tropy and the cratic entropy.[14] The data are presented in Table IV.

Table IV

| | AgCl | | AgBr | | AgI | |
	H₂O (25°)	melt (172°)	H₂O (25°)	melt (172°)	H₂O (25°)	melt (172°)
	H_2O (25°)	melt (172°)	H_2O (25°)	melt (172°)	H_2O (25°)	melt (172°)
Entropy of crystal	23.0	28.9	25.6	31.2	27.1	33.0
Entropy of solution	52.5	43.8	67.6	51.7	88.8	62.9
Partial molal entropy	75.5	72.7	93.2	82.9	115.9	95.9
Cratic entropy	60.6	40.5	72.3	50.0	89.6	59.9
Difference in unitary entropy	...	...	6.0	0	11.4	4

The last item in Table III is the difference between the unitary entropy of AgCl and each of the other halides. As is evident from these data, there is in water a progressive increase in entropy associated with the halide ion and its co-sphere. This increase is of the form $Cl^- <$ $Br^- < I^-$. In molten Li–K nitrate eutectic, however, the difference between Cl^- and Br^- is essentially zero and between Cl^- and I^- only 4 e.u. This may be interpreted to mean that the three halides behave quite alike in the nitrate melt, whereas they exhibit great differences in an aqueous solution.

These results are not unexpected since water is a polar solvent and the molten nitrate is completely ionic. It is interesting, however, that the ion–ion interaction in the nitrate melt is essentially the same regardless of which halide is present. This may be associated, in part at least, with the low polarizability of the nitrate ion.

One may pursue this comparison still further by comparing the standard unitary entropies for each of the

(14) In the interest of space the details of the calculation are not given since they are extensively covered by Gurney, ref. 13.

solvents at the same temperatures. The values of ΔS^0 are presented in Table III. The values for H_2O at this temperature were calculated from extrapolated data as mentioned above. Standard cratic entropies were calculated according to the method of Gurney.[12] The values of 10 and 16 e.u. were obtained for the Li–K nitrate eutectic and water solutions, respectively, at 172°. The standard unitary entropies are presented in Table V.

Table V

STANDARD UNITARY ENTROPY OF SOLUTION, E.U.

Li–K nitrate eutectic (172°)			Aqueous solution (172°)		
AgCl	AgBr	AgI	AgCl	AgBr	AgI
−6	−8	−6	−10	−4	+3

It is interesting to note that the unitary part of the standard entropy increases with the size of the anion in aqueous solution but shows almost no variation in the molten nitrate solvent. The negative entropies in Table V signify an increase of order in the co-spheres; hence, in water, at this temperature, the chloride ion has the most ordered co-sphere. In the molten solvent, the differences between each of the anions is so small that one cannot say which anion exerts the greatest influence on the solvent molecules in its vicinity. These conclusions are in agreement with those discussed above.

It seems apparent, from this investigation, that when chloride, bromide, or iodide ions are present in very low concentrations in molten Li–K nitrate eutectic, each of these ions behaves in essentially the same fashion with respect to the solvating anions. That this is the case is very apparent when the molten solution is contrasted to analogous aqueous solutions. While not completely unexpected, it is still somewhat surprising in view of the large differences in size and polarizabilities among the three halide ions. These factors apparently are only important in their influence on the over-all solvation as evidenced by the variation in solubility.

The Vibrational Spectra and Structure of the Vanadyl Ion in Aqueous Solution

BY J. C. EVANS

It is concluded from a study of the Raman and infrared spectra of aqueous solutions of vanadyl salts that, in solutions of the chloride, fluoride, and perchlorate, the vanadyl ion has the structure $[OV(OH_2)_n]^{+2}$ where n is not determined. In vanadyl sulfate solutions, association between the vanadyl and sulfate ion occurs, the sulfate ions replacing one or more of the water molecules in the vanadium coördination sphere.

Introduction

Early oxidation–reduction potential studies of the V^{+4}–V^{+5} system were interpreted in terms of the structures VO^{+2} for the vanadyl ion and VO_2^+ for the pervanadyl ion.[1] Later, Rossotti and Rossotti[2] concluded

from spectrophotometric (electronic spectra) and from potentiometric measurements on vanadyl perchlorate solutions that the predominant ionic species is either

(1) A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1532 (1940).
(2) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, 9, 1177 (1955).

VO^{+2} or $V(OH)_2^{+2}$, a definite conclusion not being possible. Very recently, Ballhausen and Gray[3] have considered the accumulated data—electronic spectral data, magnetic data including paramagnetic resonance g factors and susceptibility measurements on several vanadyl complexes, the structural data as determined by the X-ray method for several compounds including vanadyl sulfate pentahydrate—and have made molecular orbital calculations for the ion $VO(H_2O)_5^{+2}$. They conclude that this structure accounts satisfactorily for the properties of the vanadyl ion in aqueous solution.

Vibrational spectroscopic studies apparently have been confined to the solid phase infrared spectra of several vanadyl complexes with organic ligands,[4-6] although vanadyl sulfate also was included.[5] This paper reports the results of a study of the Raman and infrared spectra of some vanadyl salts, the purpose being to examine the structure of the vanadyl ion in aqueous solution.

Experimental

All of the salts studied, vanadyl chloride $(VOCl_2)$, vanadyl fluoride (VOF_2), and vanadyl perchlorate $(VO(ClO_4)_2)$, were prepared from vanadyl sulfate, $VOSO_4 \cdot 2H_2O$ (Fisher Scientific Co., purified grade) and the appropriate barium salt. Solutions were maintained slightly acidic to prevent hydrolysis, but the acid concentration was too low to be detected in the spectra.

Vanadyl salts are blue in aqueous solution so that excitation of Raman spectra by 4358 Å. radiation (mercury arc) was feasible, although the absorption made fairly lengthy exposures necessary and limited the concentration range which could be covered to between 0.5 and 2.5 M. Spectra were photographed using a Hilger two-prism instrument with f/5.7 camera and reciprocal dispersion of 16 Å./mm. at 4358 A.

Infrared spectra in the 3800–450 cm.$^{-1}$ range were recorded using a prism-grating instrument.[7] Solutions were examined as thin films between silver chloride plates. The intense absorption bands of H_2O and D_2O restrict the concentration range and the spectral range of study. However, concentrations between 2.8 and 0.5 M were examined between 2500 and 450 cm.$^{-1}$. The more concentrated solutions gave spectra with but little interference from solvent absorption and it is probable that only very weak solute absorption bands could have escaped detection. With the more dilute solutions the greater thickness of solution required prevented complete coverage of the spectral range; see Fig. 2 and 3.

Results and Discussion

It is convenient to consider first those salt solutions, the spectra of which show that little or no covalent-complex formation occurs between the anion and the vanadyl ion. The chloride and perchlorate appear to be essentially unassociated while the fluoride shows some indication of association; these conclusions are in agreement with those reached earlier on other evidence.[2,8,9] Tables I to IV summarize the spectro-
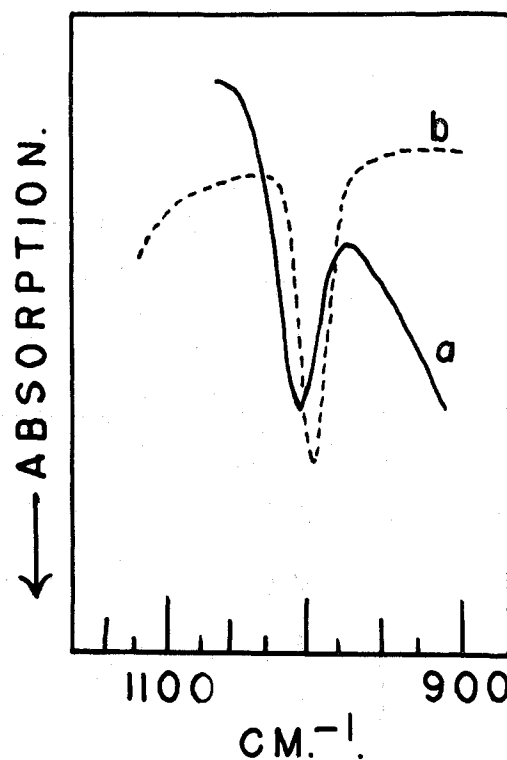
(3) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(4) K. Uneo and A. E. Martell, *J. Phys. Chem.*, **60**, 934 (1956).
(5) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).
(6) J. Selvin, L. H. Holmes, and S. P. McGlynn, *Chem. Ind.* (London), 746 (1961).
(7) L. W. Herscher, *Spectrochim. Acta*, **11**, 901 (1959).
(8) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).
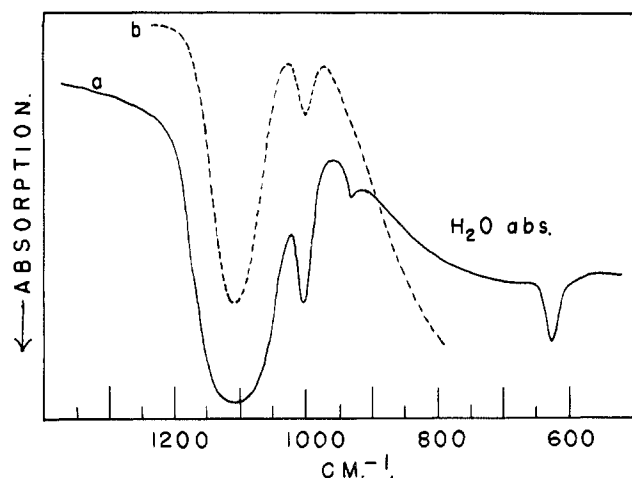(9) S. Ahrland and B. Noren, *Acta Chem. Scand.*, **12**, 1595 (1958).

Fig. 1.—The infrared absorption spectra of vanadyl chloride solutions as thin films between AgCl plates: a, in H_2O approximately 1.4 M; b, in D_2O solution.

TABLE I
THE RAMAN AND INFRARED SPECTRA OF VANADYL CHLORIDE SOLUTIONS[a,b]

——————H_2O solutions—————		————D_2O solutions————	
Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$
1001, s	1000, s	992, s	992, s
280, m,b	Not examined	275, m	Not examined

[a] s, strong; m, medium; b, broad. [b] The well known solvent bands are not quoted.

TABLE II
THE RAMAN AND INFRARED SPECTRA OF VANADYL FLUORIDE (H_2O SOLUTION)[a,b]

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Assignment
986, s	984, s	$\nu(V{=}O)$
280, m,b	Not examined	$\nu_{sym}(VO_5)$

[a] s, strong; m, medium; b, broad. [b] The well known solvent bands are not quoted.

scopic data while Fig. 1–3 illustrate some of the spectra.

Vanadyl chloride solutions show, in addition to the well known solvent bands, two bands—a fairly sharp band near 1000 cm.$^{-1}$ which appears strongly in the Raman and infrared and a weaker, broader Raman band near 280 cm.$^{-1}$. This low wave number region was not studied in the infrared. Both bands are sensitive to the change of solvent from H_2O to D_2O. Figure 1 shows the change near 1000 cm.$^{-1}$.

These data enable a choice to be made between the two alternative species proposed by Rossotti and Rossotti.[2] The ion $[HO{-}V{-}OH]^{+2}$ with the equivalent

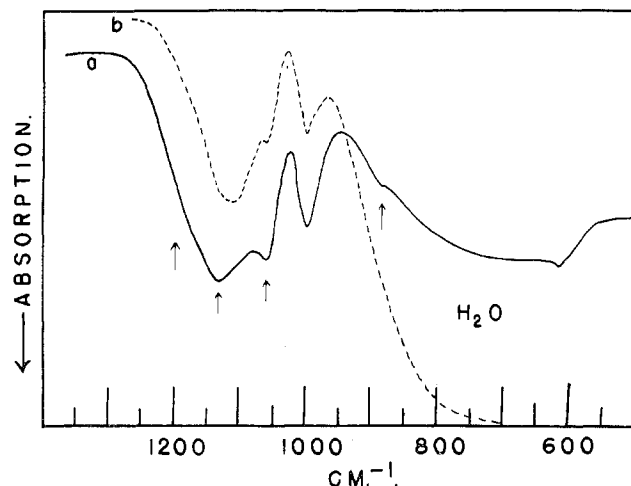Fig. 2.—The infrared absorption spectra of thin films of vanadyl perchlorate solutions in H_2O: a, 2.8 M; b, 0.5 M.

Fig. 3.—The infrared absorption spectra of thin films of vanadyl sulfate solutions in H_2O: a, 2.4 M; b, 0.5 M.

V–O bonds would yield two stretching modes of the O–V–O skeleton, the spectral activity of which would depend on the valence angle. If linear, this structure would possess a Raman-active, infrared-inactive symmetrical stretching mode and a Raman-inactive, infrared-active antisymmetrical stretching mode. A non-linear structure would have both stretching modes active in the Raman and in the infrared. In addition, a low-frequency skeletal bending mode and modes mainly confined to the OH groups should be observed, although the latter might well be obscured by the water bands. The observations, only one band in the entire valence-bond stretching-mode range, active in both Raman and infrared, show that the structure [HO–V–OH]$^{+2}$, whether it be linear or not, is very improbable. On the other hand, the diatomic ion, VO^{+2}, can give only one band which is Raman and infrared active.

Assuming the 1000 cm.$^{-1}$ band to arise from this mode yields a vanadium–oxygen bond force constant of 7.2 × 10^5 dynes/cm. Comparison of this with the corresponding force constant calculated[10] for the

(10) H. Siebert, *Z. anorg. allgem. Chem.*, **274**, 24 (1953).

TABLE III
THE RAMAN AND INFRARED SPECTRA OF VANADYL PERCHLORATE
(H_2O SOLUTION)^{a,b}

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Assignment
1110, m,b	1108, vs	ClO_4^-
1001, s	1000, m	$VO(OH_2)_5^{+2}$
934, vs	932, vw	ClO_4^-
627, m	628, m	ClO_4^-
460, m	. . .	ClO_4^-
277, w,b	Not examined	$VO(OH_2)_5^{+2}$

^{a} vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad. ^{b} The well known solvent bands are not quoted.

TABLE IV
THE RAMAN AND INFRARED SPECTRA OF VANADYL SULFATE
SOLUTIONS^a

Raman, cm.$^{-1}$	Infrared, cm.$^{-1}$	Infrared, cm.$^{-1}$	Assignment^c
	~1200, sh	Obscured	Complexed SO_4
	1130, s	1127, s	Complexed SO_4
	1115, s	1115, s	SO_4^{-2}
1060, m	1060, s	1060, s	Complexed SO_4
996, m	997, m	992 ⎫	Unresolved, $VO(OH_2)_5^{+2}$,
984, s	982, sh	976 ⎭	complex and SO_4^{-2}
	890, w	~890, w	Complexed SO_4
~604, b	~610	⎫	SO_4^{-2}
			and
440, b		⎬	complexed SO_4
282, m,b		⎪	$VO(OH_2)_5^{+2}$
		⎭	and complex

Column headers above span: the first two columns are "H_2O solutions^b" (Raman, cm.$^{-1}$ and Infrared, cm.$^{-1}$), the third column is "D_2O solutions^b" (Infrared, cm.$^{-1}$).

^{a} The well known solvent bands are not quoted. ^{b} The data were taken from the spectra of several solutions with concentrations ranging from 2.4–0.5 M. ^{c} "Complex" means here the postulated complex, $VO(H_2O)_4SO_4$; SO_4^{-2} denotes the uncomplexed sulfate ion.

VO_4^{-3} ion, 4.86 × 10^5 dynes/cm., shows that the vanadium–oxygen bond in VO^{+2} has considerable double-bond character.

We are, however, left with two other observations which require some modification of these conclusions; the band near 280 cm.$^{-1}$ and the sensitivity of this and the 1000 cm.$^{-1}$ band to the solvent change from H_2O to D_2O. These are adequately accounted for by the structure discussed by Ballhausen and Gray, VO-(OH$_2$)$_5^{+2}$. This was based on the structure determined for vanadyl sulfate pentahydrate by the X-ray method,[11] and is a tetragonal structural in which there are a VO group and five water molecules completing the vanadium coördination sphere. The vanadium–oxygen distances to the water molecules (approximately 2.3 Å.) are much longer than that in the VO group (1.67 Å.). Modes involving these long bonds should have low frequencies and the value of 280 cm.$^{-1}$ is reasonable for one of the bond-stretching modes. Presumably, since this is the strongest of these low-lying modes in the Raman spectrum, it is the totally symmetrical stretching mode of the long bonds in the ion. Justification for the assignment of these vanadium–oxygen bond-stretching modes in this region may

(11) M. B. Palma-Vittorelli, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo cimento*, **3**, 718 (1956).

be drawn from the application of Badger's rule,[12] which relates the force constant to the bond length for diatomic molecules. The bond length value of 1.67 Å. and the corresponding force constant of 7.2 × 10^5 dynes/cm. give a value for Badger's constant for the vanadium–oxygen pair, which, taken with a bond length of 2.4 Å., yields a force constant of approximately 0.7 × 10^5 dynes/cm. This is reasonably close to the value of approximately 0.6 × 10^5 dynes/cm. which emerges from a diatomic molecule calculation using the 280 cm.$^{-1}$ value. The remaining observation, the solvent sensitivity, is adequately accounted for by the mass change in the ion.

These vibrational data do not, of course, determine the number of water molecules in the ion but they do prove that the water is closely bound.

It should be noted here that vibrational spectra are not very sensitive to weak ion–ion association. Thus, for example, the vibrational spectra[13] of aqueous solutions of a series of sulfates which are known from conductivity measurements to be associated to widely differing degrees[14] are indistinguishable. It is then quite likely that the chloride and the solvated vanadyl ion may be loosely associated in vanadyl chloride solutions.

The spectra of vanadyl fluoride solutions are very

(12) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

(13) J. C. Evans, unpublished data.

(14) C. W. Davies, in "The Structure of Electrolytic Solutions," edited by W. J. Hamer, J. Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 3.

similar to those of the chloride. The higher frequency band is, however, broader in the fluoride and is shifted to lower wave number. This is indicative of considerably stronger ion–ion interaction between the vanadyl and the fluoride ions than is the case for the chloride ion.[9]

The infrared and Raman spectra of vanadyl perchlorate solutions are the same as the superposition of the spectra of the perchlorate ion and the solvated vanadyl ion; see Fig. 2 and Table III. Little or no ion–ion interaction is indicated.

Vanadyl sulfate solution spectra, however, show definite signs of complex formation between the sulfate and vanadyl ions. The spectra are concentration dependent with the more dilute solutions yielding spectra which indicate the dissociation of the complex to solvated vanadyl and sulfate ions; see Fig. 3. The structure of the complex cannot be determined unequivocally on the evidence available but the observations are in accord with the presumption that the sulfate ion displaces one of the water molecules from the vanadyl ion. Those bands indicated by arrows in Fig. 3 may be assigned to the sulfate ion bound in the complex and are reminiscent of the spectra of the HSO_4^- ion in aqueous solution, suggesting that the sulfate ion is bound at one point only. In solid $VOSO_4 \cdot 5H_2O$ this is the case.[11]

Monogermanes—Their Synthesis and Properties

BY JAMES E. GRIFFITHS

Germane and the methylgermanes CH_3GeH_3, CD_3GeH_3, $(CH_3)_2GeH_2$, $(CD_3)_2GeH_2$, and $(CH_3)_3GeH$ were conveniently prepared by the addition of an aqueous solution of sodium hydroborate to acidic solutions of GeO_2, CH_3GeBr_3, CD_3GeBr_3, $(CH_3)_2GeBr_2$, $(CD_3)_2GeBr_2$, and $(CH_3)_3GeBr$, respectively. At reaction temperatures of 30–55°, yields of 94–100% were obtained for the alkylgermanes and no side reactions were noticed. Physical properties of the CH_3 derivatives are reported. The yield of germane was virtually quantitative and temperature-independent in the 0–80° range.

Germane had been difficult to prepare until the reduction of GeO_2 with hydroborate was reported to give germane in 75% yield.[1] Other studies[2-4] under a variety of conditions failed to improve the yield and these failures were interpreted in terms of several effects. For example, a negative temperature coefficient of yield was attributed to nascent hydrogen reduction of Ge(IV) to the metal arising from the increas-

ing [H] concentration with increasing temperature. Since yields of over 90% were obtained recently at 35°, doubt was cast upon this speculation.[5]

A good method for the preparation of substituted germanes of the type R_nGeH_{4-n} ($n = 1$–3 and R = alkyl) seemed to be lacking,[6] although several methods appeared adequate.[7,8] These, however, required the use

(1) T. S. Piper and M. K. Wilson, *J. Inorg. Nucl. Chem.*, **4**, 22 (1957).

(2) E. D. Macklen, *J. Chem. Soc.*, 1989 (1959).

(3) W. L. Jolly, *J. Am. Chem. Soc.*, **83**, 335 (1961).

(4) J. E. Drake, "The Preparation of Some Germanium Hydrides," Report UCRL 9709 from the Lawrence Radiation Laboratory, University of California, Berkeley, Calif., Contract No. W-7405-eng-48, U. S. Atomic Energy Commission.

(5) T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, *Can. J. Chem.*, **40**, 739 (1962).

(6) F. Rijkens, "Organogermanium Compounds, A Survey of the Literature from Jan., 1950 to July, 1960," Institute for Organic Chemistry T.N.O., Utrecht, Holland.

(7) J. Satgé, R. Mathis-Noel, and N. Lesbre, *Compt. rend.*, **249**, 131 (1959).

(8) H. H. Anderson, *J. Am. Chem. Soc.*, **82**, 3016 (1960).