June, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *54*, *1693—1698 (1981)* 1693

The IR Spectra of $Cs_xV_2O_5$ ($x=0-0.66$)

Yoshiya KERA*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received February 23, 1980)

The IR spectra of Cs–vanadates ($C=[Cs]/[V]=0$—0.332) were recorded in the 650—1200 cm^{-1} region. In the V_2O_5, which had cautiously been purified, the V=O stretching band was found at 1022 cm^{-1}, and the V–O–V stretching band, at 815 cm^{-1}. Upon the addition of Cs, sharp new bands began to appear at 965 cm^{-1} at $C=0.0042$ and also at 1000 cm^{-1} at $C=0.0120$, and a shift in the 815-cm^{-1} band was found. Finally, at $C=0.332$ the original 1022-cm^{-1} band was replaced by the 965 and 1000 cm^{-1} bands, the intensity ratio (I_{965}/I_{1000}) of which was 2.0. The X-ray diffraction pattern of the last sample was in agreement with that of CsV_3O_8. The IR and the X-ray results suggest that the CsV_3O_8 phase appears at around $C=0.004$. Based on the band shifts of 1022→965 and 1000 cm^{-1}, the force constant and the bond strength of V=O in CsV_3O_8 were discussed. With respect to the band shift in the 815-cm^{-1} region with the increase in the Cs content, the corretion of $\Delta\tilde{\nu}$ to $C^{1/3}$ is shown in $C<0.020$.

V_2O_5 has a layer structure and has large channels along the b- and c-axes,[1-3] through which oxygen ions can be easily taken into and/or out of the lattice.[4] The property of the vanadium oxide as a catalyst has been discussed in relation to such a structural feature and behaviour of the oxygen ion.[4-8] V_2O_5 can also take many kinds of metal ion into the channels to form "vanadium bronzes;" the physico-chemical properties vary delicately and complicatedly depending upon the kind and the concentration of metal ions.[9] Recently, a big change was found in the catalytic properties of V_2O_5 when a commercial V_2O_5 (guaranteed grade) was cautiously purified.[10] This finding forces us to think that it is very important to control a small amount of impurities for a clear study of the catalytic activity and the catalytic property of vanadium oxide.

Now a series of studies of the effects of alkali metal-addition (Li–Cs) on the physico-chemical and the catalytic properties in V_2O_5 has been started. Upon the addition of Cs, the largest effects were found on the catalytic activity leading to ethanol decomposition and on the band shift in the V–O–V stretching in the IR spectrum.[11] These results could easily be expected because the Cs atom has the lowest ionization potential and the largest ionic radius of the alkali metals. However, the details of the structural change of V_2O_5 upon alkali-metal addition have not yet been made clear. In the present paper, the changes in the V=O and the V–O–V bonding properties in the original V_2O_5 lattice upon the addition of Cs are examined in especial detail. The IR spectra of the Cs–vanadates, the Cs content of which was controlled over a wide range, were measured for the purpose.

Experimental

The Cs–vanadates were prepared from Cs_2CO_3 (guaranteed grade) and NH_4VO_3 which had been purified cautiously[12] by the following procedures. The NH_4VO_3 was immersed into a aq. soln. of Cs_2CO_3, dried at 120° C, and calcined in air at 600 °C for 16—20 h. The Cs-contents of the samples are summarized in Table 1. The Cs-5 sample was prepared by grinding Cs-1 and Cs-7 well in an agate mortar, followed by heat treatment at 623 °C for 12 h and then by fusing at 700 °C for 6 h. The Cs-6 sample was prepared by grinding Cs-1 and Cs-7 well followed by heat treatment at 610 °C for 24 h; it was then fused at 623 °C for 12 h.

TABLE 1. CS-CONTENT OF CS-VANADATES

Sample	Cs-content([Cs]/[V])
Pure-V_2O_5	0.0000
Cs-1	0.0013
Cs-2	0.0042
Cs-3	0.0120
Cs-4	0.0203
Cs-5	0.100
Cs-6	0.168
Cs-7	0.332

The IR spectra of the Cs–vanadates were recorded in the frequency range from 650 to 1200 cm^{-1} by the normal KBr-disk method. The IR spectrometer used was JASCO, Model DS-402 G. The X-ray powder diffraction was checked on five samples: pure-V_2O_5 and Cs-4—Cs-7. The X-ray diffractmeter used was Rigaku Denki, Model 2001; Cu $K\alpha$-radiation (at 35 kV) and an Ni-filter were used.

Results

The IR spectra of the pure-V_2O_5 and the Cs–vanadates are shown in Fig. 1. In the spectrum of the pure-V_2O_5[8,13] a sharp band assigned to the V=O stretching vibration and a broad band assigned to V–O–V stretching are seen at 1022 and 815 cm^{-1} respectively (Fig. 1-a). The spectrum changes with the increase in the Cs–content ($C=[Cs]/[V]$): with $C=0.0042$ a new sharp band begins to appear at 965 cm^{-1} (Fig. 1-c) and with $C=0.0203$, one also appears at 1000 cm^{-1} (Fig. 1-e). In the samples with contents higher than $C=0.0203$, the bands at 965 and 1000 cm^{-1} were intensified with the Cs-content without any change in the frequencies. With $C=0.332$, finally, the original band at 1022 cm^{-1} disappeared and was completely replaced by the bands at 965 and 1000 cm^{-1} (Fig. 1-h).

On the other hand, the broad band at 815 cm^{-1} became broader and shifted toward the low frequencies from $C=0.0013$ to 0.0203 with the addition of Cs ions. In the samples with contents higher than $C=0.100$, the band split further into two peaks. With $C=0.332$,

---

* Present address: Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka 577.

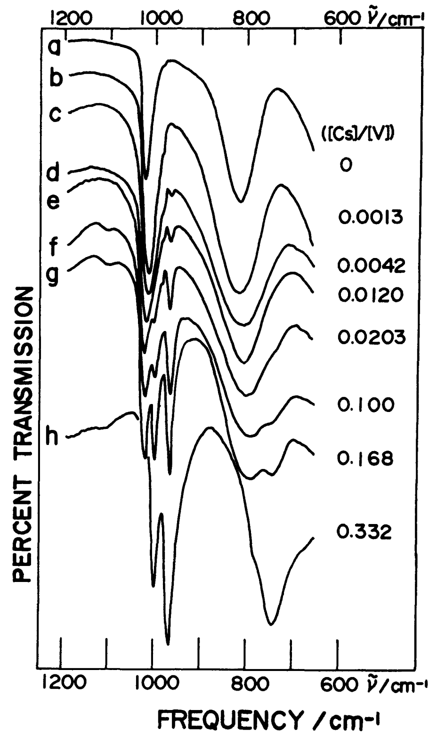

Fig. 1. IR spectra of $Cs_xV_2O_5$ (x=0—0.664), recorded in the frequency range of 1200—650 cm^{-1}. Spectrum a shows IR spectrum of the original V_2O_5, which was cautiously purified:[12] the bands at 1022 and 815 cm^{-1} have been assigned to the V=O and the V–O–V stretching, respectively.[8] The frequencies of the bands in the spectra b—h are summarized in Table 2.

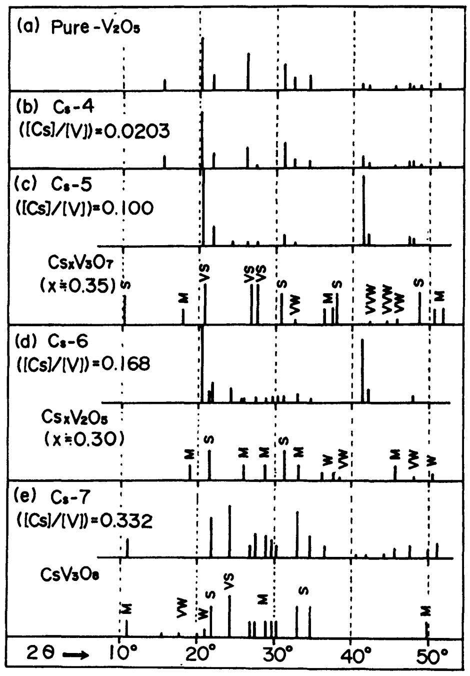

Fig. 2. The X-ray powder diffraction patterns of the pure-V_2O_5 and $Cs_xV_2O_5$ (x=0—0.664). For comparison the X-ray powder patterns of Cs–vanadates, already reported,[14–16] were added in Figs. 2-c, d, and e. In Cs-4 the patterns is almost agreement with that of the pure-V_2O_5 except for a little difference in the relative intensities. In Cs-7 the main lines of the pattern is agreement with that of Cs–hexavanadate. In Cs-5 and Cs-6 the very strong lines were seen at 20.4 and 41.2°, which have not been reported yet.

finally, the band at 815 cm^{-1} seems to be replaced by the bands at 742 and 780 cm^{-1}. The frequencies of all the bands in the spectra shown in Fig. 1 are summarized in the third column of Table 2.

The X-ray diffraction patterns of the pure-V_2O_5 and the Cs-4—Cs-7 samples are shown in Figs. 2-a—e. The pattern of Cs-4 (at C=0.0203) is almost the same as that of the pure-V_2O_5,[3] except for a very weak line appearing at 27.4° and a small change in the intensities between the corresponding peaks (Figs. 2-a and b). Strong lines appear at 20.3 and 41.3° in the diffraction patterns of Cs-5 and Cs-6. Both samples were prepared by mixing pure-V_2O_5 with Cs-7, followed by fusing and recrystallizing. Thus, the "preferred orientation" toward the (010) plane may be expected in the samples. The lines at 20.3 and 41.3° shifted just a little bit from those at 20.2 and 41.2°, which are ascribed to the diffraction from the (010) and the (020) planes respectively in pure-V_2O_5. These shifts might be caused by the formation of a non-stoichiometric phase of $Cs_xV_2O_5$ (x: too small).

In Cs-5, besides the lines at 20.3 and 41.3°, the very weak lines at 21.7, 26.2, 31.0, 32.4, and 47.3° correspond to the diffraction from pure-V_2O_5. The weak lines at

Table 2. The frequencies of the V=O and the V–O–V stretching bands in the IR-spectra of pure-V_2O_5 and Cs–vanadates, and the band shift ($\Delta\tilde{\nu}$) of the V–O–V stretching upon Cs-addition

Samples	Cs-content ([Cs]/[V])	Frequencies/cm^{-1} V=O stretching			Frequencies/cm^{-1} V–O–V stretching		$\Delta\tilde{\nu}$/cm^{-1}
Pure-V_2O_5	0	1022	—	—	815		0
Cs-1	0.0013	1017	—	—	818		−3
Cs-2	0.0042	1017	—	966	808		7
Cs-3	0.0120	1020	—	965	806		9
Cs-4	0.0203	1023	1000	965	797		18
Cs-4	0.0203	1021	1001	965	803		12
Cs-5	0.100	1022	1000	965	795	750	—
Cs-6	0.168	1020	999	965	790	743	—
Cs-7	0.332	—	1000	965	780	742	—

27.5 and 24.2° correspond well to the strong lines in Cs-7, which are ascribed to the diffractions from the (021) and the (210) planes in CsV_3O_8 respectively. However, no lines accord with the diffraction from $Cs_xV_3O_7$ (x: 0.35), given for comparison in Fig. 2. Thus, Cs-5 may be regarded as a composite phase of V_2O_5 and CsV_3O_8 or $Cs_xV_2O_5$ (x: too small) and CsV_3O_8. In Cs-6, the lines other than those at 20.3 and 41.3° which correspond to the diffraction from V_2O_5, appear at 21.7, 31.0, and 47.8°. The lines at 24.1, 27.4, 32.8, and 34.5° accord with the main lines of Cs-7. However, unknown lines appear at 25.5 and 25.8° in this samples, although they are very weak. No lines correspond to the diffraction from $Cs_xV_2O_5$ (x=0.3), given also for comparison in Fig. 2-d. This evidence suggests the formation of a new phase other than a mixed phase of V_2O_5 and CsV_3O_8 or $Cs_xV_2O_5$ (x: too small) and CsV_3O_8.

Finally, it is noteworthy that the diffraction at 27.5° was found in Cs-4 (at C=0.020), which is ascribed to the diffraction from the (021) plane in CsV_3O_8. This suggests that CsV_3O_8 phase can be already formed in such a low concentration as C=0.020 with Cs-addition to pure-V_2O_5.

The main lines of the diffraction in Cs-7 are completely in agreement with the pattern of CsV_3O_8, but none of the minor lines correspond to that of the Cs–vanadates reported hitherto. Thus, the Cs-7 sample consists of the Cs–trivanadate (CsV_3O_8), accompanied by a small quantity of an unknown compound.

Discussion

The V=O Stretching Bands. The peak intensities of the bands at 1022, 1000, and 965 cm^{-1} (I_{1022}, I_{1000}, and I_{965}) were estimated by drawing a base line smoothly under the bands in the spectra of Fig. 1. The intensities of the bands and the intensities normarized by the use of I_t ($I_{1022}+I_{1000}+I_{965}$) are summarized in Table 3.

Table 3. Intensity changes in the V=O stretching bands upon Cs-addition

Samples	C	I_{1022}	I_{1000}	I_{965}	$\frac{I_{1022}}{I_t}$	$\frac{I_{1000}}{I_t}$	$\frac{I_{965}}{I_t}$
Cs-2	0.0042	0.639	—	0.037	0.946	—	0.054
Cs-3	0.0120	0.397	—	0.042	0.904	—	0.096
Cs-4	0.0203	0.487	0.054	0.136	0.719	0.080	0.201
		0.549	0.059	0.103	0.772	0.083	0.145
Cs-5	0.100	0.492	0.124	0.301	0.536	0.135	0.328
Cs-6	0.168	0.677	0.405	0.672	0.386	0.231	0.383
Cs-7	0.332	0	0.514	1.095	0	0.319	0.681

The normalized intensities are plotted against the Cs-content in Fig. 3. The (I_{965}/I_t) and (I_{1000}/I_t) grow linearly with the Cs-content, but the ratio of I_{965} to I_{1000} remains constant at about 2 in the range of C=0.020—0.332. When the curves of (I_{965}/I_t) and (I_{1000}/I_t) *vs.* C are extrapolated to C=0, they cut the vertical axis while keeping the ratio constant at about 2. On the other hand, at contents lower than C=0.020, the curve of (I_{965}/I_t) *vs.* C cuts the point of origin. Figure 3 indicates that the fashion of the Cs-insertion in the range of C=0—0.012 differs from that in C=0.020—0.332.

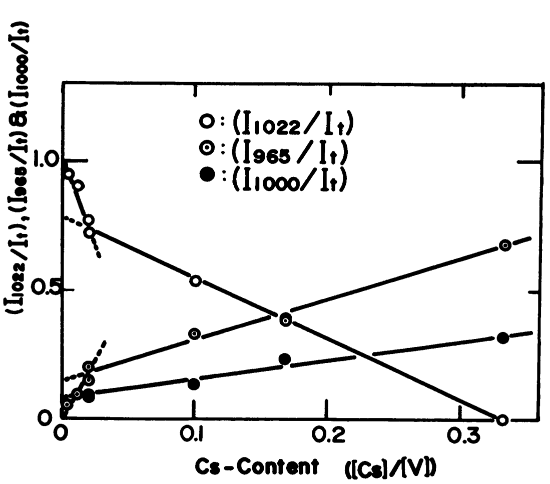

Fig. 3. The changes in the intensities of the original band at 1022 and the new bands at 1000 and 965 cm^{-1} with the increase in the Cs-content. In the Cs-content higher than C=0.020 the ratio of (I_{965}/I_t) to (I_{1000}/I_t) is kept constant at about 2.0.

According to the X-ray analysis described above, Cs-5 and Cs-6 were regarded as mixtures of V_2O_5 and CsV_3O_8, while the CsV_3O_8 phase seems to co-exist with the V_2O_5 phase in Cs-4. That is, the CsV_3O_8-content in the V_2O_5 increases with the Cs-addition in the range of C=0.020—0.332, until finally the unified CsV_3O_8 is formed at C=0.332. The X-ray results correspond completely to the IR results that the intensities of the bands at 1000 and 965 cm^{-1} increase linearly with the Cs-content without any changes in the frequencies. Therefore, the bands at 1000 and 965 cm^{-1} can be ascribed to the characteristic bands of CsV_3O_8.

The results of the X-ray analysis by Walterson *et al.*[14,15] showed that the Cs ion occupies one kind of site in $Cs_xV_3O_7$ ($x\simeq0.35$), but in $Cs_xV_2O_5$ ($x\simeq0.3$) it occupies two kinds of sites, the ratio of which is 2 : 1. Evans *et al.*[17] also showed, in CsV_3O_8, two kinds of Cs-occupation, the ratio of which was 2 : 1. The ratio of the Cs-occupation corresponds well to the intensity ratio of the bands at 965 and at 1000 cm^{-1} (I_{965}/I_{1000}) in the samples of Cs-4—Cs-7. Thus, the bands at 965 and 1000 cm^{-1} could be ascribed to the stretching bands of V=O groups, affected by the nearest-neighbored Cs ions, which are placed in two kinds of sites.

An application of the Bond-Strength-Bond-Length-Parameters of Brown an Shannon to the band shifts from 1022 to 1000 and to 965 cm^{-1} will now be tried. The bond strength, S, is defined as Eq. 1;

$$S = S_0(R/R_0)^{-N}. \tag{1}$$

The bond strength is evaluated as S=1.848 for the V=O bond in pure-V_2O_5 by the use of the values in Table 3 of Ref. 18 : S_0=1.25, R_0=1.700, and N=4.8. The V=O bond length, R, was regarded as 1.567 Å, which is the average of the values given by Ketelaar,[1] Byström,[2] and Bachmann.[3] The bond strength, S, is assumed to be proportional to the force constant, k. Thus, the IR-frequency, f, is proportional to $S^{1/2}$

because the $f=(k/\mu)^{1/2}$ relation, holds, where μ denotes a reduced mass. From the isotope shift of the V=O stretching band with the replacement of ^{16}O for ^{18}O, the reduced mass for the band has been regarded exactly as 16.[18] This means that the oxygen ion bonds to a large body with an infinite mass. For this reason, the V=O stretching mode is prevented from the interuption of the other modes, thus giving a very sharp band. The same situation could remain in the V=O groups of such Cs–vanadates as Cs-3—Cs-7 because the bands at 965 and 1000 cm^{-1} of the samples are also very sharp, as is the original band at 1022 cm^{-1}.

The changes in the bond strength and the subsequent changes in the V=O bond length with the Cs-addition, therefore, can be estimated exactly from the band shifts from 1022 to 1000 and 965 cm^{-1} based on the relation, $f\propto S^{1/2}$. For the shift from 1022 to 1000 cm^{-1},

$$(1000/1022) = \{S(1000)/1.848\}^{1/2},$$

where the 1.848 value is $S(1022)$, which was evaluated above for the V=O bond in pure-V_2O_5; thus, the bond strength corresponding to the band at 1000 cm^{-1}, $S(1000)$, became 1.769. For the shift from 1022 to 965 cm^{-1},

$$(965/1022) = \{S(965)/1.848\}^{1/2}.$$

Thus, the bond strength corresponding to the band at 965 cm^{-1}, $S(965)$, became 1.648. By substituting the values of $S(1000)$ and $S(965)$ into Eq. 1, the V=O bond lengths corresponding to the bands at 1000 and 965 cm^{-1}, $R(1000)$ and $R(965)$, were estimated as 1.581 and 1.605 Å respectively. These values are consistent with the V=O bond distances in the CsV_3O_8, 1.575 and 1.624 Å, as deduced from X-ray analysis by Evans *et al.*[17] This agreement confirms that, in CsV_3O_8, the V=O stretching band is subjected to shifts from 1022 to 1000 and 965 cm^{-1} by the Cs ions in two different sites.

Recently, Blasse[19] found a linear correlation between the Ti–O symmetric stretching frequencies in titanates of several metals and the bond strength, P, as estimated by Pauling's Electrostatic Valence Rule. The linear correlation means that the bond strength, P, is proportional to the square root of the force constant, because the $P\propto f=(k/\mu)^{1/2}$ relation holds. Under the assumption of $f\propto S$ according to Blasse, the bond lengths of the V=O are estimated as 1.574 and 1.586 Å by a procedure similar to that described above. The values are less consistent with those in CsV_3O_8 than those estimated above under the assumption of $f\propto S^{1/2}$. From a physical analogy, the bond strength seems to correspond directly to the force constant itself rather than the square root of the force constant. In Fig. 1 in Ref. 19 by Blasse, the plots of $P^{1/2}$ against f seem, in fact, to give a better linearity than that of P against f.

The crystal structure of the Cs–vanadates (C= 0.100—0.50) has been determined by X-ray diffraction;[14–17,20,21] the V=O bond length has also been estimated. The bond length expands linearly with the Cs-content, as is indicated by the open circles in Fig. 4. The bond lengths estimated above at C=0.332 are shown by the closed circles. They are located near the linear line.

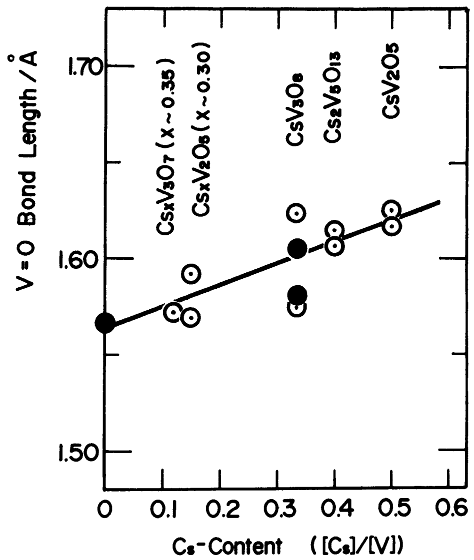

Fig. 4. The expansion of the V=O bond with the Cs-addition to V_2O_5. The open circles indicate the V=O bond lengths for the Cs–vanadates: $Cs_xV_3O_7 (x\approx 0.35)$,[14] $Cs_xV_2O_5 (x\approx 0.3)$,[16] CsV_3O_8,[17] $Cs_2V_5O_{13}$,[20] and CsV_2O_5,[21] which have been determined by the X-ray analysis. The closed circles at C=0.332 indicates the V=O bond lengths, estimated by the application of the Bond-Strength-Bond-Length parameters by Brown and Sahnnon to the band shifts from 1022 to 1000 and to 965 cm^{-1}. The closed circle at C=0 indicates the reference for the estimation of the V=O bond length mentioned above and the values (1.567 Å) is the average of the values determined by Ketelaar,[1] Byström *et al.*,[2] and Backmann *et al.*[3]

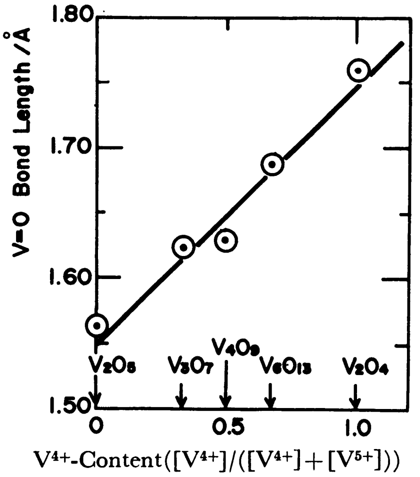

Fig. 5. The expansion of the V=O bond with the reduction of V_2O_5. In V_2O_5 the average of the values by Ketelaar,[1] Byström *et al.*,[2] and Backmann *et al.*,[3] and in V_2O_4 the value by Anderson[25] were given. In the intermediate phases, V_3O_7,[22] V_4O_9,[23] and V_6O_{13},[24] the V^{4+}-content was evaluated under the assumption that the V-ions take a mixed valency of V^{4+} and V^{5+}. In the phases there are two or three kinds of the V=O group and thus the averages of the V=O bond length were given.

Therefore, it is confirmed that Cs-ions occupy two kinds of sites, which are close to the V=O groups in the CsV_3O_8 crystalline lattice, and that the bond strengths of the V=O groups are weakened by the Cs ions inserted; thus, the stretching frequency decreases from 1022 to 1000 cm^{-1} and to 965 cm^{-1}.

With the reduction in V_2O_5, the VO_6 polyhedral unit changes in symmetry from a distorted trigonal bipyramid toward an octahedron.12) The V=O bond expands linearly with the reduction, as is shown in Fig. 5; the expansion in the V=O bond is accompanied by a decrease in the valence state of the vanadium ion and then by a change in the symmetry around the vanadium ion. In other words, the bond expansion is caused by the formation of the V^{4+} ion, that is, V^{4+}=O. The curve of the V=O bond length *vs.* the V^{4+}-content in Fig. 5 corresponds well to that of the V=O bond length *vs.* the Cs-content in Fig. 4. The complete transfer of electrons from alkali metals such as Li and Na to vanadium ions has, in fact, been observed in alkali–vanadates by NMR and ESR spectrometry.26) With Cs–vanadates, electron transfer could occur more favorably because Cs atom has the lowest ionization potential of all the alkali metals. Therefore, it can be concluded that the expansion in the V=O bond by the Cs-addition is caused not only by its steric effect, but also by the electron transfer from Cs to the vanadium ion to form the V^{4+}=O group.

The V–O–V Stretching Bands. With respect to the V–O–V stretching vibration in pure-V_2O_5, the original band itself was too broad. The band broadened further and also shifted toward the low frequencies upon the Cs-addition. The band shifts from 815 cm^{-1}, $\Delta\tilde{\nu}$, are summarized in the last column of Table 2. In the three samples of C=0.100—0.332, in which the band is split into two peaks, the band shift could not be estimated. The plot of $\Delta\tilde{\nu}$ *vs.* C is shown in Fig. 6-a. In the range of C=0—0.020, there is a good correlation between the band shift, $\Delta\tilde{\nu}$, and the cubic root of the Cs-content, $C^{1/3}$, as is shown in Fig. 6-b.

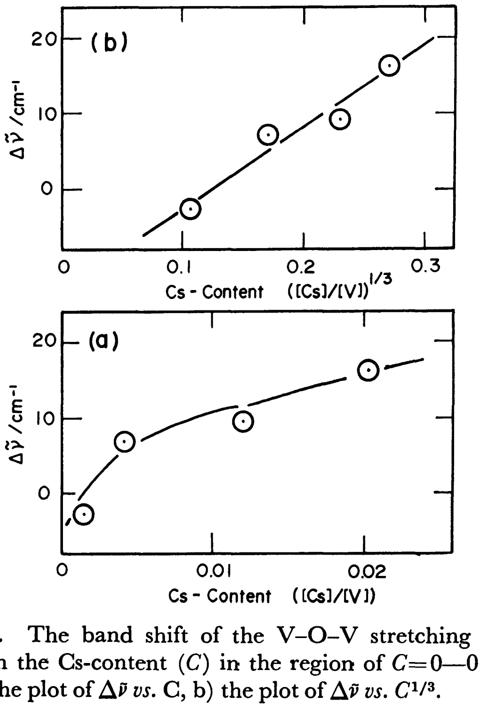

Fig. 6. The band shift of the V–O–V stretching ($\Delta\tilde{\nu}$) with the Cs-content (C) in the region of C=0—0.020; a) the plot of $\Delta\tilde{\nu}$ *vs.* C, b) the plot of $\Delta\tilde{\nu}$ *vs.* $C^{1/3}$.

In samples of Cs-4—Cs-6, the phases of V_2O_5 or $Cs_xV_2O_5$ and CsV_3O_8 co-exist, as was clearly shown above in the discussion of the V=O stretching band. In Cs-3 (C=0.012) the characteristic bands of CsV_3O_8 appear at 965 and 1000 cm^{-1}. In Cs-2 (C=0.0042), the 965 cm^{-1} band appeared, but the 1000 cm^{-1} band did not appear; it might have been masked under the steep part of the 1022 cm^{-1} band of pure-V_2O_5. If so, CsV_3O_8 would already be formed in such a low concentration as C=0.0042. In such a situation, the broadening and the shifts in the 815 cm^{-1} band might arise for the mixing of the 815 cm^{-1} by V_2O_5 with the 780 and the 742 cm^{-1} by CsV_3O_8 even though it is very weak. Furthermore, the intensities of the 780 and the 742 cm^{-1} bands grow relatively with the increase in the Cs-content; thus, the band shifts may be expected to become larger.

In fact, the region where the non-stoichiometric phase of $Cs_xV_2O_5$ (x=too small) can exist stably and the Cs-content, at which the CsV_3O_8 phase begins to appear, can not be exactly determined in the present paper. Therefore, even in the region of C=0—0.020, where the linear correlation of $\Delta\tilde{\nu}$ to $C^{1/3}$ holds as is shown in Fig. 6-b, the x in the $Cs_xV_2O_5$ could not be simply regarded as varying with the changes in the Cs-content. The physical meanings of the correlation can not be discussed further.

The author wishes to express his appreciation to Mr. Shinichi Ishikawa and Mr. Tetuo Yamamoto for their measurements of the IR spectra, and to Professor Keiji Kuwata for his continued interest in this work and for his valuable suggestions.

References

1) J. A. A. Ketelaar, *Z. Kristallogr.*, **95**, 9 (1936).

2) A. Byström, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, **4**, 1119 (1950).

3) H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr.*, **115**, 110 (1961).

4) E. Gillis, *C. R. Acad. Sci.*, **258**, 4765 (1964).

5) G. L. Simard, J. F. Steger, R. J. Arnott, and L. A. Siegel, *Ind. Eng. Chem.*, **47**, 1424 (1955).

6) E. R. S. Winter, *Adv. Catal.*, **10**, 196 (1958); G. K. Boreskov, *ibid.*, **15**, 285 (1964).

7) T. Toda, K. Kosuge, and S. Kachi, *Nippon Kagaku Zasshi*, **87**, 1311 (1966).

8) Y. Kera and K. Hirota, *J. Phys. Chem.*, **73**, 3973 (1969); Y. Kera, S. Teratani, and K. Hirota, *Bull. Chem. Soc. Jpn.*, **40**, 2458 (1967).

9) For instance, P. Hagenmuller, "Chem. Extend. Defects in Non-Metal. Solids," Amsterdam (1970), pp. 91—108; *Prog. Solid State Chem.*, **5**, 71 (1971); M. Nygren, *Chem. Commun. Univ. Stockholm*, No. 11 (1973); T. Horlin, *ibid.*, No. 6 (1977); K. Waltersson, *ibid.*, No. 7 (1976).

10) Y. Kera, *Bull. Chem. Soc. Jpn.* **52**, 888 (1979); **50**, 2841 (1977).

11) Y. Kera, unpublished.

12) Y. Kera and K. Kuwata, *Bull. Chem. Soc. Jpn.*, **52**, 1268 (1979).

13) L. D. Frederickson, Jr., and D. M. Hansen, *Anal. Chem.*, **35**, 818 (1963).

14) K. Waltersson and B. Forslund, *Acta Crystallogr., Sect.*

B, **33**, 775 (1977).

15) A. D. Kelmers, *J. Inorg. Nucl. Chem.*, **21**, 45 (1961).

16) K. Waltersson and B. Forslund, *Acta Crystallogr.*, *Sect. B*, **33**, 780 (1977).

17) H. T. Evans, Jr., and S. Block, *Inorg. Chem.*, **5**, 1808 (1966).

18) I. D. Brown and R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, **29**, 266 (1973).

19) G. Blasse, *J. Solid State Chem.*, **20**, 217 (1977).

20) K. Walterson and B. Forslund, *Acta Crystallogr.*, *Sect. B*, **33**, 784, (1977).

21) K. Walterson and B. Forslund, *Acta Crystallogr.*, *Sect. B*, **33**, 789 (1977).

22) K. Waltersson, B. Forslund, and K. A. Wilhelmi, *Acta Crystallogr.*, *Sect. B*, **30**, 2644 (1974).

23) K. A. Wilhelmi and K. Waltersson, *Acta Chem. Scand.*, **24**, 3409 (1970).

24) K. A. Wilhelmi, K. Waltersson, and L. Kihlborg, *Acta Chem. Scand.*, **25**, 2675 (1971).

25) G. Andersson, *Acta Chem. Scand.*, **10**, 623 (1956).

26) For instance, J. Gendel, R. M. Cotts, and M. J. Sienko, *J. Chem. Phys.*, **37**, 220 (1962); R. N. Pletnev, V. K. Kapustkin, and V. L. Volkov, *Sov. Phys.-Solid State*, **15**, 1700 (1974).