820. *Infra-red Spectrum of Crystalline Potassium Perchlorate. Re-assignment of the lower Fundamental Frequencies of the Perchlorate Ion.*

By (the late) HENRY COHN.

The infra-red spectrum of crystalline potassium perchlorate contains a strong band at 628 cm.$^{-1}$ and a strong double band at 1090, 1140 cm.$^{-1}$. Crystalline nitronium perchlorate shows the same bands. These frequencies are found also in the Raman spectra. However, the other two Raman frequencies, 935 and 460 cm.$^{-1}$, do not appear in the infra-red. It is concluded that the assignments of frequencies to the two stretching vibrations of the perchlorate ion have been correctly made in the past, but that the two bending frequencies have been wrongly assigned, and must be interchanged.

THE perchlorate ion, as a tetrahedral XY_4 molecule, has its nine vibrational degrees of freedom distributed in four normal modes of vibration, as shown in the Table below.

No.	Class	Description
1	A_1	Totally symmetrical, stretching : the four bonds extend synchronously.
2	E	Doubly degenerate, bending : external atoms converge in pairs.
3	F_2	Triply degenerate, stretching : such that external atoms move towards a common direction.
4	F_2	Triply degenerate, bending : the bonds bend over towards a common direction.

All four vibrations are allowed in the Raman spectrum. Observations of the Raman spectra of aqueous solutions of perchlorates have established the existence of three strong Raman frequencies, while the expected fourth is replaced by a diffuse band. Redlich, Holt, and Biegeleisen (*J. Amer. Chem. Soc.*, 1944, **66**, 13) have assigned these frequencies as follows :

(1) A_1 stretching	(2) E bending	(3) F_2 stretching	(4) F_2 bending
935	630	1050—1170	460 cm.$^{-1}$

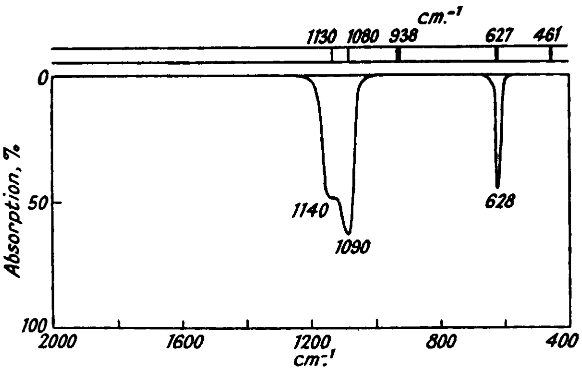
However, the arguments underlying these assignments are not all equally convincing.

On account of the outstanding intensity of the Raman frequency 935 cm.$^{-1}$, its assignment to vibration no. 1 may be considered well founded. For a time there was doubt about the origin of the band, 1050—1170 cm.$^{-1}$: it was not obvious why vibration no. 3 should produce a broad band. However, Millen accounted for this (*J.*, 1950, 2606), when he found the band replaced by two lines, of frequencies 1080 and 1130 cm.$^{-1}$, in the Raman spectra of crystalline perchlorates. As he noted, this is the simplest result which could arise from near-degeneracy between a degenerate fundamental F_2 at about 1120 cm.$^{-1}$ and the highly degenerate combination $E + F_2$ at $630 + 460 = 1090$ cm.$^{-1}$; for in the symmetric force-field of a crystal, the resulting resonance could yield only two degenerate Raman-active energy levels, while in the instantaneously dissymmetric and fluctuating field of a solution, the degeneracies of these levels would become split, and the split levels broadened, to give six, individually diffuse, Raman-active levels, that is, a band. This is such a consistent interpretation, that the correlation of the band, or of the doublet, with vibration no. 3 seems well confirmed.

It could be considered almost certain, simply on grounds of intensity, that the Raman frequencies 460 and 630 cm.$^{-1}$ belong collectively to the bending vibrations, nos. 2 and 4. This conclusion receives some confirmation from their joint involvement in the above explanation concerning vibration no. 3. However, the reason given by Redlich, Holt, and Biegeleisen for distributing these two frequencies as they did between the two vibrations was not convincing. Herzberg arranged them, though apparently arbitrarily, in the opposite way (" Infra-red and Raman Spectra," van Nostrand, New York, 1945, p. 167). Millen pointed out that the question was open.

Of the four vibrations of the perchlorate ion, only two, namely, the F_2 vibrations, nos. 3 and 4, are allowed in the infra-red spectrum. Therefore this spectrum should furnish a clear distinction between the bending frequencies : vibration no. 4 should record its frequency, while no. 2 should not. If the assignment of frequencies to vibration no. 3 is thought to want further support, then the reappearance of these frequencies in the infra-red would supply the needed confirmation. If any doubt remained as to the assignments of the strongest Raman frequency to vibration no. 1, support for the assignment would follow from the non-appearance of this frequency in the infra-red.

The infra-red spectrum of crystalline potassium perchlorate is shown in the Figure.



Below : *Infra-red spectrum of crystalline potassium perchlorate.*
Above : *Diagram of Raman frequencies for comparison.*

There is a strong single band at 628 cm.$^{-1}$, and also a strong double band with a peak at 1090 cm.$^{-1}$ and a nearly resolved second component at 1140 cm.$^{-1}$. No other band was found over the range 450—2000 cm.$^{-1}$, though a very weak band was observed at about 2050 cm.$^{-1}$. The strong single band, shifted however to 620 cm.$^{-1}$, and the strong double band, have been found again in the infra-red spectrum of crystalline nitronium perchlorate, which will be described in detail later.

These results make it certain that the frequencies of the two bending vibrations of the perchlorate ion have been wrongly assigned in the past, and must be interchanged. The new data confirm previous assignments to the two stretching vibrations. The revised assignments are summarised below (frequencies in cm.$^{-1}$) :

	(1) A_1	(2) E	(3) F_2 *	(4) F_2
Raman (soln.)	935	460	1050—1170	630
,, (cryst.)	938	461	1080, 1130	627
Infra-red (cryst.)	— †	— †	1090, 1140	624

* Resonance with (2) + (4). † Forbidden

The weak infra-red band at about 2050 cm.$^{-1}$ can be understood as the allowed combination (1) + (3).

EXPERIMENTAL

A paste of potassium perchlorate in " Nujol " was spread in a thin layer on a plate of sodium chloride or potassium bromide. A comparison plate was prepared in which the scattering effect of the solid perchlorate in the relevant spectral region was approximately imitated by previous grinding of the plate surface.

A Hilger D 209 spectrometer was used, with fluorite, rock salt, and potassium bromide prisms. However, in these experiments the automatic recording arrangements were not employed. Instead, the experimental and comparison plates were mounted side by side, so that either could be inserted in the optical path, and a point-by-point determination of the bands was made by interchanging the plates, and noting the deflections of the secondary galvanometer.

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