# EXAMINATION OF MASS-RADIUS EFFECTS, HYDROGEN BONDING AND $\nu_b$ SPLITTING IN INFRARED SPECTRA OF Zr-Hf HOMOLOGS

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## ABSTRACT

Infrared absorption spectra of homologous hafnium and zirconium sulfate tetrahydrates refute the idea that vibrational frequencies of functional molecules in crystals are affected by the mass of the external cation. The frequency shift of the $SO_4^{2-}$ stretching modes is evidently caused by a slight change in ionic radius produced by cation substitution. The OH frequencies indicate hydrogen-bond formation. The shift of the O-H $\cdots$ O stretching mode frequency reflects a decrease in the H-bonded oxygen-oxygen distance, thus evidently conforming to the change in cation size. The apparent splitting of the O-H $\cdots$ O bending mode may be explained as arising from resolution of a degeneracy of the $\nu_2$ fundamental of an unsymmetrical linear O-H $\cdots$ O group. This interpretation requires abandonment of the conventional concept of proton-oxygen vibrations based on the bent $H_2O$ model. The data indicate that cation substitution in isomorphous mineral systems may be expected to affect the strength of the H bond, the relationship being generally one of increasing H-bond energy with decreasing cation size.

## INTRODUCTION

Early in the application of infrared absorption spectroscopy to minerals it was recognized that the environmental metallic ions surrounding a functional molecule influenced the constancy of characteristic group frequencies. The infrared spectra of structurally related minerals having a common functional ionic molecule although generally alike were without exception observed to differ slightly in absorption frequency. This difference has been related to changes in the ionic radius and mass of the substitutional extramolecular ions bonded to the vibrating ionic group through a mutual oxygen atom.

For some time mineralogists have used this concept of environmental interaction to explain the absorption-band shifts observed for isomorphous mineral species without ascertaining the degree of influence of each of the contributing factors. One obvious reason for this is the lack of a "mineral system" in which mass and radius characteristics may be independently manipulated. Such a system is, of course, restricted to only a few elements which because of lanthanide-type contractions have ionic radii that are nearly identical. This has the effect of making their chemical behavior extremely similar and simplifies the problem of establishing the existence or absence of a "secondary" mass dependency.

The main purpose of this study is to dispel some uncertainties regarding the role of mass of the environmental cations in altering the vibrational frequencies of anionic molecules in minerals. However, the mineral kingdom does not provide suitable species that can be applied to the problem.

The requirements of this study are best fulfilled by zirconium and hafnium which differ markedly in atomic weight, have nearly identical ionic radii but otherwise differ only so slightly in few other respects that the chemistry of these elements is generally accepted as being comparable. The zirconium sulfate tetrahydrate, $Zr(SO_4)_2 \cdot 4H_2O$, and its hafnium analogue were chosen for convenience.

This paper is also concerned with the characterization of the spectral region identified with stretching and bending motions of O-H $\cdots$ O groups in these homologous salts and with interpretation of the peculiar splitting of the bending mode.

## PREVIOUS STUDIES

An earlier study of the vibrational spectra of carbonate minerals by the writer (Adler, 1950) provided data indicating a relationship between the shifting frequency of the carbonate vibrations and compositional variation among the isostructural calcite-group and aragonite-group carbonates involving changes in the ionic radius and atomic weight of the substitutional cations bonded to the functional $CO_3^{2-}$ ion. From the strikingly anomalous spectral position of the normal modes of cerussite, $PbCO_3$, it was possible to conclude with some confidence that an environmental factor other than ionic radius must contribute to the localization of the absorption bands. It was natural to attribute this alteration to the relatively high atomic weight of lead inasmuch as the shift in frequency of the four normal modes conforms to the conventional effect of an increase in mass for functional molecules. Almost simultaneously, Hunt and his co-workers (1950) found that the absorption shift in the out-of-plane carbonate bending region (11 $\mu$) to longer wavelengths is nearly linear with increasing atomic weight.

Other studies of carbonates that followed, although furnishing no new corroborative data, also pointed to a possible association between the absorption frequency of the molecular group and the ionic radius and atomic mass of the attached cations. In evaluating the connection Keller and his associates (1952) concluded that although the carbonate spectra appeared to be affected by the cation, the effect is neither regular nor simple. Huang and Kerr (1960) concluded that while calcite- and dolomite-group minerals manifest an ionic-radius dependency, the spectral shift for the aragonite group follows a sequence of increasing atomic weight.

The anhydrous normal carbonate systems were reinvestigated by Weir and Lippincott (1961) along with vaterite and structurally analogous rare-earth borates and nitrates. The irregularities in frequency variation for the carbonates were attributed by them to a change in ionic char-

acter of the cation-oxygen bond, with increasing covalency possibly enhancing the role of cation mass in altering the internal vibrations of the functional group. On the other hand, congeneric frequencies of the borates were found to increase with decreasing cation radius but show no evident response to the simultaneously increasing mass of the cation. The idea of a conventional mass effect was rejected on this basis. The evidence furnished is, however, not as conclusive as one might hope for. For the rare-earth vaterite compounds, the ionic radius decreases by about 15 per cent, with a comparable per cent increase in mass, as the cation is changed from $Sm^{3+}$ (1.00 Å, 150) to $Lu^{3+}$ (.85 Å, 175). A little reflection will show that since the frequency of a vibrational mode conventionally decreases with increasing mass and increases with decreasing ionic radius, the mass effect may simply attenuate the radius effect and might, therefore, not be readily discernible in the spectra of rare-earth compounds. Unfortunately, the data for $YBO_3$ (.92 Å, at. wt. = 89) and $DyBO_3$ (.92 Å, at. wt. = 162) also do not convincingly demonstrate the absence of a mass effect inasmuch as absorption spectra of these compounds do not conform in many respects. The only valid conclusion that can be drawn from this study is that the radius of the extramolecular cation exerts a much more pronounced influence than atomic mass on the vibration frequency of the functional ion. It leaves in doubt the question whether there is any genuine mass effect.

On re-examination of the anhydrous carbonates Adler and Kerr (1963a) found that the inconsistencies in absorption trends were not attributable entirely to either radius or mass effects. It was suggested that the anomalous position of absorption bands of the Mn, Fe and Zn carbonates might in some way be related to their electron structures which differ from those of the Group II elements comprising the calcite group, and that this might also account for the deviation of the $PbCO_3$ spectrum from those of other aragonite-type carbonates.

Olivine in different compositional conditions has also been studied. The frequency of absorption of the silicate ion in olivine was observed (Duke and Stephens, 1964) to vary systematically with the ratio of the substituting cation because of differences in ionic mass and radius. However, other factors such as electronegativity and polarizability appeared to be equally important.

It is evident that there is an appreciable difference in the opinions of individual researchers concerning the existence of a mass effect, which is in part due to the lack of rigorous control over the variables. The system selected for this study differs from others already examined in that it makes it more probable that any mass effect will be recognizable, *i.e.*, distinguishable from the radius effect.

MASS-RADIUS EFFECTS

The complex internal motions of the sulfate ion in the crystalline zirconium and hafnium sulfate tetrahydrates give rise within the rock-salt region of the infrared spectrum to absorption bands between 8 and 10 microns (Fig. 1). The spectra appear to contain no anomalies and except for minor differences in absorption frequency, to be discussed, are remarkably alike. The peaks at 3 $\mu$ and 6 $\mu$ correspond to normal vibrational modes of "lattice water" and differ sufficiently in frequency from hydroxyl modes to be attributable to hydrogen bonding. The frequencies of 1136 cm$^{-1}$ (8.80 $\mu$) and 1088 cm$^{-1}$ (9.19 $\mu$) for the zirconium salt correspond to the stretching mode $\nu_3$ of the $SO_4^{2-}$ ion (Fig. 1, Table 1). The frequency of 1031 cm$^{-1}$ (9.70 $\mu$) is assigned to the $\nu_1$ stretching mode. Corresponding modes for the hafnium salt give rise to absorption at 1136 cm$^{-1}$ (8.80 $\mu$) ($\nu_3$), 1099 cm$^{-1}$ (9.10 $\mu$) ($\nu_3$), and 1040 cm$^{-1}$ (9.62 $\mu$) ($\nu_1$).

The splitting of the fundamental stretching mode $\nu_3$ arises from partial resolution of its triply degenerate vibrations. The three vibrations of this mode normally have exactly the same frequency when the $SO_4^{2-}$ molecule is perfectly tetrahedral. However, they assume different frequencies if the molecular symmetry is lowered in conforming to the symmetry of the site. According to the relationships between molecular symmetry, site symmetry and vibrational activity of the sulfate ion
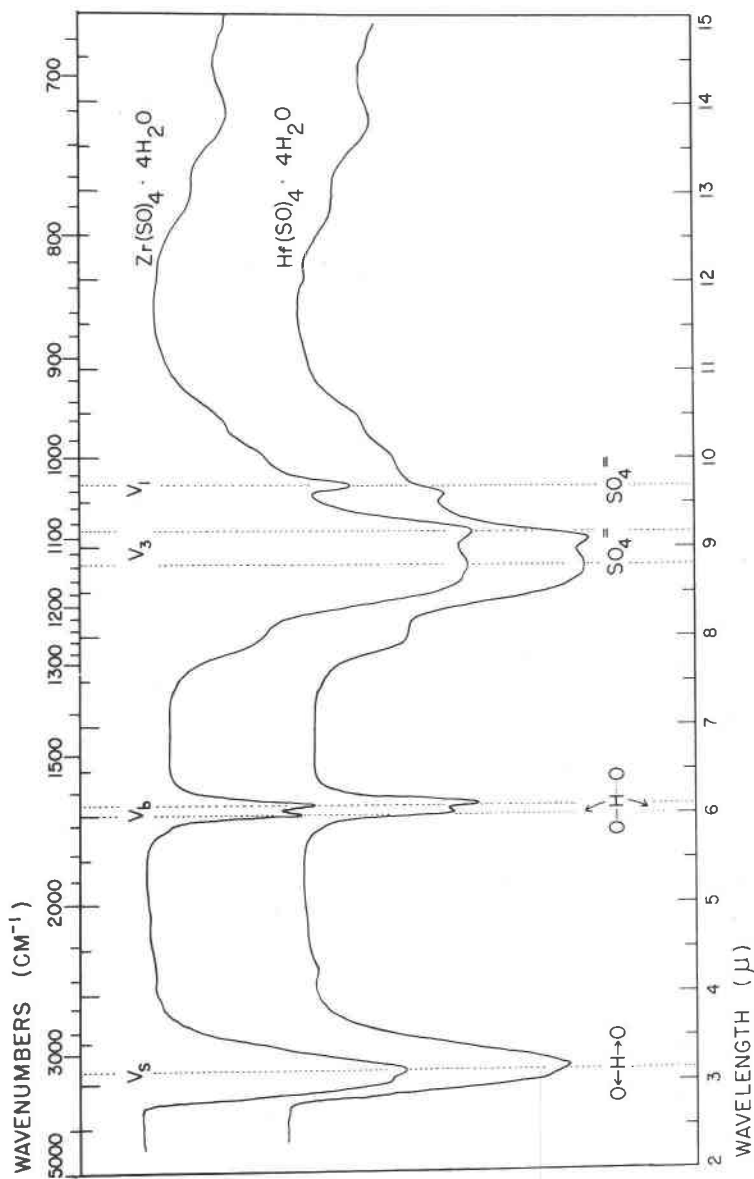
FIG. 1. Infrared spectra of isomorphous Hf and Zr sulfate tetrahydrates showing absorption bands corresponding to $SO_4^{2-}$ and $O-H \cdots O$ vibrational modes.

observed by Adler and Kerr (1965), the two $\nu_3$ bands and single $\nu_1$ band for $Zr(SO_4)_2 \cdot 4H_2O$ and $Hf(SO_4)_2 \cdot 4H_2O$ are indicative of $C_{3v}$ or lower symmetry of the sulfate ion. The $\nu_1$ mode is non-degenerate.

The small divergence in frequency of corresponding sulfate bands of the two salts is significant (Fig. 1). The slight shift to higher frequency observed for both $\nu_3$ and $\nu_1$ of $Hf(SO_4)_2 \cdot 4H_2O$ is readily explained by the smaller ionic radius of $Hf^{4+}$ (0.78 Å; Green, 1959) which is only about 1 per cent smaller than that of $Zr^{4+}$ (0.79 Å). This points up the extreme sensitivity of these vibrations to a very small change in ionic radius of the environmental cation.

On the other hand, the mass of the cation appears to have no ap-

TABLE 1. OBSERVED INFRARED FREQUENCIES OF $Zr(SO_4)_2 \cdot 4H_2O$ AND $Hf(SO_4)_2 \cdot H_4_2O$
(DATA ARE IN $cm^{-1}$ AND $\mu$)

| | Assignment | | | | | |
|---|---|---|---|---|---|---|
| | O-H $\cdots$ O | | | $SO_4^{2-}$ | | |
| | $\nu_s$ | $\nu_b$ | | $\nu_3$ | | $\nu_1$ |
| $Zr(SO_4)_2 \cdot 4H_2O$ | 3185 | 1667, | 1629 | 1136, | 1088 | 1031 |
| | (3.14) | (6.00), | (6.14) | (8.80), | (9.19) | (9.70) |
| $Hf(SO_4)_2 \cdot 4H_2O$ | 3145 | 1656, | 1632 | 1136, | 1099 | 1040 |
| | (3.18) | (6.04), | (6.13) | (8.80), | (9.10) | (9.62) |

preciable effect on the frequency of these modes. In spite of the fact that the atomic weight of Hf (178) is 96 per cent greater than that of Zr(91), there is no evidence of a correlative shift. One may assume in view of the substantial difference in atomic weight that if the mass of the cation were indeed effective in producing a change in the frequency of $SO_4^{2-}$ vibrations, the $\nu_3$ and $\nu_1$ modes would occur at lower rather than higher frequencies. Certainly, considering the magnitude of shifts attributed elsewhere to a mass effect, the Hf salt would be expected to absorb at much lower frequency than its Zr homolog. This is not to say that molecular vibration is completely independent of cation mass; however, the data indicate that for practical purposes mass is a non-functional property in the sense that it is not useful in explaining the shift of the vibrational frequency of the stretching modes. Whether the bending modes $\nu_2$ and $\nu_4$, which occur at lower frequencies, are similarly affected remains to be determined.

## HYDROGEN BONDING

The general spectral characteristics of many H-bonded organic and inorganic compounds are well known. The typical stretching frequency range for OH with H bonding varies from 2.95 to about 5.8 $\mu$, whereas without H bonding it is 2.7 to 2.85 $\mu$. The shift of the stretching mode $\nu_s$ (collectively $\nu_1$ and $\nu_3$) to lower frequency appears to be related to an increase in energy of the H bond and a corresponding lengthening of the O-H bond and decrease in the O-O distance.

The frequency of the $\nu_s$ mode of the Zr and Hf sulfate tetrahydrates occurs where absorption has been generally found in compounds in which hydrogen bonding is present. The tetrahydrates of Zr and Hf absorb at 3.14 $\mu$ (3185 cm$^{-1}$) and 3.18 $\mu$ (3145 cm$^{-1}$) respectively (Fig. 1, Table 1). Because $Hf(SO_4)_2 \cdot 4H_2O$ absorbs at the lower frequency, it may be expected to have the stronger H bond and shorter H-bonded O-O distance. It is reasonable to suppose that the O-O distance decreases because of overall oxygen-oxygen repulsion caused by shrinkage of the cation-oxygen bond (generally reflected by diminished lattice constants, but in this case inferred on the basis of smaller cation size). This is manifest in the sulfate absorption frequencies, which are higher for the Hf salt. The subject is discussed further in the following section.

The in-plane bending mode $\nu_b$ (or $\nu_2$) of the two salts falls near 6 $\mu$ (Fig. 1, Table 1). This mode is ordinarily shifted to a higher frequency with stronger H-bond formation, but the magnitude of the shift is smaller than that of $\nu_s$. There is no noticeable shift upward of $\nu_b$ for the hafnium salt suggestive of a stronger H bond probably because of this inherently weak response. Both peaks of the doublet near 6 $\mu$ (Fig. 1) are presumably associated with the $\nu_b$ mode. Although this assignment was not confirmed, $\nu_b$ splitting of O-H $\cdots$ O groups has been observed by many workers investigating various alcohols.

In general, splitting of normal modes of molecular ions may arise from the resolution of normally degenerate vibrations of fundamentals and from nonequivalent ions in the unit cell (Adler and Kerr, 1963b). Band enrichment in the OH stretching region has been attributed to interaction among OH$^-$ ions in close proximity causing them to have several different orientations and bonding energies (Boutin and Bassett, 1963). Usually, however, multiplicities of O-H $\cdots$ O absorptions have been ascribed to coupling with other modes enhanced by Fermi resonance. Although there is ample reason for this, it is possible to account for $\nu_b$ splitting in another way. The writer proposes the following alternative explanation.

The vibrational frequencies of water in various compounds are gener-

ally considered as originating from the vibrational motions of the bent $H_2O$ group. In this configuration a molecule can have only three normal modes of vibration as prescribed by the relation 3N-6, where N is the number of participating atoms. Hence, only $\nu_1$, $\nu_2$, and $\nu_3$ modes are allowed. All three are infrared active and non-degenerate. In this circumstance, splitting of $\nu_2$ can be associated only with accidental degeneracy related to coupling, etc., or to the presence of nonequivalent $H_2O$ groups in the crystal lattice.

On the other hand, the bonding relations suggest that hydrogen-bonded oxygen and hydrogen atoms may have vibrational motions more like those of a linear XYX or XYZ molecule. Although deviation from linearity has been recognized in a few compounds, the linear arrangement of the O-H $\cdots$ O group is energetically favored. In this case, 3N-5 or four normal vibrations, namely $\nu_1$, $\nu_3$, $\nu_{2a}$, and $\nu_{2b}$, are possible. If the nuclei carry out the motions characteristic of linear triatomic molecules, the $\nu_2$ (or $\nu_b$) mode would comprise two perpendicular vibrations $\nu_{2a}$ and $\nu_{2b}$ which are normally degenerate, *i.e.*, they vibrate with the same frequency and are indistinguishable.

As mentioned at the outset of this section, one O-H bond is lengthened and the other increased in strength as a result of H-bond formation. Hence, the O-H $\cdots$ O group may be functionally equivalent to an unsymmetrical triatomic linear molecule. Although the ideal symmetry ($C\infty\nu$) of this configuration normally produces a doubly degenerate $\nu_2$ mode, the vibrational symmetry may be lowered and the degeneracy removed if the group is on a site of orthorhombic or lower symmetry. This might cause the two $\nu_2$ component modes, $\nu_{2a}$ and $\nu_{2b}$, to vibrate at slightly different frequencies without any distortion of internal symmetry to $C_s$ or $C_{2v}$ (bent triatomic configuration) which would rule out the possibility of two vibrations. It is also conceivable that the proton in some cases may approach a symmetrical position between the two oxygen atoms thus imparting $D\infty h$ symmetry to the O-H $\cdots$ O group with the result that $\nu_1$ would become inactive.

Although this explanation for splitting of $\nu_b$ seems quite plausible in view of the large number of symmetrically different sites that a given functional group may occupy in mineral structures (Adler and Kerr, 1963b, 1965), the exact cause, nevertheless, remains ambiguous.

## CONCLUSIONS

Differences in vibration frequency of congeneric modes of the $SO_4{}^{2-}$ ion in the tetrahydrated sulfates of Hf and Zr can be explained by cation substitution. The magnitude and direction of frequency shift are found

to be reasonable if attributed to a change in radius of the substitutional cation but can not be satisfactorily explained by the mass change. In accordance with the concept advanced by Weir and Lippincott (1961) the decrease in the cation-oxygen distance, as the cation radius becomes smaller, causes increased repulsion between oxygen atoms of neighboring sulfate ions attached to the cation. This, in turn, causes shortening of the S-O bond and an increase in frequency of sulfate vibrations.

The absorption related to stretching and bending modes of OH are as expected in a hydrogen-bonded system. The shift of the fundamental stretching mode of $Hf(SO_4)_2 \cdot 4H_2O$ to lower frequency reflects an increase in the H-bond strength as well as a decrease in the H-bonded oxygen-oxygen distance.

The shift correlates well with that observed for the sulfate bands. Both polyatomic vibrational systems evidently respond harmoniously to the change in cation radius. It may be concluded, therefore, that the strength of binding of oxygen atoms by hydrogen is a function of the size of the metallic ion or, more directly, the volume of the unit cell.

Consequently, it is reasonable to suggest, but not certain, that for all isomorphous mineral groups the frequency of the O-H $\cdots$ O stretching mode $\nu_s$ will be materially lowered and the H-bond energy correspondingly increased by a reduction in size of the substituting cation. Conformably, the frequency of the bending mode $\nu_b$ will be raised but usually less conspicuously. It is also reasonable to expect that the change in frequency of these modes will conform to the complex and unexplained variations exhibited by other functional molecules of isostructural minerals having replaceable cations belonging to different periodic groups (Adler and Kerr, 1963a).

Splitting of the $\nu_b$ mode may be interpreted as arising from an unsymmetrical linear O-H $\cdots$ O group occupying a site of orthorhombic or lower symmetry. This favors removal of the degeneracy which is inherent in all molecules having $C \infty \nu$ symmetry.

It is interesting to note that a number of minerals yield spectra that show doubling of the $\nu_b$ band. The splitting is perhaps most conspicuous for gypsum, nahcolite and $KHSO_4$ (mercallite). It is apparent but less distinct in the spectra of epsomite, goslarite, bieberite and melanterite. The splitting of $\nu_b$ of gypsum has been attributed by Hass and Sutherland (1956) to interaction between the water molecules in the unit cell. The spectra of some hydrated salts of polyatomic ions examined by Miller and Wilkins (1952) also show this phenomenon. The majority of hydrated minerals for which spectra are available do not show this feature.

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