VIBRATIONAL PROPERTIES OF SURFACE HYDROXYLS: NONEMPIRICAL MODEL CALCULATIONS INCLUDING ANHARMONICITIES

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

Complete sets of harmonic, semidiagonal cubic as well as diagonal cubic and quartic force constants are reported for the internal coordinates of terminal, ≡SiOH, and bridging, ≡SiOH··Al≡, surface hydroxyls on silica and zeolites. They are obtained by numerical differentiation of analytically calculated gradients of the energy (SCF approximation, 6-31G* basis set). A GF vibrational analysis is performed and after making a nonlinear transformation of the force constants into normal coordinates the anharmonicity constants are evaluated by perturbation theory. Comparison is made with the D_2OH^+ ion and the DOH molecule. The calculated anharmonicities of the OH bonds in the systems studied are remarkably constant and vary between -76 and -84 cm^{-1}, only in agreement with the values observed for DOH (-83 cm^{-1}) and surface silanols, ≡SiOH (-90 ± 15 cm^{-1}).

Thanks to the development of powerful gradient techniques[1] quantum chemical *ab initio* calculations do nowadays efficiently assist the work of spectroscopists[2]. It belongs to the power of the theoretical approach that it yields, in the same straightforward way as the diagonal force constants, non-diagonal force constants and anharmonic corrections, which are difficult to obtain from experiments since there are commonly not enough observed data. This is particularly true for investigations of active sites of surfaces and solids[3,4] where IR spectroscopy encounters specific difficulties. Studies of surface hydroxyls on zeolites, silica and other oxidic catalysts in the near-IR region raised interest in the anharmonicities of these groups[4-6]. Fortunately, *ab initio* calculations are feasible not only for molecules in the gas phase but also for bulk and surface sites of solids provided that suitable molecular models can be found[7-9]. The present study aims at predicting theoretically the anharmonicity constants of surface hydroxyls from *ab initio* calculations of cubic and quartic force

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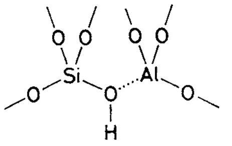
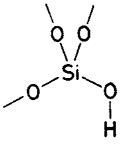
constants. In another paper the vibrational properties of zeolitic surface hydroxyls and framework units will be analyzed in the harmonic approximation[10].

This paper is organized as follows. First, we outline the spectroscopic problem which stimulated our study. Next, the theoretical procedures are described, details of calculations are given and the models of the surface hydroxyls used in the calculations are specified. The theoretical procedure consists of two steps, namely (i) calculation of the force constants by quantum chemical *ab initio* methods and (ii) solving the nuclear motion problem by the GF matrix analysis and perturbation theory. In the last section the results are presented and conclusions are drawn. To assess the reliability of the procedures used, a comparison is made with the observed[11,12] and high-level theoretical data[12] using the HDO molecule as a benchmark.

Surface hydroxyls are of interest because they are the origin of Brönsted acidity of catalysts. Among acidic catalysts high-silica zeolites such as ZSM-5 proved particularly efficient[13]. Their active sites are bridging hydroxyls, *I*, which are formed when protons are attached to aluminosilicate frameworks to compensate the negative excess charge of the latter. The outer surfaces of the microcrystallites are terminated by silanols ("terminal" hydroxyls), *II*, which are only very weakly acidic. They are also present on the surfaces of various forms of silica. The O—H bond stretching vibrational frequency is well separated from other bands and therefore used routinely to distinguish different types of hydroxyl sites (typical wavenumbers are 3 610 cm^{-1} for bridging, e.g. ref.[14] and 3 745 cm^{-1} for terminal hydroxyls, e.g. ref.[5]). Moreover, this band is used to monitor changes of the environment of the bridging groups, i.e. variations in structure and composition of the catalyst.



I



II

Previous quantum chemical studies[15,16] have dealt with the O—H oscillator only. However, the recently performed complete vibrational analysis[10] revealed that the Si—O—H bending mode shows a much larger shift between different types of sites and would be possibly more sensitive to differences of structure and composition of the catalysts. There were also indications from experiments that bending vibrations may be better suited to characterize the properties of surface hydroxyls[5,14]. However, the measurement of bending vibrations encounters experimental difficulties. Since their wavenumbers are in the range between 700 and 1 100 cm^{-1} they cannot be observed directly on the background of strong adsorption bands of the

Al—O and Si—O framework vibrations. Therefore, Kustov et al.[5,14] suggested to measure combination bands and overtones in the near-IR region and employed the diffuse reflectance technique on powdered samples. In addition, one cannot get the fundamental wavenumbers from the overtones and combination bands without knowing the respective anharmonicity constants. This stimulated the present work.

THEORETICAL

The anharmonicity constants x_{rs} are defined by the following power series expansion of the vibrational energy E_{n_ν,n_δ} of the coupled O—H stretching (ν) and Si—O—H bending (δ) oscillators (n are the quantum numbers, $\tilde{\nu}^0$ the harmonic wavenumbers, $\boldsymbol{h}$ and $\boldsymbol{c}$ are the Planck constant and the velocity of light):

$$E_{n_\nu,n_\delta}/\boldsymbol{hc} = \tilde{\nu}_\nu^0(n_\nu + \tfrac{1}{2}) + x_{\nu\nu}(n_\nu + \tfrac{1}{2})^2 + \\ + \tilde{\nu}_\delta^0(n_\delta + \tfrac{1}{2}) + x_{\delta\delta}(n_\delta + \tfrac{1}{2})^2 + 2x_{\nu\delta}(n_\nu + \tfrac{1}{2})(n_\delta + \tfrac{1}{2})\,. \tag{1}$$

For the combination band $\tilde{\nu}_{\nu+\delta}$ of the O—H stretch and Si—O—H bend we obtain

$$(E_{1,1} - E_{0,0})/\boldsymbol{hc} = \tilde{\nu}_{\nu+\delta} = \tilde{\nu}_\nu + \tilde{\nu}_\delta + 2x_{\nu\delta}\,. \tag{2}$$

For the second combination band $\tilde{\nu}_{2\nu+\delta}$ we have

$$(E_{2,1} - E_{0,0})/\boldsymbol{hc} = \tilde{\nu}_{2\nu+\delta} = \tilde{\nu}_{2\nu} + \tilde{\nu}_\delta + 4x_{\nu\delta}\,, \tag{3}$$

while for the O—H fundamental $\tilde{\nu}_\nu$ and overtone $\tilde{\nu}_{2\nu}$ we obtain

$$(E_{1,0} - E_{0,0})/\boldsymbol{hc} = \tilde{\nu}_\nu = \tilde{\nu}_\nu^0 + 2x_{\nu\nu} + x_{\nu\delta} \tag{4a}$$

and

$$(E_{2,0} - E_{0,0})/\boldsymbol{hc} = \tilde{\nu}_{2\nu} = 2\tilde{\nu}_\nu + 2x_{\nu\nu}\,, \tag{4b}$$

respectively.

For terminal silanols all four quantities are known (4 550, 8 117, 3 745 and 7 310 cm^{-1}, respectively) and Eqs (*2*)–(*4*) yield the following estimates: $\tilde{\nu}_\delta = 803 \pm 70\ \mathrm{cm}^{-1}$, $x_{\nu\delta} = 1 \pm 25\ \mathrm{cm}^{-1}$ and $x_{\nu\nu} = -90 \pm 15\ \mathrm{cm}^{-1}$ (ref.[17]). The observed wavenumbers[17] are in agreement with both the results of Shen and Klier[18] ($\tilde{\nu}_{2\nu} = 7\,305 - 7\,321\ \mathrm{cm}^{-1}$ and $\tilde{\nu}_{2\nu+\delta} = 8\,810 - 8\,123\ \mathrm{cm}^{-1}$) and of Kustov et al.[5] ($\tilde{\nu}_{2\nu} = 7\,320$ and $\tilde{\nu}_{\nu+\delta} = 4\,540\ \mathrm{cm}^{-1}$). In most applications selected overtones or combination bands are measured only and there are not enough observed data to derive the fundamental frequencies. Therefore, predictions of $x_{\nu\nu}$ and $x_{\nu\delta}$ become topical. The present study provides theoretical data on anharmonicity constants for bridging, *I*, and terminal, *II*, hydroxyls. Agreement with the above experimental estimates for terminal hydroxyls could strengthen confidence in these values. Of particular interest is to see whether there are significant differences between the results of different types of hydroxyls.

Force Constant Evaluation

The harmonic, F_{ij}, cubic, F_{ijk}, and quartic, F_{ijkl}, force constants are defined as the second, third and fourth derivatives, respectively, of the potential energy of a molecular system with respect to curvilinear internal coordinates, $\mathscr{R}_i$ (see e.g., ref.[11]):

$$F_{ij} = \left.\frac{\partial V}{\partial \mathscr{R}_i \partial \mathscr{R}_j}\right|_{\mathscr{R}=0} \tag{5}$$

$$F_{ijk} = \left.\frac{\partial V}{\partial \mathscr{R}_i \partial \mathscr{R}_j \partial \mathscr{R}_k}\right|_{\mathscr{R}=0} \tag{6}$$

$$F_{ijkl} = \left.\frac{\partial V}{\partial \mathscr{R}_i \partial \mathscr{R}_j \partial \mathscr{R}_k \partial \mathscr{R}_l}\right|_{\mathscr{R}=0} . \tag{7}$$

They are the coefficients of a Taylor series expansion of the potential energy V of the system with respect to curvilinear internal coordinates:

$$\begin{aligned} V(\mathscr{R}) = V(\mathbf{0}) &+ \tfrac{1}{2}\sum_{ij} F_{ij}\mathscr{R}_i\mathscr{R}_j + \tfrac{1}{6}\sum_{ijk} F_{ijk}\mathscr{R}_i\mathscr{R}_j\mathscr{R}_k + \\ &+ \tfrac{1}{24}\sum_{ijkl} F_{ijkl}\mathscr{R}_i\mathscr{R}_j\mathscr{R}_k\mathscr{R}_l + \ldots . \end{aligned} \tag{8}$$

Although, in principle, second and also higher derivatives of the energy can be calculated analytically from the SCF wavefunction, only the first derivatives,

$$g_i = \left.\frac{\partial V}{\partial \mathscr{R}_i}\right|_{\mathscr{R}=0} , \tag{9}$$

are routinely available and the force constants are obtained as finite differences.

If energies, $V(x_i)$ and $V(-x_i)$, and gradient vectors, $\mathbf{g}(x_i)$ and $\mathbf{g}(-x_i)$, are calculated for all structures which are obtained when each internal doordinate $\mathscr{R}_i$ is distorted by an increment x_i in plus and minus direction, the full matrix of harmonic force constants, F_{ij}, the diagonal and semidiagonal cubic force constants, F_{iij}, and the diagonal quartic force constants, F_{iiii}, can be evaluated according to

$$F^g_{ij} = \frac{g_j(x_i) - g_j(-x_i)}{2x_i} \quad (i \neq j) \tag{10}$$

$$F_{iij} = \frac{g_j(x_i) + g_j(-x_i) - 2g_j(0)}{x_i^2} \qquad (11)$$

$$F_{ii} = 2F_{ii}^V - F_{ii}^g \qquad (12)$$

$$F_{iiii} = \frac{12}{x^2}(F_{ii}^g - F_{ii}^V) \qquad (13)$$

with

$$F_{ii}^V = \frac{V(x_i) + V(-x_i) - 2V(0)}{x_i^2} \qquad (14)$$

and

$$F_{ii}^g = \frac{g_i(x_i) - g_i(-x_i)}{2x_i}\,. \qquad (15)$$

The energy and the gradient vector of the equilibrium structure are denoted by $V(0)$ and $\mathbf{g}(0)$. Since expression (*10*) yields slightly different values for F_{ij}^g and F_{ji}^g, a symmetrization is made according to

$$F_{ij} = F_{ji} = \tfrac{1}{2}(F_{ij}^g + F_{ji}^g)\,.$$

For some calculations it turned out that the numerical accuracy was not sufficient to get reliable results from Eqs (*12*) and (*13*). In this case energies and gradients were calculated for a second pair of distortions, y and $-y$, (we drop the index i; the first pair of distortions is x and $-x$) and the following formulas (gradients only) were used for numerical differentiation:

$$F_{ii} = F_{ii}^x - \frac{x^2}{y^2 - x^2}(F_{ii}^y - F_{ii}^x)\,, \qquad (16)$$

$$F_{iiii} = \frac{6}{y^2 - x^2}(F_{ii}^y - F_{ii}^x)\,. \qquad (17)$$

F_{ii}^y and F_{ii}^x are given by Eq. (*15*) for distortions y and x, respectively. In addition, from the available gradient values a more accurate estimate of the cubic diagonal force constant is possible:

$$F_{iii} = F_{iii}^x - \frac{x^2}{y^2 - x^2}(F_{iii}^y - F_{iii}^x)\,. \qquad (18)$$

F_{iii}^y and F_{iii}^x are given by Eq. (*11*) ($j = i$) for distortions y and x, respectively.

As models of terminal and bridging hydroxyls in zeolites we adopted the H_3SiOH molecule and the $H_3SiOH{\cdot}AlH_3$ complex, respectively, suggested previously[15] (Fig. 1). They proved successful in describing diffeences between the two types of hydroxyls[15,16,19]. For comparison, the H_2O molecule and the H_3O^+ ion are considered. Our calculations of the energies and gradients were performed by the HONDO5 program[20] and the transformations between curvilinear internal and cartesian coordinates were made by means of the BMAT link of the program TEXAS[21]. In all calculations we employed the 6-31G* basis set[23] (see ref.[19] for details). In ref.[19] the equilibrium structures of H_3SiOH and $H_3SiOH{\cdot}AlH_3$ were reported for this basis set. For H_3O^+ the data were taken from a previous 6-31G* study[24] of the harmonic vibrational frequencies. We took these geometries as reference structures and made distortions of the internal coordinates by 5 pm (for bond lengths) and by 5° (for bond angles). Additional distortions were made for O—H and Si—O bonds (±3 pm) and for the Si—O—H angle (±3°).

Molecular Vibrations

In the first step of the theoretical treatment of molecular vibrations the harmonic problem is solved, i.e. the normal coordinates, $\tilde{q}_r$, and the harmonic wavenumbers, $\tilde{\nu}_r^0$, are obtained by diagonalizing the GF matrix[25]. A standard program[22] was employed.

The anharmonicity constants, x_{rs}, which appear in the expression for the energy levels, E, of the (anharmonically) vibrating molecule (cf. Eq. (*1*), $\{n\}$ denotes a set of $(3N\text{-}6)$ vibrational quantum numbers),

$$E_{\{n\}}/hc = \sum_r \tilde{\nu}_r^0 (n_r + \tfrac{1}{2}) + \sum_{rs} x_{rs} (n_r + \tfrac{1}{2})(n_s + \tfrac{1}{2}) \,, \qquad (19)$$

FIG. 1

Silanol molecule and silanol aluminiumhydrid complex — models of terminal and bridging hydroxyls in zeolites can be obtained by a perturbation expansion[26,27] in terms of the (normalized) normal coordinates, $\tilde{q}_r$. For example the diagonal anharmonicity constant, x_{rr}, is[26,27]

$$x_{rr} = \frac{1}{16}\tilde{\Phi}_{rrrr} - \frac{1}{16}\sum_t \tilde{\Phi}_{rrt}^2 \frac{8\tilde{\nu}_r^{0\,2} - 3\tilde{\nu}_t^{0\,2}}{\tilde{\nu}_t^0(4\tilde{\nu}_r^{0\,2} - \tilde{\nu}_t^{0\,2})}\,. \qquad (20)$$

The force constants $\tilde{\Phi}_{rrrr}$ and $\tilde{\Phi}_{rrt}$ which appear in the latter expression are defined as Taylor expansion coefficients of the potential energy with respect to the normalized normal coordinates

$$V/hc = \tfrac{1}{2}\sum_r \tilde{\nu}_r^{0\,2}\tilde{q}_r^2 + \tfrac{1}{6}\sum_{rst}\tilde{\Phi}_{rst}\tilde{q}_r\tilde{q}_s\tilde{q}_t + \tfrac{1}{24}\sum_{rstu}\tilde{\Phi}_{rstu}\tilde{q}_r\tilde{q}_s\tilde{q}_t\tilde{q}_u\,. \qquad (21)$$

The crucial problem from the practical point of view is the transformation of the cubic and quartic force constants F_{ijk} and F_{ijkl} with respect to internal coordinates (Eqs (5)–(7)) into the force constants $\tilde{\Phi}_{rst}$ and $\tilde{\Phi}_{rstu}$ with respect to normal coordinates. Namely, this transformation is nonlinear and requires programming of the rather complex expressions for the **L**-tensor elements[11]. Alternatively one may obtain $\tilde{\Phi}_{rst}$ and $\tilde{\Phi}_{rstu}$ directly by numerical differentiation (using Eqs (*10*)–(*15*) but making gradient calculations for geometries which are obtained by distortions in the direction of the normal coordinates). It requires, however, too many gradient calculations since all non-diagonal elements of $\tilde{\Phi}_{rst}$ and $\tilde{\Phi}_{rstu}$ enter the perturbation expression. In contrast, it is a fair assumption that most significant anharmonicity effects are accounted for by including semidiagonal cubic and diagonal cubic and quartic force constants only provided that they are defined with respect to curvilinear internal coordinates. This approximation is adopted in the present work. For the transformations of cubic and quartic force constants into normal coordinates the program of Hoy, Mills and Strey[11] is employed.

RESULTS AND DISCUSSION

Table I shows diagonal force constants for the molecular models considered in this study and Table II the harmonic wavenumbers calculated from the harmonic force constants. The modes are characterized by the internal coordinate the change of which dominates the respective normal motion. Table II also shows the results of GF calculations assuming a simpler models for the treatment of the motions of the nuclei but using the same force constants. The terminating hydrogen atoms are introduced to avoid boundary effects when solving the electronic problem[7–9,15,19]. When dealing with nuclear motions other boundary effects are present and the motions of the light hydrogen atoms may affect the vibrations of the atoms of the surface site in an undesirable way. To avoid such effects and, moreover, to reduce the number of the normal modes to be included in the nonlinear transformation for getting the anharmonicity constants the simple Si—O—H model was studied. For the ≡SiOH·Al≡ site the harmonic Si—O—H and Si—O frequencies obtained for the different models vary by up to about 50 cm^{-1}. The O—H stretching frequency is much higher than all the other modes and therefore the O—H oscillator can be treated as isolated without any loss of accuracy. This is illustrated by the results of Table II.

TABLE I

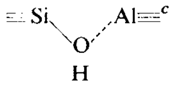
Harmonic, cubic and quartic diagonal force constants (Eqs (*16*)–(*18*))

Force constant	Model	Internal coordinate		
		OH	SiO	SiOH
F_{ii}[a]	H_3SiOH	9·579	5·427	0·402
	$H_3SiOH \cdot AlH_3$	9·360	4·347	0·627
F_{iii}[b]	H_3SiOH	−66·14	−27·79	−0·791
	$H_3SiOH \cdot AlH_3$	−63·98	−21·81	−0·425
F_{iiii}[c]	H_3SiOH	423·6	129·7	−0·015
	$H_3SiOH \cdot AlH_3$	410·2	99·4	0·036

[a] In 10^{2} N m^{-1} (stretch) or 10^{-18} N mrad^{-2} (bend); [b] in 10^{12} N m^{-2} (stretch) or 10^{-18} N . mrad^{-3} (bend); [c] in 10^{22} N m^{-3} (stretch) or 10^{-18} N mrad^{-4} (bend).

TABLE II

Wawenumbers $\tilde{\nu}^0$ (cm^{-1}) for different models adopted in the GF calculations (harmonic force constants from Table I)

Hydroxyl site	Model	Vibrational mode[a]		
		1 (OH)	2 (SiO)	3 (SiOH)
≡SiOH[b]	H_3SiOH	4 140	908	958
	Si—O—H	4 140	896	937
	O—H	4 141		
	$H_3SiOH \cdot AlH_3$	4 091	1 197	875
	Si—O—H	4 093	1 138	835
	O—H	4 093		

[a] The normal modes are characterized by the dominating internal coordinate; [b] force constants calculated for H_3SiOH; [c] force constants calculated for $H_3SiOH \cdot AlH_3$.

To check the reliability of the SCF approximation and the 6-31G* basis set for calculations of anharmonicity constants, calculations are performed for the HDO molecule (Table III). For this molecule comparison can be made with both the observed data[11,12] and the results of extended basis set SCF and CI calculations[12]. Overestimation of the hamonic vibrational frequencies by 6–11% (Table III) is a well known systematic shortcoming of the SCF/6-31G* approach[2]. In contrast, the SCF/6-31G* anharmonicity constants differ by only a few cm^{-1} from the observed ones, presumably because of the cancellation of basis set and correlation effects.

To estimate the numericl accuracy of the calculated anharmonicity constants we compare two sets of diagonal force constants. The first one is obtained from Eqs (*11*)–(*13*) (two energies and two gradients) while the second one results from Eqs (*16*)–(*18*) (four gradients). In the case of $H_3SiOH{\cdot}AlH_3$ only the second procedure yields stable results, while for H_3SiOH both types of results are very similar. The largest difference met (x_{11}) is 3 cm^{-1}, all other are of 1 cm^{-1} or less. The results shown in the tables were obtained by the second procedure. In the following discussion, the differences between anharmonicity constants are considered significant only if they are at least of 5 cm^{-1}.

Table IV shows anharmonicity constants of the SiOH models for ≡SiOH and ≡SiOH·Al≡ surface hydoxyl groups and Table V shows the results for the O—H diatomic oscillator model. Firstly, we note that contributions from cubic and quartic force constants are of the same order of magnitude but have opposite signs. Secondly, as expected, the anharmonicity of the Si—O stretching mode and all its coupling

TABLE III

Observed and calculated (different quantum chemical approaches) harmonic vibrational wavenumbers and anharmonicity constants of HDO (cm^{-1})

Spectroscopic parameter	SCF/6-31G*[a]	SCF/39-STO[b]	CI/39-STO[b]	Obs.[c]
$\tilde{\nu}_1^0$(OH)	4 132	4 184	3 909	3 889·8
$\tilde{\nu}_2^0$(HOD)	1 600	1 553	1 479	1 440·2
$\tilde{\nu}_3^0$(OD)	2 999	3 040	2 839	2 824·3
x_{11}	−82·3	−85·1	−73·7	−82·9
x_{22}	−12·4	−18·4	−13·7	−11·8
x_{33}	−43·1	−49·6	−42·5	−43·4
x_{12}	−17·3	+6·4	−19·2	−20·1
x_{13}	−5·7	−7·0	−15·0	−13·1
x_{23}	−12·6	−19·2	−7·3	−8·6

[a] This work; [b] ref.[12]; the basis set comprises 39 Slater type functions; [c] refs[11,12].

terms are below 5 cm^{-1} and can safely be ignored. The calculated values for the x_{11} and x_{12} constants of ≡SiOH groups, −81 and −2 cm^{-1}, respectively, fall into the range of values inferred from experiments (vide supra), −90 ± 15 and 1 ± 25 cm^{-1}, respectively. Our prediction for the anharmonicity constant of the Si—O—H bening mode is −17 cm^{-1} which is close to the value for the D—O—H bending in the

TABLE IV

Anharmonicity constants of surface hydroxyls[a] and individual contributions to the second order perturbation term (cm^{-1})

x_{rs}	≡SiOH			≡SiOH·Al≡		
	total[b]	contribution from		total[b]	contribution from	
		cubic f.c.[c]	quartic f.c.[c]		cubic f.c.[c]	quartic f.c.[c]
x_{11}	−81	−179	98	−78	−175	97
x_{22}	−17	−117	100	−4	−73	69
x_{12}	−2[b]	320	−324	−20[b]	254	−276
x_{33}	−3	−7	4	−4	−8	4
x_{13}	−4[b]	34	−39	2	1	1
x_{23}	−3	−54	51	0[b]	−1	0

[a] Normal modes from the Si—O—H dynamical model (cf. Table II), force constants from H_3SiOH and $H_3SiOH·AlH_3$ models, respectively (for diagonal terms cf. Table I); [b] small differences between the total value and the sum of the contributions from cubic and quartic f.c. are due to a small contribution from the rotational term (refs[26,27]) which is zero in all other cases; [c] f.c. force constant.

TABLE V

Anharmonicity constants of O—H bonds, x_{11}, obtained for the diatomic oscillator model and its individual contributions from cubic and quartic force constants (cm^{-1})

Species	Total	Contribution from	
		cubic f.c.[a]	quartic f.c.[a]
D_2OH^+	−83·6	−181·0	97·4
DOH	−80·7	−179·3	98·6
≡SiOH	−78·3	−176·6	98·3
≡SiOH.Al≡	−75·7	−173·1	97·4

[a] f.c. Force constant.

HDO molecule (-12 cm^{-1}, calculated and observed, cf. Table III). The differences between terminal $\equiv$SiOH, and bridging $\equiv$SiOH·Al$\equiv$ hydroxyls are small (Table IV) and below the limits of uncertainty of experimental estimates. For the bridging hydroxyl groups the calculations indicate a negligible anharmonicity (4 cm^{-1}) of the bending mode but a nonnegligible coupling term x_{12} (-20 cm^{-1}). In particular, the anharmonicities of the O—H stretching modes are virtually identical for both types of surface hydroxyls (Table IV). Moreover, Table V shows that the anharmonicities of the O—H bonds in surface hydroxyls do not differ significantly from those of the DOH molecule or the D_2OH^+ ion. We conclude that the anharmonicity of an O—H bond is not changed even if the coordination of the oxygen is altered from two to three by formation of an additional chemical bond (DOH → D_2OH^+) or by formation of an electron pair donor acceptor bond ($\equiv$SiOH → $\equiv$SiOH·Al$\equiv$). This invariance of the anharmonicity of O—H bonds with respect to the change of the bonding state of oxygen contrasts sharply with its sensitivity to the formation of hydrogen bonds with proton acceptors[4,6].

As far as the investigations of surface hydroxyls on silicates, aluminosilicates and different types of zeolites is concerned we conclude from the results of this study that the same anharmonicity constants can safely be assumed independent of the type or the environment of the hydroxyl group.

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REFERENCES

1. Pulay P. in the book: *Ab initio Methods in Quantum Chemistry — II* (K. P. Lawley, Ed.), *Advances in Chemical Physics*, Vol. 69, p. 241. Wiley, Chichester 1987.
2. Hess jr B. A., Schaad L. J., Čársky P., Zahradník R.: Chem. Rev. *86*, 7709 (1986).
3. Bell A. T., Hair M. L.: *Vibrational Spectroscopies for Adsorbed Species, ACS Symposium series 137 (1980)*. American Chemical Society, Washington 1980.
4. Kazansky V. B.: Kinet. Katal. *18* (5), 1179 (1977).
5. Kustov L. M., Borovkov V. Yu., Kazansky V. B.: J. Catal. *72*, 149 (1981).
6. Böhm P. H., Knözinger H. in the book: *Catalysis — Science and Technology* (J. R. Andersen and M. Boudart, Eds), Vol. 4, p. 39. Springer, Berlin 1984.
7. Gibbs G. V.: Am. Mineral. *67*, 421 (1982).
8. Sauer J., Zahradník R.: Int. J. Quantum Chem. *26*, 793 (1984).
9. Sauer J.: Chem. Rev., submitted.
10. Sauer J., Mix H., Hill J.-R., Pfeifer H.: Unpublished results.
11. Hoy A. R., Mills I. M., Strey G.: Mol. Phys. *24*, 1265 (1972).
12. Ermler W. C., Rosenberg B. J., Shavitt I. in the book: *Comparison of ab initio Quantum Chemistry with Experiment for Small Molecules* (R. Bartlett, Ed.), p. 171. D. Reidel, Dordrecht 1985.
13. Marakami Y., Jijima A., Ward J. W. (Eds): *Proceedings of the 7th International Zeolite Conference*. Kodansha, Tokyo 1986.

14. Kazansky V. B., Kustov L. M., Borovkov V. Yu.: Zeolites *3*, 77 (1983).
15. Mortier W. J., Sauer J., Lercher J. A., Noller H.: J. Phys. Chem. *88*, 905 (1984).
16. Datka J., Geerlings P., Mortier W. J., Jacobs P.: J. Phys. Chem. *89*, 3488 (1985).
17. Mix H.: *Thesis.* Karl Marx University, Leipzig 1987.
18. Shen J. H., Klier K.: J. Colloid Interface Sci. *75*, 56 (1980).
19. Sauer J.: J. Phys. Chem. *91*, 2315 (1987).
20. Dupuis M., Rys J., King H. F.: Nat. Resour. Comput. Chem. Software Cat. *1*, Progr. No. QHO2 (HONDO5), (1980).
21. Čársky P., Hess jr. B. A., Schaad L. J.: J. Am. Chem. Soc. *105*, 396 (1983).
22. Čársky P.: *Program* GF. Prague 1981.
    McIntosh D. F., Michaelian K. H.: Can. J. Spectrosc. *24*, 35 (1979).
23. Francl M. M., Pietro W. J., Hehre W. J., Binkley J. S., Gordon M. S., De Frees D. J., Pople J. A.: J. Chem. Phys. *77*, 3654 (1982).
    Gordon M. S.: Chem. Phys. Lett. *76*, 163 (1980).
24. Swanton D. J., Bacskay G. B., Hush N. S.: Chem. Phys. *107*, 9 (1986).
25. Wilson E. B., Decius J. C., Cross P. C.: *Molecular Vibrations.* McGraw-Hill, New York 1955.
26. Nielsen H. H. in the book: *Handbuch der Physik* (S. Flügge, Ed.), Bd. 37/1. Springer Verlag, Berlin 1959.
27. Mills I. M. in the book: *Molecular Spectroscopy — Modern Research* (K. N. Rao and C. W. Mathews, Eds). Academic Press, New York 1972.