

Low and High Raman Frequencies for Water

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which originate from the same absorption line of the free ion, some are polarized strongly in one direction and some strongly in another.

We reproduce in Fig. 1 some typical absorption photographs which show the polarization. The crystals are monoclinic, and the upper and the lower halves in each photograph correspond to light vibrating respectively along the two extinction lines in the particular crystal plane selected for study.

The strong polarization, and the variation in its direction, observed among the members of a Stark group, show that the electric fields which produce the Stark splitting should be strongly asymmetric. Since there are 8 rare earth ions in the unit cell of the crystal, and the principal axes of the electric fields acting on these 8 ions may not be all parallel, the noncubic parts of the fields may be even much larger than the observed polarizations would suggest.

We are studying the polarization of the lines in some detail in the hope that the results may be helpful in the analysis of these complicated spectra.

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Indian Association for the Cultivation of Science,
210 Bowbazar Street,
Calcutta, India,
January, 24, 1938.

¹ Several papers in this journal, 1937.

² K. S. Krishnan and A. Mookherji, *Nature* **140**, 549 (1937), and paper in course of publication in *Phil. Trans. Roy. Soc. A*.

The Infra-Red Absorption Spectrum of Nickel, Carbonyl Vapor

We have examined the infra-red absorption spectrum of nickel carbonyl between 1 and 20 μ . The bands observed are shown in Table I, and compared with the Raman spectrum as observed by Duncan and Murray.¹

The figures in parentheses indicate two complex and extended regions of absorption near 7.5 and 10 μ ; the former appears to have six or seven peaks at intervals of approximately 20 cm⁻¹.

The question at once arises as to whether free CO was present. The fundamental band of this substance as determined with a fluorite prism² has its center at 2146, with *P* and *R* branches easily resolvable at a separation of some 46 cm⁻¹; the Raman line³ lies at 2155 10 cm⁻¹. A weak frequency in the Ni(CO)₄ infra-red spectrum shows as a side maximum at 2134 on the 2051 band. We found no trace of structure in the side band but cannot definitely say that it is not due to carbon monoxide. We propose to examine the effect of additions of small quantities of the gas on the spectrum in this region.

Evidence from electron diffraction measurements favors a tetrahedral model;⁴ in this case the numbers of frequencies and their spectral characteristics are:

*A*₁: Two; Raman active, polarized;
E: Two; doubly degenerate, Raman active, depolarized;
*F*₁: One; triply degenerate, inactive in both Raman and IR;
*F*₂: Four; triply degenerate, active in both Raman and IR, depolarized.

TABLE I. The Raman and infra-red spectrum of Ni(CO)₄.

Raman	Intensity Polarization Frequency	100 <i>P</i> 82	20 <i>P</i> 382	8 <i>D</i> 463	—	4 601	—
IR	Frequency Intensity	—	—	—	542 <i>m</i>	—	655, 669, 684 <i>w</i>
Raman	Intensity Polarization Frequency	0	—	—	2 833	2 872	2 913
IR	Frequency Intensity	—	757 <i>s</i>	787 <i>m</i>	826, 842 <i>m</i>	—	917 <i>m</i>
Raman	Intensity Polarization Frequency	—	—	—	—	0 1609	—
IR	Frequency Intensity	(983) <i>m</i>	(1340) <i>m</i>	—	1589 <i>m</i>	—	1677 <i>w</i>
Raman	Intensity Polarization Frequency	30 <i>P</i> 2043	—	5 2132	1 2223	—	—
IR	Frequency Intensity	2051 <i>v.s.</i>	—	2134 <i>w</i>	—	2326 <i>m</i>	2476 <i>s</i>

The coincidence of the high frequencies at 2043 and 2051 cm⁻¹ would make it necessary to attribute these to the out-of-phase CO motions in *F*₂; the in-phase motion might then be 2223 cm⁻¹ but this line should be powerful in the Raman effect and highly polarized. Further inspection of the data will show that other difficulties exist.

The plane square model was discussed by Bright Wilson⁵ who showed that there should be 7 active Raman lines and 6 infra-red with no coincidences. Although those observed lie in the shorter wave region of the spectrum where one might anticipate their chance occurrence in combination tones due to many fundamentals, on the whole the evidence seems to support the tetrahedral model.

An approximate estimate of the Ni-C and C-O bond force constants gives 2.35 and 17.35 × 10⁸ dynes/cm.

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ROY R. GORDON

The Sir William Ramsay and Ralph Forster Laboratories,
University College, London, England,
February 15, 1938.

¹ *J. Chem. Phys.* **2**, 636 (1934).

² E. von Bahr, *Verhand. Deutsch. Physikal. Gesell.* **15**, 710 (1913).

³ F. Rasetti, *Proc. Nat. Acad. Sci.* **15**, 234 (1929).

⁴ L. O. Brockway and P. C. Cross, *J. Chem. Phys.* **3**, 828 (1935).

⁵ *J. Chem. Phys.* **3**, 59 (1935).

Low and High Raman Frequencies for Water

I have read with some delay the remarks of I. Ramakrishna Rao and P. Koteswaran published by this journal¹ on "Low and High Raman Frequencies for Water." These authors state that of the Raman bands of water: 172, 510, 780, 1645, 2150, 3990 cm⁻¹, observed since 1933 by different workers using as exciting line the 2537A of the mercury arc, only the band 1645 cm⁻¹ is genuine.² The authors consider all other bands as excited by lines of the mercury arc excepting 2537A, with an average shift of 3400 cm⁻¹, corresponding nearly to the center of gravity of the well-known very intense group of frequencies 3200, 3435, 3620 cm⁻¹.

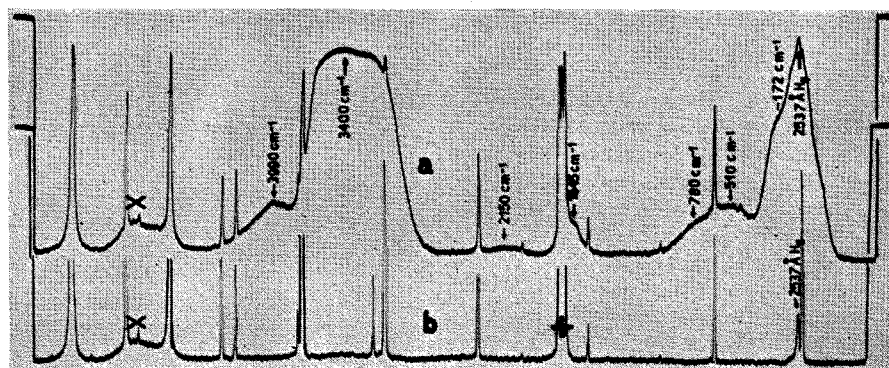


FIG. 1. The Raman bands of water (curve *a*) fall off (curve *b*) when the resonance line 2537 Å of the employed low pressure mercury arc is absorbed.

Without any doubt, this statement is to be attributed, as indicated by J. H. Hibben,³ to the great differences between the mercury lamps at low pressure, exclusively used by the former workers, and the ordinary lamps, apparently used by Rao and Koteswaran. In the first type of lamps the resonance line 2537 Å is remarkably sharp and particularly intense (a thousand times more than any neighboring line); in the other type of lamps the same line, instead, is greatly weakened by self-reversal, so that it does not at all assume a prominent position between the other lines.

For that reason, and because the lines accompanying the 2537 Å are too numerous, and some are diffused, the ordinary lamps are absolutely unallowable in Raman work in ultraviolet. With their use to study the Raman spectrum of water, one cannot do better than observe the very intense group of frequencies at 3400 cm^{-1} excited by the various lines, and so do Rao and Koteswaran. The weak frequencies 172, 510, 780, 1645, 2150, 3990 cm^{-1} indeed, either are not photographed or, if photographed, are masked by the numerous bands corresponding to the quoted intense group of frequencies.

Independently of these considerations, it is to be noted that in 1933, when I have observed the frequencies in question, I have carried out and published an experiment to decide definitely its assignment.⁴ In my experiment, a filter of mercury vapor at about 200°C was used in order to absorb, in the exciting spectrum of the low pressure mercury arc, the resonance line 2537 Å. I am giving in Fig. 1 two microphotometric curves of a plate made in 1933: *a* is the complete Raman spectrum of water obtained *without* the mercury filter, *b* is obtained *with* the mercury filter (3h, 30m and 3h exposures, respectively). I feel that no doubt will remain that the frequencies 172, 510, 780, 1645, 2150, 3990 cm^{-1} *really exist*: it is a fact that they fall off when the line 2537 Å is absent in the exciting spectrum.

The band indicated with a cross in both the curves has been considered by M. Magat⁵ corresponding to a frequency 5100 cm^{-1} , as excited by the line 2537 Å. It is evident that it should be considered as excited by the

group of lines at 2653 Å (indicated with plus sign in *b*), with the resulting displacement of about 3400 cm^{-1} .

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March 4, 1938.

¹ I. Ramakrishna Rao and P. Koteswaran, J. Chem. Phys. 5, 667 (1937).

² There are some discrepancies, generally not essential, between the values given by different authors. I am referring the values given by me in Nuovo Cimento 10, 101 (1933); in this paper I have also measured the low frequency 60 cm^{-1} , not afterwards observed by other authors. On this frequency and on the pointed discrepancies I will return elsewhere.

³ J. H. Hibben, J. Chem. Phys. 5, 994 (1937).

⁴ G. Bolla, Nuovo Cimento 10, 101 (1933), §3.

⁵ M. Magat, J. de phys. 5, 347 (1934).

Viscosity of Monomolecular Films

There have appeared in the numbers of *Nature* of September 11, 1937 and of the *Journal of Chemical Physics* of January, 1938, two editorial letters by Harkins and Myers, and Harkins and Kirkwood, respectively, concerning a surface viscosimeter. We wish to call attention to the previous results that we have obtained with a viscosimeter of the same type.¹

We have shown experimentally that the surface flow per second, Q , is in fact proportional to the difference of pressure and inversely proportional to the length of the canal, but we think it necessary to insist that there is no law analogous to Poiseuille's law concerning the width of the slit. The corresponding Poiseuille equation for a two-dimensional fluid should contain a factor d^3 (d =width of slit). The results of our systematic study with canals of different widths show clearly that the problem is much more complicated. There is no doubt that we have simultaneous entrainment of the water and that the viscosity of the substrate becomes the preponderant factor as soon as canal widths of the order of one centimeter are reached, i.e. the flows per unit time become independent of the nature of the fluid as the diameter increases, finally reaching the same value. The relation with d^3 would be valid only as a limiting law for very narrow canals, since, as the diameter decreases, we find *linear* variation until