Raman Spectra of Hydrogen Peroxide in Condensed Phases. I. The Spectra of the Pure Liquid and Its Aqueous Solutions*

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The Raman spectrum of liquid 99.5% H_2O_2 has been obtained at 30° and −40°C and compared with the spectrum of 90% D_2O_2 at −40°C. Three bands not previously reported were observed and their assignment, together with that of the remaining bands, is discussed.

Raman spectra were also obtained for aqueous solutions at 30° and −40°C over the complete concentration range. The interpretation is qualitatively in agreement with the results of other work which indicate that the addition of hydrogen peroxide to water results in more extensive hydrogen bonding and an increased degree of order in the solutions.

INTRODUCTION

HYDROGEN peroxide is a simple compound which is strongly hydrogen bonded in its condensed phases. Its vibrational spectrum under such conditions is therefore not only of interest in the study of the molecule but also in the comparative study of associated liquids. The infrared spectrum of the liquid has been reported fairly recently[1-3] but apparently the Raman spectrum has not been examined since the work of Simon and Feher[4,5] over fifteen years ago. These workers were primarily interested in locating the fundamental frequencies of the molecule and did not concern themselves with what may be termed intermolecular effects nor with the effect of temperature on the appearance of the spectrum.

In the case of water, which is the liquid most closely resembling hydrogen peroxide, the Raman spectrum exhibits several bands[6,7] which cannot be explained in terms of the fundamental frequencies of the molecule. These have been attributed to intermolecular motions in the quasi-crystalline lattice maintained in the liquid by the hydrogen bonds between the individual molecules. Observation of similar frequencies in hydrogen bonded liquids other than water is of interest since they afford direct evidence regarding the freedom of motion of the individual molecules. Such bands have not previously been reported in the case of hydrogen peroxide.

EXPERIMENTAL

Hydrogen peroxide containing approximately 10% by weight of water was kindly donated by the Buffalo Electrochemical Company. It was concentrated in the

manner described by Gross and Taylor[8] to give material containing 0.5% or less of water. Solutions were prepared by dilution of this material with special high-purity conductivity water. In all cases it was found essential to evaporate the sample *in vacuo* directly into the pretreated Raman cell just prior to an exposure. If this was not done, trace decomposition under the arcs invariably produced bubbles which reflected stray light into the spectrograph and reduced the quality of the spectrum. Deuterium peroxide was prepared by per-sulfate oxidation of heavy water in a closed system[9]; the most concentrated solution examined contained about 90% D_2O_2 and 10% D_2O.

Spectra of the pure peroxide were obtained with a Gaerntner two prism glass spectrograph with a $f/3.5$ camera lens while the solution spectra, which were obtained in the early stages of the investigation, were photographed with a medium Hilger spectrograph with glass optics and an aperture of about $f/10$. The dispersion of the first instrument is about 38 angstroms per mm in the blue region and that of the latter about 13 angstroms per mm. Type AH-11 mercury arcs were used in the light source and the incident light was heavily filtered with $NaNO_2$ and Rhodamine 5GDN Extra solutions so as to give as clean spectra as possible. Temperature control of the sample was achieved by placing the

TABLE I. Raman bands of liquid hydrogen and deuterium peroxides.

H₂O₂, liq. 30°C	H₂O₂, liq. −40°C	D₂O₂, liq. (90%) −40°C	Assignments	Polariz.
⋯	200±25 cm⁻¹	⋯		
⋯	525±25	⋯		
880±0.5	880±0.5	880±0.5	$\nu_3(a)$	pol.
1400±5	1402±5	1013±5	$\nu_2(a)$	pol.
⋯	2815±15	2038±10	$2\nu_2(A)$	⋯
3410±8	3364±8	2472±7	$\nu_1(a)$	pol.

* The initial stages of this work were carried out at Brown University under contract N6ori-88 with the Office of Naval Research.
[1] P. A. Giguere, J. Chem. Phys. **18**, 88 (1950).
[2] R. C. Taylor, J. Chem. Phys. **18**, 898 (1950).
[3] O. Bain and P. A. Giguere, Can. J. Chem. **33**, 527 (1955).
[4] A. Simon and F. Feher, Z. Elektrochem. **41**, 290 (1935).
[5] F. Feher, Ber. deut. chem. Ges. **72B**, 1778 (1939).
[6] J. H. Hibben, J. Chem. Phys. **5**, 166 (1937).
[7] Cross, Burnham, and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

[8] P. M. Gross, Jr. and R. C. Taylor, J. Am. Chem. Soc. **72**, 2075 (1950).
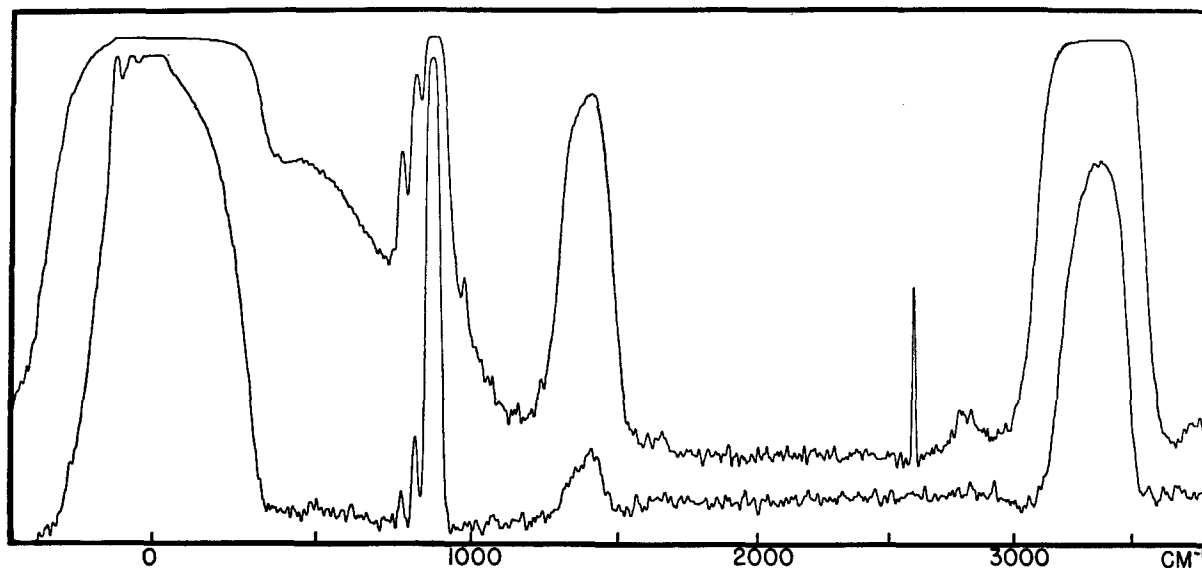[9] F. Feher, Ber. deut. chem. Ges. **72**, 1789 (1939).

FIG. 1. The Raman spectrum of liquid hydrogen peroxide at −40°C (short and long exposures).

Raman cell in a small Dewar flask with windows in the bottom and passing air of the desired temperature up around it. The temperature gradient along the cell was approximately 5–7 degrees.

EXPERIMENTAL RESULTS

The values measured for the band maxima in the spectra of pure H_2O_2 and 90% D_2O_2 are tabulated in Table I. Since all the bands except one were broad and rather diffuse, most of the measurements were made on microphotometer tracings. The uncertainties listed in the table consequently reflect primarily the difficulty in choosing the maxima. Microphotometer tracings of the Raman spectrum of 99.5% H_2O_2 at −40°C are shown in Fig. 1 for both long and short exposures.

In the case of peroxide-water mixtures, significant changes occurred in the shape of the O−H stretching band but otherwise, the spectra of the solutions are satisfactorily interpreted in terms of the spectra of the pure compounds. The systematic changes in the shape of the OH band as water is added to hydrogen peroxide are shown in Fig. 2. Table II lists the measured maxima of the bands arising from hydrogen motions in solutions at −40°C. The exposures in the case of the solutions

were not sufficiently long to allow reliable measurements to be made of the weaker bands observed in the pure peroxide spectrum. The O−O stretching band of hydrogen peroxide at 880 cm^{-1} was not shifted in any of the solutions.

DISCUSSION

The bands in the spectrum of pure hydrogen peroxide at 880, 1400, and 3410 cm^{-1} have been reported previously[4] as have also the corresponding bands of the deuterated compound.[5] On the basis of the C_2 model commonly accepted for this molecule, the six normal vibrations may be described as a symmetrical and unsymmetrical hydrogen bending motion, a symmetrical and unsymmetrical hydrogen stretching motion, an oxygen-oxygen stretching motion, and a torsional motion of the OH groups around the O−O axis. Feher[5] has suggested, and the evidence seems to support the fact, that because of the particular geometry of the molecule the two hydrogen bending motions, ν_2 and ν_6, have very nearly the same frequency, and likewise in the case of the two hydrogen stretching motions, ν_1 and ν_5. Although Simon and Feher originally reported[4] the 1400 cm^{-1} band split into a close doublet, this phenomenon was not found in their deuterium work[5] and also was not observed in the present investigation. Since the 1400 cm^{-1} band was observed to be fairly strongly polarized, it appears to be due largely to the symmetrical bending motion, ν_2. The microphotometer tracing shows a shoulder on the low-frequency side of this band at approximately the position due to the unsymmetrical bending motion which one would normally expect to be more intense in the infrared. In the Raman spectrum of the crystal, these two bands are clearly resolved and sharp.[10]

TABLE II. Raman bands arising from hydrogen motions in mixtures of water and hydrogen peroxide at −40°C.

Mol. ratio $H_2O_2:H_2O$	Bending motions H_2O_2	Bending motions H_2O	Stretching motions Shoulder	Stretching motions Main max
9:2	1411 cm^{-1}	⋯	⋯	3373 cm^{-1}
2:1	1422	1625	⋯	3377
1:1	1431	1630	⋯	3395
1:2	1465	1638	3260±20	3412
1:4ᵃ	1455	1640	3240±20	3417
1:9ᵇ	1445	1630	3345±20	3417

ᵃ −25°C.   ᵇ −8°C.

10 R. C. Taylor (unpublished work).

In a similar way, the high degree of polarization of the 3410 cm^{-1} band indicates that it must be ascribed chiefly to the symmetrical hydrogen stretching motion, ν_1. In this case the position of the infrared band coincides with that of the Raman band and no asymmetry is apparent, although the accidental degeneracy again is removed in the crystal and both bands are well resolved in the latter's Raman spectrum.[10] No ambiguity exists in the assignment of the 880 cm^{-1} band to the O—O stretching motion.

The remaining three bands at 200, 525, and 2815 cm^{-1} in the Raman spectrum of pure peroxide have not been previously reported. The infrared spectra of both the liquid and vapor show a band in the general region of 2700 cm^{-1} whose assignment has not been clearly established. Deuterium studies show that it is primarily a hydrogen motion and the simplest explanation of this infrared band is that it is a combination band of the two bending modes, ν_2 and ν_6, although there is some discrepancy in the calculated and observed positions. On the other hand, the Raman band in the liquid at 2815 cm^{-1} would appear more likely to be the overtone of ν_2, the symmetrical bending motion, with perhaps some contribution from $2\nu_6$ which belongs to the same class. In fact, the small discrepancy between the observed and calculated positions of this band may be due to a weak Fermi resonance between the two overtones acting to increase the frequency of $2\nu_2$. This band was observed excited by both the e and k lines of the mercury arc.

The bands observed at approximately 200 and 525 cm^{-1} in the Raman spectrum fall in the range normally associated with intermolecular frequencies of compounds with light atoms. The Raman spectrum of water, for example, contains two broad and diffuse bands centered roughly around 200 and 600 cm^{-1} which have been attributed respectively to hindered translational and rotational motions.[7] The least moment of inertia of the hydrogen peroxide molecule around an axis nearly coincident with the O—O axis is the same order of magnitude as the moments of inertia of the water molecule. Inasmuch as the intermolecular forces in the liquid must be very similar to those in liquid water, a band in the general region of 500 cm^{-1} might be predicted. Also, the two halves of the peroxide molecule may execute a torsional motion around the O—O axis, the frequency of which has been predicted theoretically to lie in this same region. Since this internal torsional motion would be very strongly coupled to any restricted rotational motion around the same axis, it seems probable that the scattering in the region between 400 and 700 cm^{-1} cannot be attributed solely to any simple type of vibration.

The low-frequency scattering lying between the exciting line and about 300 cm^{-1} is fairly intense and can be assigned either to restricted rotational motions involving the larger motions of inertia or to translatory oscillations, or both. The Raman spectrum of the crystal[10] shows at least seven well-defined lines in this
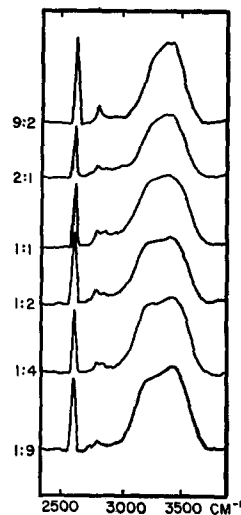

FIG. 2. The O—H stretching band in hydrogen peroxide—water solutions at −40°C for various values of the mole ratio $H_2O_2:H_2O$.

region, some of them approaching the 880 cm^{-1} line in intensity, which must involve both rotatory and translatory types of lattice vibrations. Apparently the hydrogen bonding present in liquid is sufficient to maintain some sort of a three-dimensional quasi-lattice network in which these vibrations can occur in strongly perturbed forms. Unfortunately, the D_2O_2 spectra were not of sufficient quality to allow the position of these rather diffuse bands to be distinguished with any certainty.

There are two points of interest in the spectra of the aqueous solutions, both consistent with the same general conclusion. As hydrogen peroxide is added to water, the shoulder on the low-frequency side of the O—H stretching band progressively increases in intensity until it becomes a distinct maximum in the concentration range of approximately twenty to forty mole percent hydrogen peroxide (Fig. 2); at a temperature of 30°C the shoulder increases in intensity but does not reach a maximum. A discussion of the origin of this second component of the OH band will not be given here. Instead it will merely be pointed out that its intensity has been shown empirically to correlate very well with the extent to which hydrogen bonding occurs in the liquid.[11]

Secondly, inspection of Table II shows that the positions of both the 1400 cm^{-1} band of H_2O_2 and the 1630 cm^{-1} band of water shift with concentration, the highest frequencies for both bands being observed in the same concentration range mentioned above. It is generally accepted that an increase in the amount of hydrogen bonding in a liquid shifts the position of hydrogen bending bands such as these to higher frequencies. The spectral data presented here thus are in good agreement with the results of freezing point measurements,[12] dielectric constant measurements[8] and thermodynamic

[11] See, for example, reference 6 and also: J. Burnham and P.A. Leighton, J. Am. Chem. Soc. **59**, 424 (1937); J. Chien, J. Am. Chem. Soc. **69**, 20 (1947), and others.

[12] W. T. Foley and P. A. Giguere, Can. J. Chem. **29**, 123 (1951).

data[13] all of which indicate that the addition of hydrogen peroxide to water in concentrations up to around 40 mole percent results in an increase in the number of hydrogen bonds and a greater degree of order in the solution.

[13] A. G. Mitchell and W. F. K. Wynne-Jones, Discussions Faraday Soc. No. 15, 161 (1953).

Note added in proof.—Simon and Kriegsmann, Naturwissenschaften 42, 12 (1955) have recently reported a band at 228 cm⁻¹ in the Raman spectrum of the liquid at 5°C.

Influence of Fermi Resonance on the Centrifugal Stretching Constant of a Linear Molecule*

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A theory of the influence of Fermi resonance on the centrifugal distortion constant of a linear molecule has been developed and its predictions for CO_2 compared with experiment. The theory of those bands which exhibit simultaneous Fermi resonance and l-type doubling is also discussed.

INTRODUCTION

A GENERAL quantum-mechanical study of the rotation-vibration energy levels of molecules has previously been given,[1] but as is well known, this theory is essentially a nondegenerate perturbation analysis which must be modified to cope with accidental degeneracies. One of the most interesting theoretically, and commonly encountered experimentally, of these degeneracies occurs when a molecule possesses a normal mode of vibration whose fundamental frequency is approximately equal to one half the frequency of one of the other normal modes. If, in addition to this condition, the eigenfunctions of two almost equal vibrational energy levels belong to the same symmetry species, the vibrational interaction known as Fermi resonance occurs. In the present paper we examine the effects of this interaction on the rotational energy levels of a linear molecule.

Let V_1, V_2, $\cdots$, V_s be the principal vibrational quantum number associated with the fundamental frequencies ω_1, ω_2, $\cdots$, ω_s of a linear molecule. We suppose that $\omega_1 \approx 2\omega_2$; that the corresponding wave functions are of the same symmetry species, and that ω_1 is nondegenerate whereas ω_2 may be either degenerate or nondegenerate. Under these conditions, the vibrational energy levels of the molecule fall into resonance polyads[1] whose components have approximately equal energies. The levels of a polyad are characterized by some fixed

value of $2V_1 + V_2$ and, if ω_2 is degenerate, a value of l_2, the quantum number of angular momentum associated with ω_2. In the presence of first-order anharmonic resonance interaction (Fermi resonance), the vibrational energies X_k of the members of a given polyad may be obtained as roots of the secular equation:

$$\begin{vmatrix} E_{V1}-X & W_{12} & 0 & \cdots \\ W_{21} & E_{V2}-X & W_{23} & \cdots \\ 0 & W_{32} & E_{V3}-X & \cdots \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \\ \cdot & \cdot & \cdot & \end{vmatrix} = 0 \qquad (1)$$

where E_{V1}, E_{V2}, $\cdots$ designate the unperturbed vibrational energies given by:

$$E_V/hc = \sum_s (V_s + g_s/2)\omega_s$$
$$+ \sum_{ss'} x_{ss'}\left(V_s + \frac{g_s}{2}\right)\left(V_{s'} + \frac{g_s'}{2}\right) + \sum_s x_{l_s l_s} l_s^2, \quad (2)$$

g_s being the degree of degeneracy of ω_s and where the $W_{i,i\pm1}$ are the matrix elements:

$$(V_1 V_2 | hc K_{122} q_1 q_2^2 | V_1 \mp 1, V_2 \pm 2)$$

in which K_{122} is the coefficient of a cubic term in the potential energy. If ω_2 is twofold degenerate, as will be true in our calculations, one finds[1]:

$$(V_1 V_2 | hc K_{122} q_1 q_2^2 | V_1 - 1, V_2 + 2)$$
$$= -\frac{hc K_{122}}{2}[(V_2+2)^2 - l_2^2]^{\frac{1}{2}}\left(\frac{V_1}{2}\right)^{\frac{1}{2}}.$$

[1] H. H. Nielsen, Phys. Rev. **68**, 181 (1945); Revs. Modern Phys. **23**, 90 (1951).