ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

THE STRUCTURE OF THE PERRHENATE ION

by

Howard H. Claassen and A. J. Zielen

CHEMISTRY DIVISION

September 8, 1953

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE STRUCTURE OF THE PERRHENATE ION

by

Howard H. Claassen* and A. J. Zielen

ABSTRACT

Raman and infrared spectra have been obtained for aqueous solutions of perrhenic acid and sodium perrhenate. The spectra are interpreted satisfactorily with the assumption that the perrhenate ion in dilute solutions has the tetrahedral symmetry, ReO_4^-.

INTRODUCTION

The Raman spectra of solutions of perrhenic acid and sodium perrhenate, and of crystalline sodium and potassium perrhenate, have been investigated by Fonteyne.[1] He observed only three Raman bands for dilute perrhenic acid and for solutions of sodium perrhenate and concluded that the anion in solution may be ReO_6^{5-} with an octahedral structure, rather than ReO_4^- with a tetrahedral structure as the ion exists in alkali perrhenate crystals.[2] After a study of the ultraviolet absorption spectra of perrhenate solutions, as well as some of the chemical properties, J. C. Hindman suggested that the Raman spectra should be reinvestigated.

MATERIALS AND EXPERIMENTAL PROCEDURE

Rhenium heptaoxide was obtained from the Department of Chemistry of the University of Tennessee. Spectrochemical analysis[3] of a sample of this material did not reveal the presence of any impurities. Stock solutions of perrhenic acid were prepared by dissolving the heptaoxide in doubly distilled water. Weight analyses of the $HReO_4$ content were carried out by titration with standard sodium hydroxide to the methyl red end point. Utilizing a Cary Recording Spectrophotometer, absorption spectra of diluted

---

*Department of Physics, Wheaton College, Wheaton, Illinois. Participating Institution Appointment.

[1] R. Fonteyne, Natuurw. Tijdschr. Belg. 20, 20 (1938).

[2] J. Beintema, Z. Krist. 97A, 300 (1937).

[3] Kindly performed by J. A. Goleb of this Laboratory.

aliquots of the perrhenic acid stock solutions were obtained. These did not indicate the presence of any lower oxidation states of rhenium and were in quantitative agreement with the results reported by Hindman and Wehner.[4]

The sodium perrhenate solution was prepared by adding a slight excess of perrhenic acid to CP grade sodium hydroxide pellets. The pH of the solution was then adjusted to 6 by the addition of dilute sodium hydroxide.

A Hilger E612 Raman Spectrograph, having two 63° glass prisms, camera aperture F/5.7, and inverse dispersion on the plate of 16Å per mm at 4358Å, was used. The Raman excitation unit was obtained from Applied Research Laboratories; it has been described by Kemp, Jones, and Durkee.[5] A 21 ml Raman tube was used. It was filled by forcing the solutions through fine fritted glass filters by means of compressed air.

Raman spectra were recorded on Kodak 103a-J and III-J plates. Sodium nitrite solutions were used as light filters. Frequencies were determined by linear interpolation between nearby lines on an adjacent iron arc spectrum. Measurements were made using a Gaertner Model M1205C comparator modified by the addition of the photoelectric setting device described by Tomkins and Fred.[6] A Leeds and Northrup photoelectric microphotometer was used to trace some of the spectra. Qualitative information about the state of polarization of Raman bands was obtained by taking two equal exposures with polaroid sheets around the Raman tube, one transmitting the electric vector perpendicular to and one parallel to the axis of the tube.

Infrared spectra were obtained by means of a Model 21 Perkin-Elmer Spectrophotometer with NaCl prism. Silver chloride windows 0.25 mm thick and coated with silver sulfide were used to contain the sample. A drop of solution was placed on one window, the other window was laid on, and they were held pressed together with thumb and finger and clamped between brass collars.

RESULTS AND DISCUSSION

Raman spectra were obtained for six different concentrations of perrhenic acid solutions and for one of sodium perrhenate. For all except the most concentrated acid only three Raman shifts were observed in

---

[4] J. C. Hindman and P. Wehner, J. Am. Chem. Soc. 75, 2869 (1953).

[5] Kemp, Jones, and Durkee, J. Opt. Soc. Am. 42, 811 (1952).

[6] F. S. Tomkins and M. Fred, J. Opt. Soc. Am. 41, 641 (1951).

addition to the diffuse scattering due to the water. The averages of the measured frequency shifts and the Kohlrausch designations of the exciting Hg lines for which each shift was observed are given in Table I. The relative intensities and widths of the bands may be estimated from Figure 1A, a photograph of a microphotometer trace showing the three shifts from 4358Å for the 70% perrhenic acid solution. The spectra for the more dilute solutions are essentially identical to this one. For the most concentrated solution, however, several new bands were observed. These are shown, and their frequencies listed, in Figure 1B. An additional weak band, whose assignment must be considered doubtful, was observed shifted 1612 cm^{-1} from 4358Å.

Table I

RAMAN FREQUENCIES AND THE EXCITING Hg LINES FOR WHICH EACH WAS OBSERVED, FOR VARIOUS PERRHENATE SOLUTIONS

$NaReO_4$, 25.4%	331 $\pm$ e,k	920 e,k,i	970.7 e,k,i
$HReO_4$, 6%	331 $\pm$ e,k	919 e,k	970.3 $\pm$ e,k,i
$HReO_4$, 10.0%	331 $\pm$ e,k	920 e,k	970.7 $\pm$ e,k,i
$HReO_4$, 28.5%	332 $\pm$ e,k,i	918 e,k,i	970.7 $\pm$ e,k,i
$HReO_4$, 70.0%	332 $\pm$ e,k,i	916 e,k,i	971.8 $\pm$ e,k,i,l
$HReO_4$, 80.1%	333 $\pm$ e	916 e	974.8 e,k

The great difference in exposure times for Figures 1A and 1B was necessary because of absorption in the 87.7% sample. This solution appeared yellowish green; the 80.1% solution appeared slightly yellowish, but all the more dilute solutions were colorless. Because of the absorption, the relative intensity of the 338 cm^{-1} band is probably considerably greater than indicated in Figure 1B.

Polarization exposures were made on a 10% $HReO_4$ solution. These showed the 971 cm^{-1} band to be polarized and indicated the other two to be depolarized. This is as one would expect by noting the high intensity and sharpness of the 971 cm^{-1} band.

The infrared spectrum was scanned from 700 to 1400 cm^{-1} for the sodium perrhenate solution and for three different concentrations of perrhenic acid. Only one absorption maximum due to the perrhenate ion was found in each case, a strong band at 914 cm^{-1}.

The data of Fonteyne[1] agree well with the present Raman data for dilute solutions, but some differences may be noted for the most concentrated solutions. Thus he lists a band at 1102 cm^{-1} which we did not observe, and we find bands at 886 and 989 cm^{-1} which he apparently did not resolve from

the neighboring stronger bands. More puzzling is the disagreement in regard
to the concentrations at which extra bands may be observed. Fonteyne lists
a band at 840 cm^{-1} for 30% HReO$_4$, whereas we found the corresponding band
only at 87.7% concentration. For example, in the case of the 70% solution,
exposures 30 times as great as the one shown in Figure 1A showed no evidence
of this band.

STRUCTURE CONSIDERATIONS

Fonteyne[1] has suggested that the perrhenate ion in dilute solution
may be octahedral rather than tetrahedral. The number of fundamental
vibrations of each symmetry species and the selection rules for their obser-
vation are listed in Table II both for XY$_4$ molecules of T$_d$ symmetry and XY$_6$
molecules of O$_h$ symmetry. Fonteyne[1] believed that only three Raman bands
could be ascribed to the ion, and that therefore the O$_h$ structure was most
plausible. When the absence of a fourth Raman band, except in very con-
centrated solutions, was verified in the present work, an infrared investiga-
tion was attempted. The Raman band at 971 cm^{-1}, since it is polarized,
sharp, and intense, must be due to a totally symmetric vibration, and would
be observable by absorption neither for the T$_d$ nor for the O$_h$ structures.
The band at about 918 cm^{-1}, on the other hand, must belong to species F$_2$
and be infrared active if the symmetry is T$_d$, but cannot be infrared active
if it is O$_h$, since for that symmetry no vibrational mode can be active in
both infrared and Raman spectra. Fortunately, water has no strong absorp-
tion bands in this region, and it was possible to observe an infrared band
at 914 cm^{-1} due to the perrhenate ion. This is so close to the observed
918 cm^{-1} Raman band that it is quite plausible they are both due to the same
vibrational mode.

The experimental data leave two choices: (1) The symmetry is T$_d$
and the reason one does not observe four R-bands is that the E and one of
the F$_2$ vibrations happen to lie so close together that one cannot resolve
them, or (2) The symmetry is O$_h$ and the close agreement between the one
Raman and the infrared band is accidental; they are actually due to vibra-
tional modes of different species. Either choice requires the assumption
of an accidental coincidence, the first perhaps more probable since the
observed Raman band at 331 cm^{-1} is quite broad, as shown in Figure 1.

Further light on this question may be obtained by calculation. Heath
and Linnett[7] have shown that for several types and many individual molecules
and anions it is possible to calculate frequencies to within one or two per cent,

---

[7] D. F. Heath and J. W. Linnett, Trans. Faraday Soc. 44, 873, 878, 884
(1948); 45, 264 (1949).

using an intramolecular force field between bonded atoms in accordance with
modern theories of directed valency plus an assumed Van der Waals type
of repulsion between non-bonded atoms. They have given equations both for
tetrahedral XY_4 and for octahedral XY_6 types of molecules. In either case
the vibration frequencies for one molecule are given in terms of three
potential constants. These equations have been used for the present problem.

Table II

SELECTION RULES FOR THE TWO MODELS CONSIDERED

Symmetry Species	Number of Vibrations	Selection Rules		Assignment
		Raman	Infrared	
T_d symmetry, ReO_4^-				
A_1	1	Allowed	Forbidden	971
E	1	Allowed	Forbidden	331
F_2	2	Allowed	Allowed	918, 331
O_h symmetry, ReO_6^{5-}				
A_{1g}	1	Allowed	Forbidden	(971)
E_g	1	Allowed	Forbidden	(918)
F_{2g}	1	Allowed	Forbidden	(331)
F_{2u}	2	Forbidden	Allowed	-
F_{1u}	1	Forbidden	Forbidden	-

First, assuming an O_h ion, ReO_6^{5-}, the three observed Raman bands
at 971, 918, and 331 cm^{-1} were assigned to species A_{1g}, E_g, and F_{2g}, respec-
tively, and three potential constants evaluated: $k_1 = 7.59$, $k_\beta = 0.337$ and
$A = 0.162 \times 10^5$ dynes/cm. Then the two frequencies of species F_{1u}, which
should be infrared active, were calculated. The result was 315 and 1000 cm^{-1}.

Second, assuming a T_d ion, ReO_4^-, the Raman bands at 971, 918, and
331 cm^{-1} were assigned to A_1, F_2, and E, respectively, and three potential
constants evaluated: $k_1 = 6.52$, $k_\alpha' = 0.400$, $A = 0.295 \times 10^5$ dynes/cm. The
other F_2 frequency could then be calculated. The result was 343 cm^{-1}.

These calculations seem definitely to favor the tetrahedral assumption. The fourth frequency calculated for this assumption is only 12 cm^{-1} from the observed peak at 331 cm^{-1}, so that it is very plausible that this observed Raman band at 331 cm^{-1} is a superposition of two bands too close to resolve, particularly in view of the width of the observed band. On the other hand, the octahedral assumption leads to a calculated value for the high infrared frequency of 1000 cm^{-1}, which is 86 cm^{-1} or 9% from the observed band at 914 cm^{-1}. This deviation between calculated and observed is much greater than Heath and Linnett[7] found in any of their examples.

On the basis of the spectroscopic evidence, then, it seems most likely that the perrhenate ion in dilute solution is tetrahedral. The source of the additional Raman bands and of the green color in concentrated solutions may well be the undissociated acid, $HORO_3$. The difference in Raman spectra of dilute and highly concentrated perchloric acid presents a very similar case.[8,9]

ACKNOWLEDGMENTS

[8]J. H. Hibben, The Raman Effect and its Chemical Applications (Rheinhold Publishing Corp., New York, 1939) p. 376.
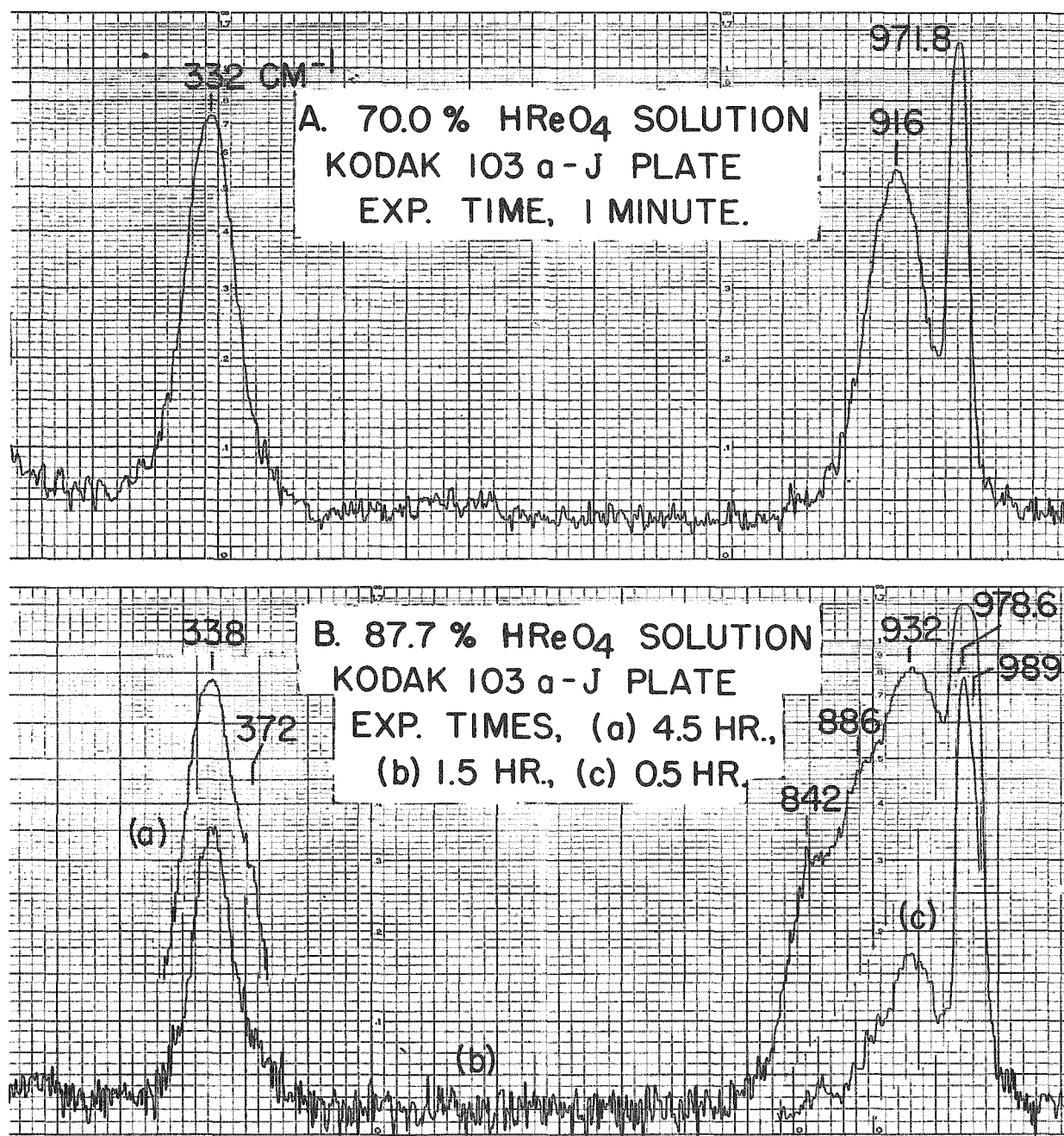
[9]Redlich, Holt, and Bigeleisen, J. Am. Chem. Soc. 66, 13 (1944).

FIGURE 1.

MICROPHOTOMETER TRACES OF RAMAN SPECTRA.