was shown that the 4358 Hg line was accompanied by a series of close companions, corresponding to rotations of the HCl molecule, and it was further shown that the infrared frequencies corresponding to these lines were of very nearly the same wave-length as the *alternate* lines observed by Czerny. An interpretation of these results was given by several investigators independently.[2] Rasetti[1] studied with great success the Raman effect of other diatomic gases at atmospheric or higher pressures.

With the same tube, and with a platinum diaphragm as was employed in the earlier experiment, but with a recently constructed spectrograph equipped with two interchangeable camera lenses, one a large Steinheil portrait objective (F2.5) and the other a Cooke objective of one meter focus, some superior spectrograms of the Raman effect in HCl have been obtained.

A better alignment of the tube was secured and greater precautions taken to exclude all parasitic light. Six, or possibly seven rotation bands appeared on the long wave-length side of Hg 4355 and three (anti-Stokes) on the other side. Rotation bands also appeared on both sides of the 4046 line, but the "*Q* branch" line excited by 3650–3655 and 3663 appeared in triplicate mixed in with these rotation bands.

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[1] F. Rasetti, Nature **123**, 205, 757 (1929). Proc. Nat. Acad. Sci. **15**, 234, 515, (1929). Phys. Rev. **34**, 367 (1929).

[2] G. H. Dieke, Nature **123**, (1929). F. Rasetti reference 1. E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Sci. **15**, 387 (1929), and others. All these papers are simply an interpretation of the formulas of the dispersion theory developed first by Kramers and Heisenberg in 1925.

An enlargement of the entire spectrum is reproduced in Fig. 1. and a highly enlarged portion of the part showing the *Q* branch excited by 4046 and the rotation bands to the right and left of the 4358 line in Fig. 2.

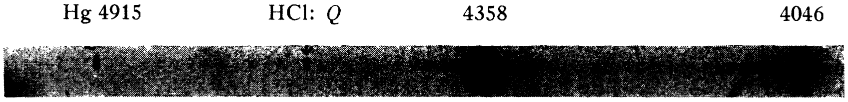

Fig. 1. Enlargement of entire spectrum.

Fig. 2. Highly enlarged portion of spectrum.

INTERPRETATION OF THE RESULTS

The Raman effect of HCl furnishes an excellent opportunity to compare the theoretical predictions with the experimental results, for the HCl molecule is very simple, and furthermore we know its entire infrared absorption spectrum. The situation is therefore much more favorable than for the organic molecules, the exact structure of which is generally not known, so that it is impossible to say what we ought to expect theoretically.

The experimental data are given in Table I.

TABLE I.

λ	$\Delta\nu$	Transition	$\Delta\nu$ infrared
—	—	0→2	62.69
4377.60	101.1	1→3	104.29
85.6	142.7	2→4	146.03
94.2	187.5	3→5	187.45
4402.4	229.4	4→6	228.87
10.4	271.0	5→7	270.03
18.6	312.9	6→8	311.23
26.5	353.0	7→9	352.23
4314.7	143.8	4→2	146.03
23.8	183.3	5→3	187.45
31.2	232.2	6→4	228.87
4581.8	2886.0	j→j	2885.4*

* This line is excited by λ4047. The corresponding line excited by λ4358 would fall in a region where the plate is very insensitive. The infrared datum is the zero line of the absorption band at 3.4μ. The wave-length of the Raman *Q*-branch has been taken from the previous work because the dispersion was then greater. We find now a value about 3 cm^{-1} less, but think it less reliable.

The first column gives the observed wave-lengths of the Raman lines. The second column gives the frequency differences with the exciting line λ4358.

In the third column we find the rotational transitions in the molecule to which the lines correspond, and the fourth column gives a comparison with the infrared data (see farther down).

The dispersion theory of Kramers and Heisenberg[3] published in 1925 contains, as is well known now, a complete theory of the Raman effect. The more rigid radiation theory of Dirac leads essentially to the same formulae. The essential feature of this theory is, that the intensity of a Raman line which corresponds with a transition of the molecule from the level a to the level b, has no connection at all with the transition probability between these two levels, which would determine the intensity of the corresponding absorption line. In order to find the intensity of a Raman line we must consider virtual transitions with a certain third level c. If this level c can be reached in an ordinary transition from both the levels a and b, the Raman line is allowed. The Raman line can therefore be considered as the difference between two lines of the molecule, one of which must be an absorption line. The theory gives further the exact intensities of the lines expressed in terms of the transition probabilities between the different levels of the molecule, but we need not go here into details of the theory.

If we consider now a HCl molecule in its normal electronic and vibrational state and with a value j of the rotational quantum number, we have to consider first the possible absorption transitions in order to find which Raman lines we have to expect. In any transition the change of j can be only zero or ± 1. From the theory of the spectra of diatomic molecules it is well known[4] that those states to which the molecule can go if $\Delta j=0$ are of a different nature from those for which $\Delta j=\pm 1$.

Let us consider the latter ones first. The molecule would be either in a state with $j+1$ or with $j-1$ after the virtual absorption act. It has to fall back in a virtual emission act to the *normal* electronic level, and the change of j can only be ± 1 in this transition. After the emission of the Raman line the molecule can therefore only be in a state with the rotational quantum number j or $j\pm 2$. If we take into account also those virtual absorption acts for which $\Delta j=0$, (such transitions would occur when the upper electronic state is a Π-state), nothing will be changed in this result. For in the virtual reemission act j must remain likewise unchanged, so that in this particular kind of Raman transition no change of j can occur. As we have to take the sum over all possible third levels c, our result is that in any Raman transition j can change only zero or ± 2. As for any infrared absorption line of HCl we must have $\Delta j=\pm 1$, we see that not a single Raman line can correspond to an absorption line.

As was shown by Van Vleck[5] the possible changes of the vibrational quantum number are zero or ± 1 only, even if intermediate levels c with high

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[3] H. A. Kramers and W. Heisenberg Zeits. f. Physik **31**, 681 (1925).

[4] E. Hulthén, Zeits. f. Physik **46**, 349 (1927). R. de L. Kronig Zeits. f. Physik **46**, 814 (1928).

[5] J. H. Van Vleck, Proc. Nat. Acad. Sci. **15**, 754 (1930).

values of the vibrational quantum number are taken into account. A higher electronic level of the HCl molecule than the normal one is as yet unknown. From the behavior of similar molecules we have reason to expect that an absorption act will result in such a case into dissociation. There seems to be no reason why these dissociated states cannot act in just the same way as the discrete levels as intermediate states in the Raman effect. The considerations which determine the selection rule for j hold just as well for this kind of transition. It may be expected that the probability for the ultraviolet absorption is much greater than that for the infrared absorption so that the transitions via the dissociated states play the most important part in the Raman effect of HCl. But other factors ought also to be considered, so that this point cannot be settled yet with the present material.

If the vibrational quantum number does not change, we can notice only a change ±2 of the rotational quantum number for $\Delta j=0$ gives the unmodified line. If *j increases* two units we have what is called the normal Raman effect,[6] i.e., lines on the red side of the directly scattered line and as the table shows, the transitions up to 7→9 have been observed except the first one which would come too close to the strong unmodified line so that it cannot be detected. We can obtain the same rotational differences also from the infrared data of the vibrational rotational bands *nl.* as differences $R(j-1)-P(j+1)$ of lines of the R- and P-branch, and these differences are given in the fourth column of the table.[7] The agreement is as good as it can be expected from measurements of such faint lines.

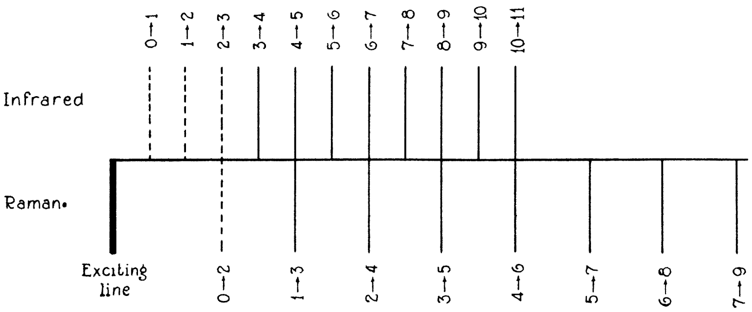

Fig. 3. Diagram showing the connection between the Raman and the infrared rotational spectrum of HCl.

In the former communication and in the beginning of this paper it was mentioned that these lines correspond with alternate lines of the rotational absorption band in the far infrared observed by Czerny.[8] But this correspondence is only accidental as can be seen immediately from Fig. 3 in which

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[6] A sequence for which in the Raman effect $j\to j+2$ is called an O-branch. It would be similar to an ordinary P-branch with double spacing. Similarly a sequence of lines for which $j\to j-2$ is called an S-branch.

[7] Taken from C. F. Meyer and A. A. Levin, Phys. Rev. **34,** 44 (1929).

[8] M. Czerny Zeits. f. Physik **34,** 227 (1925); **44,** 235 (1927).

both the Raman and the far infrared absorption spectrum of Czerny are plotted and the corresponding transitions indicated. The fact that the Raman lines coincide with alternate infrared lines is only due to the fact that the rotational energy can be represented with good approximation by $Bj(j+1)$, from which follows that the Raman lines due to the transitions $j+1\rightarrow j-1$ coincide with the absorption lines $2j+1\rightarrow 2j$. This agreement is not exact as one would find deviations if one takes into account also the higher terms in the rotational energy. These deviations are however too small to be noticeable with the accuracy of the present observations.

The conditions for the observation of the Raman lines corresponding to transitions $j\rightarrow j-2$ (anti-Stokes lines, S-branch) were much less favorable, as the first lines are covered by the companions of $\lambda 4358$. However, the three lines given in the table can clearly be recognized. Obviously the distance of a line $j\rightarrow j-2$ from the unmodified line must be the same as that for the line $j-2\rightarrow j$. The intensity of the $j\rightarrow j-2$ transition seems to be less than that of the $j\rightarrow j+2$ transition. This asymmetry can also be accounted for theoretically. For a $\Sigma\rightarrow\Sigma$ transition the probability for a transition $j+1\rightarrow j$ is equal to that for $j\rightarrow j+1$ and proportional to $j+1/2$. For a Raman transition the intensity is determined by expressions in which the product of the probabilities for the virtual absorption and emission act occur. Therefore for a transition $j\rightarrow j-2$ the intensity would be proportional to $(j-1/2)(j-3/2)$ whereas for the transition $j\rightarrow j+2$ the intensity would be proportional to $(j+1/2)$ $(j+3/2)$. That means that a line of the O-branch must be stronger than the line of the R-branch which has the same initial state, and that is in agreement with the observed intensities.

If the vibrational quantum number increases one unit, we have to expect transitions $j\rightarrow j+2$ (O-branch) $j\rightarrow j-2$ (P-branch) and $j\rightarrow j$ (Q-branch). The O and P branches were too weak to be noticeable on the plates, which indicates that a Raman transition in which the vibrational quantum number increases one unit is *much* less probable than the transition in which it remains unchanged in accordance with Van Vleck's calculations. All the lines of the Q-branch fall so close together that they cannot be separated and are seen as one somewhat diffuse line. As the moment of inertia is larger in the final state of the Raman transition (on account of the stronger vibration) the Q-branch ought to be degraded towards the exciting line, i.e. towards the violet. It can clearly be seen on the plate that this is actually the case.

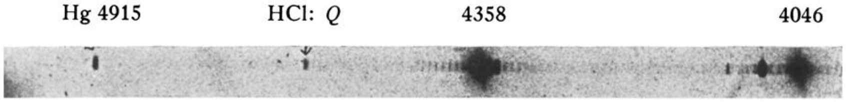

Fig. 1. Enlargement of entire spectrum.

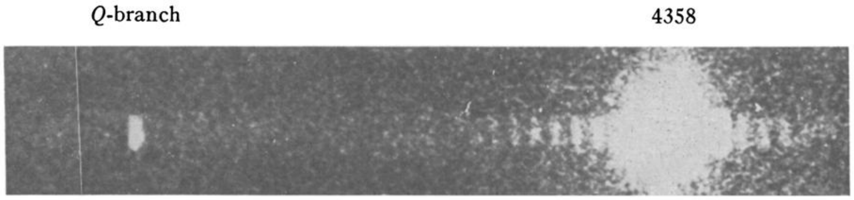

Fig. 2. Highly enlarged portion of spectrum.