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Vibrational Spectra and Structures of Xenate(VI) and Perxenate(VIII) Ions in Aqueous Solution[1]

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Aqueous solutions 1.1 *M* in sodium xenate(VI) have been prepared, and their Raman spectra have been studied. The results indicate that $HXeO_4^-$ is the predominant anion present. The Raman and infrared spectra of aqueous solutions 1.8 *M* in cesium perxenate(VIII) have been investigated, and the Raman spectrum of solid sodium perxenate has also been examined. These spectra suggest a high concentration of symmetrical XeO_6^{4-} ions in the solutions, but certain details imply the presence of other ionic forms.

Introduction

The reaction of XeF_4 or XeF_6 with water or dilute acid yields aqueous Xe(VI).[2] The solutions are stable, and their Raman spectra indicate that the primary xenon species is molecular XeO_3.[3] Aqueous XeO_3 behaves as a weak, monobasic acid,[2] and alkali salts of "xenic acid" can be prepared.[4,5] The infrared spectra and X-ray powder patterns of these alkali xenates have been obtained but have not been interpreted in detail.[4,5] No structural data at all have been reported for the xenate anions in solution, and the extent of their hydration is not known. The predominant ion in solution may be $HXeO_4^-$ or $H_5XeO_6^-$ or possibly something else.

Alkaline Xe(VI) solutions may be oxidized to Xe(VIII), perxenate.[2] Solid, hydrated perxenates have been well characterized. Complete structures from X-ray diffraction data have been reported for $Na_4XeO_6 \cdot 6H_2O$,[6] $Na_4XeO_6 \cdot 8H_2O$,[7] and $K_4XeO_6 \cdot 9H_2O$.[8] In all of these the XeO_6^{4-} ion exists as a nearly symmetrical octahedron with Xe–O bond lengths of 1.84–1.86 Å and O–Xe–O angles between 87 and 93°. Infrared spectra of solid sodium, silver, lead, and uranyl perxenates were studied by Gruen.[9] He found in each case an intense absorption in the region 650–680 cm^{-1}, which he interpreted as the $\nu_3(f_{1u})$ fundamental of an octahedral XeO_6 group. Neither infrared nor Raman spectra have been reported for aqueous perxenates, but the ultraviolet absorption spectra of sodium perxenate solutions were studied by Appelman and Malm, who interpreted their results in terms of the anions $H_2XeO_6^{2-}$, predominant at pH 7–10, and $HXeO_6^{3-}$, predominant at higher pH.[2] This interpretation was supported by the results of potentiometric titrations.[2] As in the xenate case, however, the actual degree of hydration of the ions has been unknown.

The present investigation involved the use of Raman and infrared spectroscopy to study both the xenate and perxenate anions in solution. It was important for both techniques to use rather concentrated solutions; hence the fairly soluble sodium xenate and cesium perxenate were chosen. Inasmuch as the structures of solid perxenates were known, the Raman spectrum of solid sodium perxenate was also investigated.

Experimental Section

Materials.—An XeO_3 solution was prepared by hydrolysis of XeF_6, using methods described elsewhere.[2] It was concentrated by evaporation under vacuum at room temperature. The sodium xenate solutions were made by adding to this XeO_3 solution enough NaOH to neutralize the small amount of strong acid present[2] and then adding exactly 1 mol of NaOH per mole of XeO_3.

Sodium perxenate was prepared from XeO_3 by oxidation with ozone in alkaline solution.[2] A 0.02 *M* solution of the sodium perxenate was passed through a column of cation-exchange resin (Bio-Rad AG50X8, 50–100 mesh) in the cesium form. The resulting cesium perxenate solution was evaporated to dryness in a rotary evaporator under vacuum at room temperature. The solid was redissolved in the least possible quantity of water to give the concentrated cesium perxenate solutions used for the spectral measurements.

Spectral Measurements.—The Raman spectra of the sodium perxenate crystal powder and the cesium perxenate solution were obtained on a Cary 81 Raman spectrophotometer equipped with a Spectra-Physics 125 He–Ne laser. The solid was contained in a glass vial, while a Pyrex capillary of 0.8-mm i.d. and 1.0-mm o.d. was used for the solution.

The sodium xenate solution could not be studied in such a capillary because of bubble formation. This sample was examined with a Spex 1401 monochromator and Carson Ar^+ laser. A 5-mm i.d. sample container was used, and bubble formation was not a serious problem. Excitation was by the 4880-Å line of the laser, and the instrumentation included an ITT FW-130-S20 detector and a Victoreen 1001 dc amplifier. This apparatus could not be used for the perxenate solutions, which were decomposed by the Ar^+ laser beam.

Reference spectra of water were run both in the capillary cell and in the larger cell used for the xenate solutions. These established that the water and glass made no significant contribution to the spectra.

Because of the low intensity of most of the xenate and perxenate bands, no attempt was made to study the spectra as a function of concentration.

The infrared spectrum of the 1.8 *M* cesium perxenate solution

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

[3] H. H. Claassen and G. Knapp, *ibid.*, **86**, 2341 (1964).

[4] T. M. Spittler and B. Jaselskis, *ibid.*, **87**, 3357 (1965).

[5] B. Jaselskis, T. M. Spittler, and J. L. Huston, *ibid.*, **88**, 2149 (1966).

[6] A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 1417 (1964).

[7] J. A. Ibers, W. C. Hamilton, and D. R. MacKenzie, *ibid.*, **3**, 1412 (1964).

[8] A. Zalkin, J. D. Forrester, D. H. Templeton, S. M. Williamson, and C. W. Koch, *J. Am. Chem. Soc.*, **86**, 3569 (1964).

[9] D. M. Gruen, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 174.

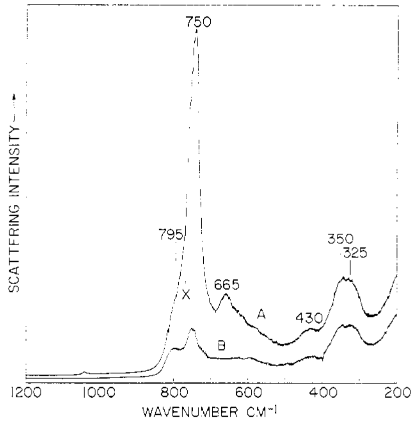

Figure 1.—Raman spectrum of 1.1 *M* sodium xenate(VI). The spike marked "X" was probably caused by a bubble in the solution.

was obtained with a Beckman IR-12 spectrophotometer. A small drop was pressed between two AgCl plates to give a very thin layer of unknown thickness.

Results and Discussion

Xenate Solution.—The Raman spectrum of a 1.1 *M* sodium xenate solution is shown in Figure 1. The direction of scattered light is at 90° to that of the incident light, and trace A is with the incident electric vector perpendicular to the plane containing the sample and the slit length, while trace B is with the electric vector parallel to that plane. In addition to the bands shown, there were broad bands around 1635 and 3425 cm^{-1}. The bands are listed and described in the first three columns of Table I. It may be noted that the shape of the broad peak around 325–350 cm^{-1} differs between traces A and B. This difference is reproducible and indicates the presence of a polarized band at about 350 cm^{-1} and a depolarized one at about 325 cm^{-1}, rather than a single broad band. There is general but not detailed agreement with the infrared frequencies of the solid alkali xenates.[4,5]

TABLE I

THE RAMAN SPECTRUM AND BAND ASSIGNMENTS OF $HXeO_4^-$, BASED ON C_{3v} SYMMETRY

Freq, cm^{-1}	Intens or description	Polarizn	Assignment
325	m	dp	ν_6, e fundamental
350	m	p	ν_3, a_1 fundamental
430	w	dp	ν_5, e fundamental
595	vb		?
665	m	p	ν_2, a_1 fundamental
750	vs	p	ν_1, a_1 fundamental
795	w	dp	ν_4, e fundamental
1042	vw	p	$\nu_2 + \nu_3$, a_1 combination
1635	b		O–H bend
3425	vb		O–H str

From the equilibrium data of Appelman and Malm,[2] we may calculate that a 1.1 *M* sodium xenate solution is about 0.03 *M* in OH^-, with some 97% of the Xe(VI) in the form of a singly charged anion.

Inasmuch as the Raman spectrum is reasonably simple, we will consider only the two likely ions, $HXeO_4^-$ and $H_5XeO_6^-$. Since the hydrogen atom motions will be above 1500 cm^{-1}, we may consider the OH^- groups as mass points for fundamental frequencies below 1000 cm^{-1}. The two possible xenate ions may be designated as $(OH)XeO_3^-$ and $OXe(OH)_5^-$, with tetrahedral and octahedral coordination to the xenon, respectively. The OH^- groups will be bound to xenon with a lower stretching force constant than will the oxygen atoms. The fact that the most intense Raman band at 750 cm^{-1} is close to the 780-cm^{-1} frequency of the most intense Raman band of aqueous XeO_3[3] certainly favors the tetrahedral model. For the octahedral model the frequency of the most intense Raman band would be controlled primarily by the Xe–OH force constant and would be expected to lie below 700 cm^{-1}. Further, the octahedral model would have eleven Raman-active fundamentals, compared to six for the tetrahedral model, and the observed spectrum seems more nearly to correspond to six. For these reasons we have based our assignments on the tetrahedral configuration with three equal bonds and a fourth with somewhat lower force constant. This model has C_{3v} symmetry, with three fundamentals belonging to species a_1 and three to species e. All six vibrations are expected to be active in both Raman and infrared spectra.

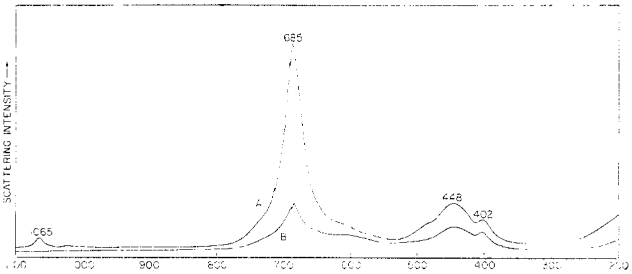

Figure 2.—Raman spectrum of 1.8 *M* cesium perxenate(VIII).

The three a_1 fundamentals, described roughly as a symmetric XeO_3 stretching, an Xe–OH stretching, and a symmetric XeO_3 bending, may be assigned immediately to 750, 665, and 350 cm^{-1}, respectively, because these are the only polarized bands in the proper regions. The three e fundamentals may be described roughly as an asymmetric XeO_3 stretching, an asymmetric XeO_3 bending, and an Xe–OH rocking. They are assigned to the depolarized bands at 795, 430, and 325 cm^{-1}, respectively. The band at 1042 cm^{-1} is definitely polarized and is very weak and sharp. Its assignment as $\nu_2 + \nu_3$ is not quite satisfactory, since the calculated sum is 1015 cm^{-1}. This may indicate a large anharmonicity, or else the band may be due to an impurity. The very broad band at 595 cm^{-1} does not fit the model and may belong to some other chemical species.

On the whole, the Raman spectrum provides impressive support for $HXeO_4^-$ as the primary anion in molar sodium xenate solutions.

The Perxenate Ion.—Figure 2 shows the Raman spectrum and Figure 3 the infrared spectrum of a 1.8 *M* cesium perxenate solution; Figure 4 shows the Raman spectrum of solid $Na_4XeO_6 \cdot 0.4H_2O$. These Raman

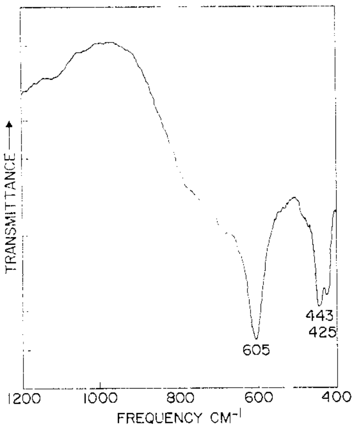

Figure 3.—Infrared spectrum of 1.8 *M* cesium perxenate(VIII).

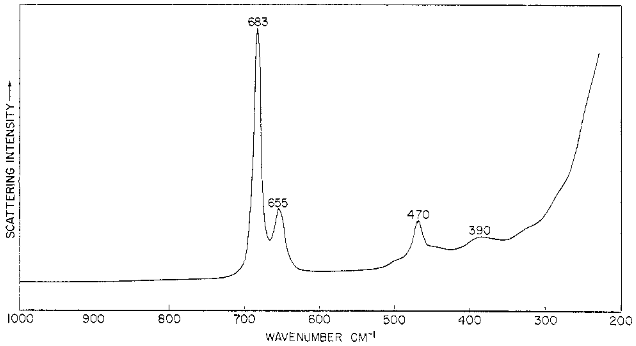

Figure 4.—Raman spectrum of solid $Na_4XeO_6 \cdot 0.4H_2O$.

spectra were obtained on the Cary 81 with a 180° scattering angle. In trace A of Figure 2 the electric vector of the exciting radiation is parallel to that of the Raman radiation, while in trace B the vectors are perpendicular. For a symmetrical XeO_6^{4-} octahedron there should be two Raman bands in the stretching region, ν_1 at higher frequency and completely polarized and ν_2 at lower frequency and depolarized; there should also be one Raman band, ν_5, in the bending region. There should be two infrared-active fundamentals, ν_3 in the stretching region and ν_4 in the bending region, and there should be no coincidences between the two spectra.

The Raman spectrum of the solid fits the predictions well except for one extra band at 390 cm^{-1}. This, however, may represent the sixth fundamental, which is forbidden for an isolated ion but may become active because of lower symmetry in the crystal.

The intense, highly polarized Raman band at 685 cm^{-1} in the solution spectrum is so close to the 683-cm^{-1} band of the solid that a symmetrically octahedral ion in the solution is strongly suggested. Several difficulties are obvious, however. The depolarized Raman band in the stretching region between 600 and 700 cm^{-1} seems very weak, if present at all, and there are two bands in the bending region in both the Raman and the infrared spectra. If one allows for complications due to hydrogen bonding and some degree of hydration, it is probably fair to say that the vibrational spectra suggest that the predominant anionic species in the perxenate solutions is a symmetrical XeO_6^{4-} ion but that other ionic forms may also be present.

Appelman and Malm[2] did not observe a 4− perxenate ion in the relatively dilute solutions with which they worked, and they concluded that sodium perxenate dissolved in water as a basic salt

$$Na_4XeO_6 + H_2O \longrightarrow 4Na^+ + OH^- + HXeO_6^{3-}$$

We might conclude by analogy that our 1.8 *M* cesium perxenate solution was 1.8 *M* each in OH^- and in $HXeO_6^{3-}$. However the equilibrium

$$HXeO_6^{3-} + OH^- \rightleftharpoons XeO_6^{4-} + H_2O$$

will be shifted to the right at high concentration, and in our solutions the XeO_6^{4-} ion may very well predominate.

Further light may be shed on this question by an examination of the changes that take place in the Raman spectrum of a perxenate solution as it is made less basic. We intend to carry out such an investigation as soon as we obtain a more intense red laser.