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ENERGY CALCULATIONS BEARING ON THE DEHYDROXYLATION OF MUSCOVITE

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ABSTRACT

Energy calculations are used to model the initial dehydroxylation of muscovite. An energetically favorable succession of states is determined for the movement of an H atom from one O atom to the other of the [HO–OH] edge shared by octahedra. Which O atom of an [HO–OH] edge will receive the extra H atom and will be expelled from the structure as an H_2O molecule depends on the local environments of the two O atoms of the initial [HO–OH] edge. In muscovite, the distribution of $^{[4]}$Al and Si on the tetrahedrally coordinated sites may be particularly important. Energy considerations indicate that hydroxyl O atoms in local environments of high $^{[4]}$Al/Si are more likely to accept an extra H atom than hydroxyl O atoms in local environments of low $^{[4]}$Al/Si. Thus OH groups in high-$^{[4]}$Al environments are more likely to be expelled, presumably at lower temperatures, than OH groups in low-$^{[4]}$Al environments.

Keywords: dehydroxylation, muscovite, site energy for H.

SOMMAIRE

Des calculs d'énergie sont utilisés pour recréer le stade initial de la déshydroxylation de la muscovite. Du seul point de vue énergétique, une succession favorable de stades ressort de ces calculs pour expliquer le mouvement d'un atome d'hydrogène à partir d'un atome d'oxygène vers l'autre de l'arête [HO–OH] de l'octaèdre. Lequel des atomes d'oxygène d'une arête [HO–OH] recevra l'atome additionnel d'hydrogène et sera libéré de la structure sous forme de molécule de H_2O dépendra des environnements locaux des deux atomes d'oxygène de l'arête [HO–OH] initiale. Dans la muscovite, la distribution de $^{[4]}$Al et Si dans les sites tétraédriques s'avère particulièrement importante à cet égard. Les considérations d'énergie indiquent que les atomes d'oxygène faisant partie des groupes OH dans les milieux à rapport $^{[4]}$Al/Si élevé sont plus propices à recevoir l'atome additionnel d'hydrogène que ceux des environnements locaux à faible rapport $^{[4]}$Al/Si. C'est donc dire que les groupes hydroxyles dans les milieux à $^{[4]}$Al élevé sont plus aptes à être libérés, et donc probablement à plus faible température, que les groupes OH associés aux milieux à $^{[4]}$Al plus faible.

(Traduit par la Rédaction)

Mots-clés: déshydroxylation, muscovite, énergie du site H.

INTRODUCTION

The behavior of dioctahedral phyllosilicates during dehydroxylation has been characterized both spectroscopically and by differential thermal analysis in a number of studies (see Guggenheim *et al.* 1987, Evans & Guggenheim 1988). For the purpose of this discussion, the process may be summarized in a general way:

$$[\mathrm{HO{-}OH}] \rightarrow [\mathrm{O}] + \mathrm{H_2O} \qquad (1)$$

For example, in muscovite the OH groups (in square brackets on the left) are shared by two octahedrally coordinated Al atoms at neighboring $M(2)$ sites (Fig. 1a). With increasing temperature, one O atom (hereafter referred to as the residual O atom) of the [HO–OH] edge loses its H atom and remains part of the dehydroxylated structure. The other O atom gains an H atom to form H_2O, either immediately before or after it starts to move out of the structure. The dehydroxylated part of the structure has corner-sharing five-coordinated Al atoms (Wardle & Brindley 1972, Udagawa *et al.* 1974, Guggenheim *et al.* 1987, Evans & Guggenheim 1988).

The movement of the residual O atom during dehydroxylation can be surmised with some measure of confidence (Guggenheim *et al.* 1987, Evans & Guggenheim 1988). However, determining the motions of the other O atom and the two H atoms is not as straightforward.

Calculations of electrostatic energy are presented here to predict the movement of the H atoms at the onset of dehydroxylation, before steric effects

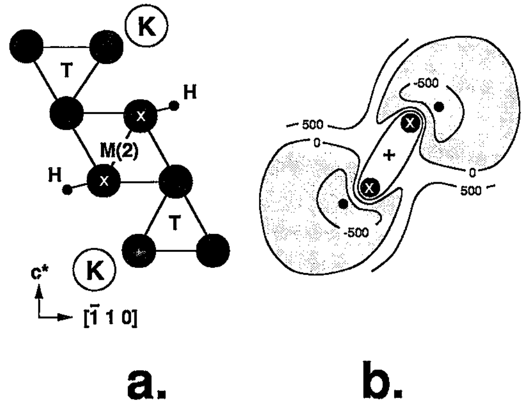

FIG. 1. a. Schematic projection onto the unit-later pseudomirror (110) of a portion of the structure of muscovite. T: tetrahedrally coordinated Si, Al; *M*(2): octahedral Al. The large filled circles are O atoms. Hydroxyl O atoms are marked with "X". The small filled circles are H atoms. The vertical arrow is parallel to $\underline{c}^*$ and 1 Å in length. The horizontal arrow is parallel to [1̄10]. b. Site-energy map for H in muscovite at 650°C. The energy calculations were based on the structure determination by Guggenheim *et al.* (1987); 2Al + 4Si were ordered according to case 10 of Abbott *et al.* (1989). Contour interval is 500 kJ/mole of H atoms. Energy is negative in shaded areas.

(Guggenheim *et al.* 1987, Evans & Guggenheim 1988) become important. The paper considers the possible influence on the process of different patterns of short-range order of $^{[4]}$Al and Si.

METHOD

Energy calculations were performed on muscovite, using the structure determined by Guggenheim *et al.* (1987) on muscovite from Panasqueira, Portugal from X-ray data collected at 650°C, and on appropriately modified variants of the structure (see below). The high-temperature structure is assumed to be the best available representation near conditions relevant to dehydroxylation.

The site energy for an H atom, W(H), is defined as follows (Abbott *et al.* 1989):

$$W(\mathrm{H}) = W_{\mathrm{C,H}} + W_{\mathrm{R,H}}, \qquad (2)$$

where $W_{\mathrm{C,H}}$ includes the Coulombic contributions to the site energy, and $W_{\mathrm{R,H}}$ includes the short-range contributions. The Coulombic contributions are given by

$$W_{\mathrm{C,H}} = \Sigma_{\mathrm{i}}\, z_{\mathrm{i}}\varepsilon^2/r_{\mathrm{iH}}, \qquad (3)$$

where the summation is over atoms other than a specific H atom, z_{i} is the formal valence of atom i, r_{iH} is the interatomic distance H–i, and ε is the magnitude of the charge of an electron. A simple Born formulation (Born & Huang 1954) for the short-range contributions was used, such that

$$W_{\mathrm{R,H}} = \Sigma_{\mathrm{i}}\, \lambda_{\mathrm{iH}}\exp(-\rho_{\mathrm{iH}}/r_{\mathrm{iH}}), \qquad (4)$$

where λ_{iH} and ρ_{iH} are parameters specific to the atom pair H–i. Values for λ_{OH} of 35050 kJ/mole of H and for ρ_{OH} of 0.2265 Å were determined empirically, using the method of Abbott (1991). For muscovite, the method requires short-range parameters for the pairs Al–O, Si–O, O–O, and K–O. These were obtained from Post & Burnham (1986) for an oxygen (O^{2-}) shell radius of 1.01 Å. The calculated values for λ_{OH} and ρ_{OH} are consistent with the observed O–H separation of 0.93 Å (Rothbauer 1971) and observed fundamental frequency of 3626–3628 cm^{-1} for O–H stretching (Vedder & MacDonald 1963, Tlili *et al.* 1989); see Appendix A. In all calculations, short-range contributions for H–i pairs involving atoms other than O atoms are negligible, because of the relatively long H–i distances. The negligible short-range contributions (H–i, where i represents a cation) were omitted by setting the relevant λ_{iH} equal to 0.

The calculations were performed on an electrostatically neutral cluster consisting of the 42 atomic sites closest to the observed (Rothbauer 1971) position for H (all sites within a radius of 4.8 Å). Justification for selection of a cluster and additional details about the calculations are given in Abbott *et al.* (1989). Among the 42 sites are the tetrahedrally coordinated sites of the six-membered ring of tetrahedra closest to the OH group and the adjacent OH group belonging to the [HO–OH] edge. Charges (+3 for Al, +4 for Si) at the six tetrahedrally coordinated sites were distributed according to ordering scheme #10 of Abbott *et al.* (1989). This ordering scheme involves 2$^{[4]}$Al + 4Si and is symmetrical with respect to the unit-layer pseudomirror plane, (110), which is defined by the O atoms of the [HO–OH] shared octahedral edge and the vacant *M*(1) site (Fig. 1a). Effects of different $^{[4]}$Al–Si ordering schemes are discussed later.

The site energy for H was calculated at points on a grid in the unit-layer pseudomirror, (110). Calculations on adjacent OH-environments of an [HO–OH] edge were done on separate clusters. Thus, each of the Figures 1b=2a, 2b, 2c, 2d, and 2e actually shows the results of calculations on two local environments, which were contoured together. Only in Figure 1b are the local structural environments symmetrically identical, related by a center at the midpoint of the [HO–OH] edge. In each of Figures 2b, 2c, 2d, and 2e, the two local environments differ with respect to the positioning of the O atoms of the [HO–OH] edge, as described below.

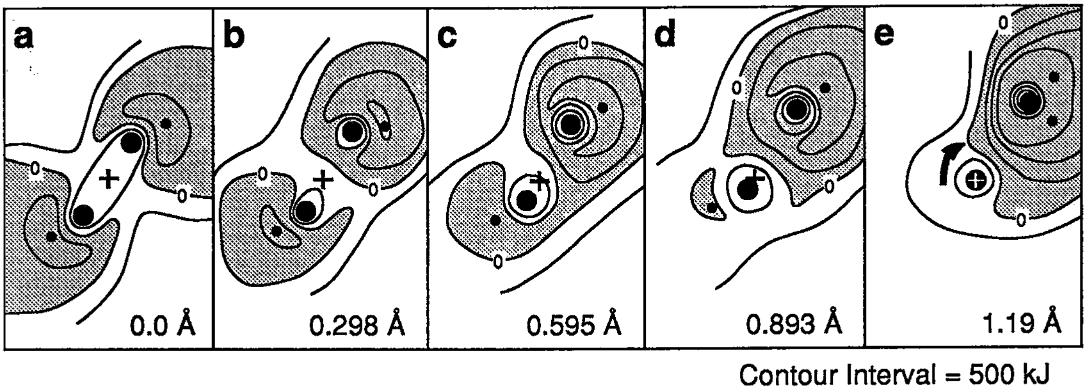

FIG. 2. Site-energy maps for H in muscovite, (110) section. The structure has been modified (relative to the configuration shown in Fig. 1b) by displacing the O–O edge toward the upper right. Amount of displacement: a. No displacement, b. 0.298 Å. c. 0.595 Å, d. 0.893 Å, e. 1.19 Å. The large filled circles are O atoms; the small filled circles are at energy minima. O–O distance is 2.38 Å. Contour interval is 500 kJ/mole of H atoms. Energy is negative in shaded areas.

MUSCOVITE AT 650°C

Figure 1b is a map of the site energy for H in muscovite at 650°C. Note three important features: (1) At 650°C, there is one energy minimum for each O atom (see Abbott *et al.* 1989). (2) The minimum-energy site is reasonably consistent with the determination of the location of the H atom by neutron diffraction (Rothbauer 1971). (3) The angle c^*–O–H from the energy calculations, approximately 68°, is somewhat less than the average of 78° observed by Rothbauer (1971). The difference may be ascribed to the specific pattern of $^{[4]}$Al–Si order used in the energy calculations or to modifications of the structure at high temperature.

EFFECTS OF DISPLACING THE O ATOMS OF THE [HO–OH] EDGE

Figure 2 gives the results of energy calculations that were intended to simulate, however imperfectly, the concerted movements of the O and H atoms during the dehydroxylation of an [HO–OH] edge. Theoretically inferred movements of the $^{[6]}$Al atoms closest to the [HO–OH] edge (Guggenheim *et al.* 1987, Evans & Guggenheim 1988) were taken into account as described below. Movements of other atoms were not modeled. Small variations in the positions of the other atoms do not alter the conclusions. Starting with the centrosymmetrical configuration (Fig. 1b=2a), the O atoms of the shared [HO–OH] edge were translated, in four increments, along the line defined by the two O atoms, without changing the O–O distance (2.38 Å). The increments of displacement were 0.298, 0.595, 0.893, and 1.19 Å (Figs. 2b, c, d, e, respectively). The lower left O atom and the upper right O atom were displaced respectively toward and away from the origin, taken to be the midpoint of the line segment connecting the two adjacent $^{[6]}$Al atoms. The movement of the upper right O atom is in the direction suggested by Guggenheim *et al.* (1987) for the departure of an H_2O molecule. The two nearest $^{[6]}$Al atoms were displaced proportionally from the observed positions in muscovite (Guggenheim *et al.* 1987), where the $^{[6]}$Al–O distances are approximately 1.8 Å, to observed positions in the dehydroxylated structure (Udagawa *et al.* 1974), where the $^{[5]}$Al–O distances are 1.62 Å. In Figure 2e, the lower left (residual) O atom is at the origin. Without the departing O atom (upper right), this configuration (Fig. 2e) is consistent with structures proposed for dehydroxylated dioctahedral phyllosilicates (Wardle & Brindley 1972, Udagawa *et al.* 1974, Guggenheim *et al.* 1987, Evans & Guggenheim 1988).

The following features are noteworthy: (1) Site energies for H change systematically as the O atoms of the [HO–OH] edge are displaced. (2) Site energies for H decrease in the vicinity of the O atom that is moving away from the origin, and increase in the vicinity of the residual O atom as it moves toward the origin. (3) There are two energy minima regardless of the displacement of the O atoms. These energy minima correspond to theoretical positions for H atoms. (4) If the O atoms of the [HO–OH] edge are fully displaced, such that the residual O atom is at the origin (Fig. 2e), both energy minima (and presumably both H atoms) are close to the off-origin O atom. Effectively, as both O atoms are displaced toward the upper right (Figs. 2a, b, c, d, e), the energy minimum associated with the residual O atom disappears at the same time as a second minimum appears near the departing O atom. (5) The final distribution of energy minima about the off-origin O atom is consistent with the positions of the H atoms in an H_2O molecule.

Because the movements of the O atoms were restricted by design in a specific local environment (*i.e.*, specific pattern of $^{[4]}$Al–Si order), the calculations pertain to a specific mechanism of dehydroxylation. The O atoms may move in some other way, depending on local structural variations. Even so, the calculations do demonstrate the plausibility of a closed [HO–OH] mechanism for initiating dehydroxylation. Regardless of the relative merits of site-hopping, tunneling, or diffusion, dehydroxylation mechanisms involving some form of an intermediate, anionic [HO–O]$^-$ edge (see Guggenheim *et al.* 1987, Evans & Guggenheim 1988) are more demanding in terms of energy than some form of a closed [HO–OH] mechanism. Calculations on stages between the O displacements 0.893 Å (Fig. 2d) and 1.19 Å (Fig. 2e) show that the path of least resistance for an H atom moving from the residual O atom to the departing O atom is clockwise along the axis of the low-energy trough. The path is indicated by the arrow in Figure 2e. Moving an H atom along the axis of the low-energy trough involves less input of energy than removing an H atom from the low-energy trough.

EFFECTS OF Al–Si ORDER

The onset of dehydroxylation in pyrophyllite should be rather uncomplicated relative to that of muscovite because all H atoms in pyrophyllite are initially in the same kind of environment with respect to nearby tetrahedrally coordinated cations. In contrast, dehydroxylation in muscovite at a given [HO–OH] edge should depend on the local environments of the two O atoms, especially with regard to the distribution of $^{[4]}$Al and Si (Abbott *et al.* 1989).

The common ratio of $^{[4]}$Al/Si = ⅓ in muscovite cannot be satisfied by any one of the possible compositions for a six-membered ring of tetrahedra (6Si, 1Al + 5Si, 2Al + 4Si, 3Al + 3Si, *etc.*). Thus a real muscovite must have different kinds of six-membered rings (Abbott *et al.* 1989). Lipsicas *et al.* (1984), Herrero *et al.* (1985), and Sanz *et al.* (1986) have shown that the principle of aluminum avoidance is obeyed in micas. Taking these factors into account, there are eighteen possible ways of arranging Al and Si on the six tetrahedral sites closest to each O atom of an [HO–OH] edge (Abbott *et al.* 1989). Although each of the eighteen patterns of Al–Si order are possible, extreme compositions of the ring (6Si and 3Al + 3Si) may be poorly represented. Because two six-membered rings of tetrahedra relate to the two OH groups of an [HO–OH] edge, in the context of Figure 3, there are eighteen possibilities for O1 and eighteen possibilities for O2, thereby producing 324 kinds of [HO–OH] edges. Many of the possibilities, however, may not be very important.

Generally, the higher the ratio of Al to Si in a ring, the lower will be the site energies for the nearest H atom (Abbott *et al.* 1989). Hence site energies for H near 3$^{[4]}$Al + 3Si are lower than sites energies for H near 2$^{[4]}$Al + 4Si, which are less than site energies for H near 1$^{[4]}$Al + 5Si, which are less than site energies for H near 6Si (Abbott *et al.* 1989). Thus:

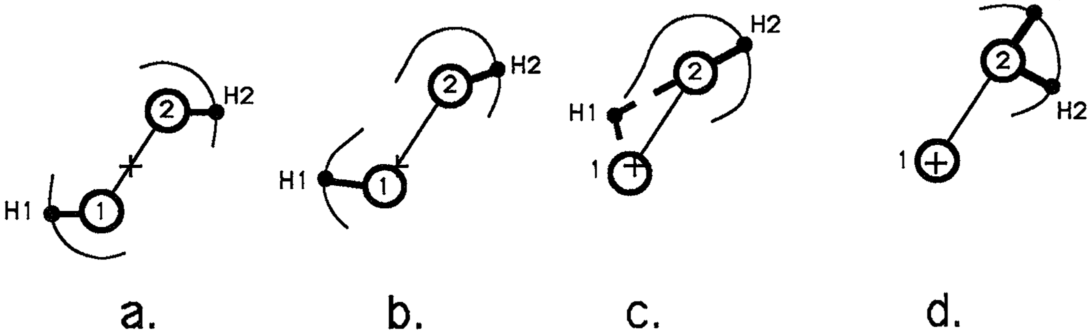

FIG. 3. Schematic representation of dehydroxylation of muscovite. a. Before initiation of dehydroxylation. O1 and O2 are O atoms of the [HO–OH] shared edge of octahedra; H1 and H2 are corresponding H atoms. b, c, d. Sequence of events during dehydroxylation.

1. Where both O atoms of an [HO–OH] edge have similar environments (*e.g.*, in Fig. 3, O1 is adjacent to $2^{[4]}$Al + 4Si, and O2 also is adjacent to $2^{[4]}$Al + 4Si), the probability is nearly the same for expulsion of either OH group (*e.g.*, O1 *versus* O2 in Fig. 3).
2. Where the O atoms of an [HO–OH] edge are in different environments, the OH group associated with the higher ratio of $^{[4]}$Al to Si (lower site-energies for H) should be liberated more readily than the OH group associated with the lower ratio of $^{[4]}$Al to Si (higher site-energies for H). In effect, hydroxyl O atoms in low-$^{[4]}$Al/Si environments (high energy) should act as H donors, whereas hydroxyl O atoms in high-$^{[4]}$Al/Si environments (low energy) should act as H acceptors. Thus hydroxyl O atoms in low-$^{[4]}$Al/Si environments are more likely to remain in the dehydroxylated structure, whereas hydroxyl O atoms in high-$^{[4]}$Al/Si environments are more likely to be liberated as H_2O. This is consistent with evidence that celadonitic muscovite ($^{[4]}$Al/Si $< 1/3$) starts to break down at higher temperatures than muscovite ($^{[4]}$Al/Si $= 1/3$) (Anderson & Rowley 1981, Thompson 1982).
3. Given so many possible patterns of Al–Si order (324 possibilities altogether) and steric effects (Guggenheim *et al.* 1987, Evans & Guggenheim 1988), it is not surprising that dehydroxylation takes place over a wide range of temperatures. If the interpretation offered in this paper is correct, as temperature increases, dehydroxylation should commence at OH groups near high-$^{[4]}$Al/Si sites.

These predictions pertain to the initiation of dehydroxylation. Obviously, the effects of one or more dehydroxylated sites on the subsequent dehydroxylation of the remaining structure, *i.e.*, the steric effects described by Guggenheim *et al.* (1987) and Evans & Guggenheim (1988), are important only after the process is initiated. Because the structural changes associated with the steric effects are severe, these effects must dominate subsequent steps of the overall dehydroxylation process.

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REFERENCES

ABBOTT, R.N., JR. (1991): A short-range O–H potential for amphiboles based on OH-stretching frequencies. *Can. Mineral.* **29**, 131-142.

———, POST, J.E. & BURNHAM, C.W. (1989): Treatment of the hydroxyl in structure-energy calculations. *Am. Mineral.* **74**, 141-150.

ANDERSON, J.L. & ROWLEY, M.C. (1981): Synkinematic intrusion of peraluminous and associated metaluminous granitic magmas, Whipple Mountains, California. *Can. Mineral.* **19**, 83-101.

BORN, M. & HUANG, K. (1954): *Dynamical Theory of Crystal Lattices.* Oxford University Press, London.

EVANS, B.W. & GUGGENHEIM, S. (1988): Talc, pyrophyllite, and related minerals. *In* Hydrous Phyllosilicates (S.W. Bailey, ed.). *Rev. Mineral.* **19**, 225-294.

GUGGENHEIM, S., CHANG, YU-HWA & KOSTER VAN GROOS, A.F. (1987): Muscovite dehydroxylation: high temperature studies. *Am. Mineral.* **72**, 537-550.

HERRERO, C.P., SANZ, J. & SERRATOSA, J.M. (1985): Tetrahedral cation ordering in layer silicates by ^{29}Si NMR spectroscopy. *Solid State Commun.* **53**, 151-154.

LIPSICAS, M., RAYTHATHA, R.H., PINNAVAIA, T.J., JOHNSON, I.D., GIESE, R.F., JR., CONSTANZO, P.M. & ROBERT, J.-L. (1984): Silicon and aluminum site distributions in 2:1 layered silicate clays. *Nature* **309**, 604-607.

POST, J.E. & BURNHAM, C.W. (1986): Ionic modeling of mineral structures in the electron gas approximation: TiO_2 polymorphs, quartz, forsterite, diopside. *Am. Mineral.* **71**, 142-150.

ROTHBAUER, R. (1971): Untersuchung eines $2M_1$-Muscovits mit Neutronenstrahlen. *Neues Jahrb. Mineral. Monatsh.*, 143-154.

SANZ, J., HERRERO, C.P. & SERRATOSA, J.M. (1986): Tetrahedral cation distribution in phyllosilicates 2:1 by ^{29}Si NMR spectroscopy. *Int. Mineral. Assoc., Abstr. Programs* **14**, 220.

THOMPSON, A.B. (1982): Dehydration melting of pelitic rocks and generation of H_2O-undersaturated granitic liquids. *Am. J. Sci.* **282**, 1567-1595.

TLILI, A., SMITH, D.C., BENY, J.-M. & BOYER, H. (1989): A Raman microprobe study of natural micas. *Mineral. Mag.* **53**, 165-179.

UDAGAWA, S., URABE, K. & HASU, H. (1974): The crystal structure of muscovite dehydroxylate. *Jap. Assoc. Mineral., Petrol., Econ. Geol.* **69**, 381-389.

VEDDER, W. & MACDONALD, R.S. (1963): Vibrations of OH ions in muscovite. *J. Chem. Phys.* **38**, 1583-1590.

WARDLE, R. & BRINDLEY, G.W. (1972): The crystal structure of pyrophyllite-1Tc and its dehydroxylate. *Am. Mineral.* **57**, 732-750.

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APPENDIX A.
SHORT- RANGE POTENTIAL FOR O-H PAIR

Results of calculation of short-range O-H potentials for muscovite, using the method of Abbott (1991) on structure determination (20°C) by Guggenheim *et al.* (1987) of muscovite from Panasqueira, Portugal.

Short-range coefficients: $\lambda_{OH} = 35050$ kJ, $\rho_{OH} = 0.2265$ Å.

Constants in anharmonic oscillator function[1], U_{OH}:

$k_1 = 4830.0$ kJ/Å^2	$k_2 = -28860.0$ kJ/Å^3	$k_3 = 104640.0$ kJ/Å^4)
(+/- 10)	(+/- 30)	(+/- 120)

	Observed	Calculated
H-O (Å)	0.93[2]	0.9289
Constants in vibrational energy functions[4], $[V(v)-U_{OH,minimum}]/h/c$:		
v_e (cm^{-1})	3793.3[3]	3789.8
$x_e v_e$ (cm^{-1})	82.8[3]	84.1
Y_{00}/c (cm^{-1})	--	-3.4
Absorption frequencies[5]:		
$\Delta(1,0)$ (cm^{-1})	3628[3]	3623
$\Delta(2,0)$ (cm^{-1})	7088[3]	7075

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1. $U_{OH}-U_{OH,minimum} = 1/2\ k_1(r-r_0)^2 + 1/6\ k_2(r-r_0)^3 + 1/24\ k_3(r-r_0)^4$

   Least-squares statistics: $R_{wp} = 0.0048$, $R_{ex} = 0.0202$, GoF = 0.0559.

   $R_{wp} = [\Sigma_i [W_{OH}(r_i) - U_{OH}(r_i)]^2 / \Sigma_i [W_{OH}(r_i)]^2]^{0.5}$, where

   $W_{OH} = \Sigma_i [z_i z_H \varepsilon^2 / r_{iH} + \lambda_{iH} \exp(-r_{iH}/\rho_{iH})] + \Sigma_{j \neq H} [z_j z_O \varepsilon^2 / r_{jO} + \lambda_{jO} \exp(-r_{jO}/\rho_{jO})]$,

   and z_i = valence of ion i, $z_H = +1$, z_j = valence of ion j, $z_O = -2$; ε = magnitude of charge on an electron; r_{iH}, r_{jO} are ion separations i-H, j-O, respectively; λ_{iH}, λ_{jO}, ρ_{iH}, ρ_{jO} are short-range parameters for pairs iH and jO, respectively. First summation is over all neighbors i of the H atom of a specific OH group; second summation is over all neighbors j of the O atom of the OH group, except the H atom of the specific OH group.

   $R_{ex} = [(N-P)/ \Sigma_i [W_{OH}(r_i)]^2]^{0.5}$, N = # samples of W_{OH}, P = 4 (# parameters)

   GoF = $(R_{wp}/R_{ex})^2$, goodness-of-fit. GoF < 1 indicates very good fit.
2. Rothbauer (1971).
3. Vedder & MacDonald (1963).
4. $[V(v)-U_{OH,min}]/h/c = v_e(v+1/2) - x_e v_e (v+1/2)^2 + Y_{00}/c$
5. $\Delta(v_2, v_1) = [V(v_2) - V(v_1)]/h/c = v_e(v_2 - v_1) - x_e v_e[(v_2+1/2)^2 - (v_1+1/2)^2]$