Potential Energy Surfaces for the Ground Electronic State of Water, Hydrogen Sulfide, and Hydrogen Selenide

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A curvilinear internal coordinate Hamiltonian is used to calculate vibrational term values of water, hydrogen sulfide, and hydrogen selenide variationally with Morse oscillator basis functions for the stretches and harmonic oscillator basis functions for the bend. Rotational parameters, α constants, are calculated with perturbation theory expressions. Potential energy parameters are optimized with the nonlinear least-squares method using vibrational term values, α constants, and Coriolis coupling coefficients as data. The model is applied to five isotopic species of water, five isotopic species of hydrogen sulfide, and to two isotopic species of hydrogen selenide. The observed vibrational and rotational data of the studied molecules are reproduced well. The potential energy surfaces obtained are in good agreement with surfaces determined by ab initio and previous empirical methods.

Introduction

Potential energy surfaces of polyatomic molecules play a key role in understanding quantitatively many structural and dynamical properties of molecular systems.[1] In the past, mainly experimental methods have been useful in obtaining information about potential energy surfaces. This situation is now rapidly changing because it has become possible to construct reliable surfaces for small molecular systems with electronic structure calculations. This development is particularly nice because often experimental data available are not adequate for these purposes. Indeed often the best surfaces can be obtained by combining the results from both experiment and theory.

The bent triatomic molecules water, hydrogen sulfide, and hydrogen selenide provide model systems for which there are large amounts of high-quality experimental spectroscopic vibration-rotation data available. In this paper we use these data to construct potential energy surfaces which are then compared with surfaces determined by high-level ab initio methods. Thus these molecules provide a test case for the empirical model used to interpret experimental data. This is important when one wants to extend empirical models to more complicated molecular systems for which it is impossible to use high-level ab initio methods.

In this work experimental vibration–rotation data of water, hydrogen sulfide, and hydrogen selenide are analyzed with a model where the vibrational problem is solved variationally and the rotational problem is solved with perturbation theory. The vibrational Hamiltonian is expressed in terms of curvilinear internal coordinates. It is obtained from an exact operator by expanding both the kinetic energy and potential energy terms as a Taylor series in terms of the Morse variable $y = 1 - \exp(-ar)$ for the stretching degrees of freedom and in terms of the curvilinear bending displacement coordinate for the bending degree of freedom.[2] The eigenvalues of this Hamiltonian are obtained by expanding the Hamiltonian in a basis whose functions are products of harmonic oscillator wave functions for the bend and Morse oscillator wave functions for the stretches. Coriolis constants, which are coefficients of rovibrational coupling terms between different vibrational levels, are calculated from the harmonic part of the potential energy surface.[3] Standard perturbation theory formulas are used to calculate vibrationally diagonal α constants, which describe the vibrational dependence of rotational constants.[4–6] The same kind of formulas are also used to calculate vibrationally off-diagonal α constants, which are coefficients of

higher order coupling terms between rotational states of different close-lying vibrational levels. The potential energy parameters are optimized with the nonlinear least-squares method. The data included in these fits consist of vibrational term values, Coriolis coupling coefficients, and α constants.

Theoretical Model

The vibrational Hamiltonian for polyatomic molecules can be written in terms of curvilinear internal coordinates $\mathbf{r}$ and their conjugate momenta $\mathbf{p}_r$ as[2,7,8]

$$H = \tfrac{1}{2}\mathbf{p}_r{}^\dagger \mathbf{g}(\mathbf{r})\mathbf{p}_r + V'(\mathbf{r}) + V(\mathbf{r}) \qquad (1)$$

where $\mathbf{g}(\mathbf{r})$, which is often called Wilson's g matrix, is a function of curvilinear internal coordinates and atomic masses.[9] $V'(\mathbf{r})$ is a kinetic energy term which does not involve momentum operators. It is of pure quantum mechanical origin. Therefore, its effect is often small.[2,8,10] $V(\mathbf{r})$ is the usual potential energy function expressed in terms of curvilinear internal coordinates.

For the present purposes a suitable Hamiltonian for bent XY_2 molecules is obtained from eq 1 by neglecting V' and expanding both the g matrix elements and the potential energy function in terms of the curvilinear internal displacement coordinate $\theta = \varphi - \varphi_e$ for the bend and in terms of the Morse variables $y_i = 1 - \exp(-ar_i)$ ($i = 1$ or 2) for the stretches. φ is an instantaneous valence angle and φ_e is its equilibrium value. $r_1 = R_1 - R_e$ and $r_2 = R_2 - R_e$, where R_1 and R_2 are instantaneous bond lengths and R_e is their equilibrium value. a is the Morse parameter which appears in the Morse potential energy function.[11] The Hamiltonian adopted in this work takes the form

$$H = T + V = \sum_{i=0}^{5} H_i \qquad (2)$$

where

$$\begin{aligned}
H_0 &= \tfrac{1}{2}g_{rr}^{(e)}(p_1{}^2 + p_2{}^2) + g_{rr'}^{(e)}p_1 p_2 + D_e(y_1{}^2 + y_2{}^2) + \\
&\quad a^{-2}f_{rr'}y_1 y_2 + T_1(y_1{}^3 + y_2{}^3) + T_2(y_1{}^4 + y_2{}^4) + \\
&\quad \tfrac{1}{2}(a^{-3}f_{rrr} + a^{-2}f_{rr'})(y_1{}^2 y_2 + y_1 y_2{}^2) \quad (3)
\end{aligned}$$

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TABLE I: Matrix Elements for the Harmonic Oscillator and for the Morse Oscillator Used in This Work[a]

$$\langle v|p_\theta|v + 1 \rangle = -i^1/_2\hbar\alpha_\theta^{1/2}[2(v + 1)]^{1/2}$$
$$\langle v|\theta|v + 1 \rangle = {}^1/_2\alpha_\theta^{-1/2}[2(v + 1)]^{1/2}$$
$$\langle v|p_\theta^2|v + 2 \rangle = -{}^1/_2\hbar^2\alpha_\theta^{1/2}[(v + 1)(v + 2)]^{1/2}$$
$$\langle v|p_\theta^2|v \rangle = \hbar^2\alpha_\theta(v + {}^1/_2)$$
$$\langle v|\theta^2|v + 2 \rangle = {}^1/_2\alpha_\theta^{-1}[(v + 1)(v + 2)]^{1/2}$$
$$\langle v|\theta^2|v \rangle = \alpha_\theta^{-1}(v + {}^1/_2)$$
$$\langle v|p_\theta\theta + \theta p_\theta|v + 2 \rangle = -i\hbar[(v + 1)(v + 2)]^{1/2}$$
$$\langle v|p_\theta\theta + \theta p_\theta|v \rangle = 0$$
$$\langle v|p_\theta\theta p_\theta|v + 3 \rangle = -{}^1/_2\hbar^2\alpha_\theta^{1/2}[{}^1/_2(v + 1)(v + 2)(v + 3)]^{1/2}$$
$$\langle v|p_\theta\theta p_\theta|v + 1 \rangle = {}^1/_2\hbar^2\alpha_\theta^{1/2}(v + 1)[{}^1/_2(v + 1)]^{1/2}$$
$$\langle v|\theta^3|v + 3 \rangle = {}^1/_2\alpha_\theta^{-3/2}[{}^1/_2(v + 1)(v + 2)(v + 3)]^{1/2}$$
$$\langle v|\theta^3|v + 1 \rangle = (3/2)\alpha_\theta^{-3/2}(v + 1)[{}^1/_2(v + 1)]^{1/2}$$
$$\langle v|p_\theta\theta^2 p_\theta|v + 4 \rangle = -(1/4)\hbar^2[(v + 1)(v + 2)(v + 3)(v + 4)]^{1/2}$$
$$\langle v|p_\theta\theta^2 p_\theta|v + 2 \rangle = 0$$
$$\langle v|p_\theta\theta^2 p_\theta|v \rangle = (1/4)\hbar^2(2v^2 + 2v + 3)$$
$$\langle v|\theta^4|v + 4 \rangle = (1/4)\alpha_\theta^{-2}[(v + 1)(v + 2)(v + 3)(v + 4)]^{1/2}$$
$$\langle v|\theta^4|v + 2 \rangle = {}^1/_2\alpha_\theta^{-2}(2v + 3)[(v + 1)(v + 2)]^{1/2}$$
$$\langle v|\theta^4|v \rangle = (3/4)\alpha_\theta^{-2}(2v^2 + 2v + 1)$$

$$\left\langle n\left|\left(\frac{1}{2}g_{rr}^{(e)}p_j^2 + D_e y_j^2\right)/hc\right|n\right\rangle = \omega(n + {}^1/_2) - \omega x(n + {}^1/_2)^2$$

$$= \frac{2a\hbar}{hc}\left(\frac{1}{2}D_e g_{rr}^{(e)}\right)^{1/2}\left(n + \frac{1}{2}\right) - \frac{a^2\hbar^2 g_{rr}^{(e)}}{2hc}\left(n + \frac{1}{2}\right)^2$$

$$\langle n + l|p_j|n \rangle = \frac{1}{2}i\hbar(-1)^{l+1}a\left\{\frac{(k - 2n - 1)[k - 2(n + l) - 1](n + 1)(n + 2)...(n + l)}{(k - n - 1)(k - n - 2)...(k - n - l)}\right\}^{1/2}$$

$$\langle n|p_j|n \rangle = 0$$

$$\langle n + l|y_j|n \rangle = -i\left(\frac{g_{rr}^{(e)}}{2D_e}\right)^{1/2}\langle n + l|p_j|n \rangle$$

$$\langle n|y_j|n \rangle = \langle n|y_j^2|n \rangle = (2n + 1)/k$$

$$\langle n + l|y_j^2|n \rangle = \left[\frac{l(2n + l + 1)}{k} - (l - 1)\right]\langle n + l|y_j|n \rangle$$

$$\langle n + l|y_j^3|n \rangle = \left\{-\frac{3l(k - 2n - l - 1)}{k} + \frac{\left[\frac{1}{2}(l + 1)(k - n - l + 1) + n(2 - l)\right](l + 2)(k - n - l) + \frac{1}{2}(2 - l)(1 - l)n(n - 1)}{k^2}\right\}\langle n + l|y_j|n \rangle$$

$$\langle n|y_j^3|n \rangle = \frac{6n(n + 1) + 1}{k^2} - \frac{2n(2n^2 + 3n + 1)}{k^3}$$

$$\langle n + l|y_j^4|n \rangle = -(1/6)[(l - 3)(l - 2)(l - 1) - (3/k)(l - 1)(l^2 - 3l - 2)(2n + l + 1) + (1/k^2)[3(2n + l + 1)^2(l^3 - 2l^2 - 4l + 1) -$$
$$4l^3 + 3l^2 + 16l + 9] - (1/k^3)l[(2n + l + 1)^2 - 4](l^2 - 4)(2n + l + 1)]\langle n + l|y_j|n \rangle$$

$$\langle n|y_j^4|n \rangle = \frac{6n(n + 1) + 3}{k^2} - \frac{2[n^3 + (n + 1)^3]}{k^3}$$

[a] $\alpha_\theta = 2\pi c\omega_\theta/\hbar g_{\theta\theta}^{(e)} = (f_{\theta\theta}/g_{\theta\theta}^{(e)})^{1/2}/\hbar$, $k = (2/a\hbar)(2D_e/g_{rr}^{(e)})_e = \omega/\omega x$; v and n are vibrational quantum numbers for the harmonic and the Morse oscillator respectively. l is an integer ≥ 1. $j = 1$ or 2.

$$H_1 = (1/2)g_{\theta\theta}^{(e)}p_\theta^2 + (1/2)f_{\theta\theta}\theta^2 + (1/2)\left(\frac{\partial g_{\theta\theta}}{\partial\theta}\right)_e p_\theta\theta p_\theta +$$

$$(1/6)f_{\theta\theta\theta}\theta^3 + (1/4)\left(\frac{\partial^2 g_{\theta\theta}}{\partial\theta^2}\right)_e p_\theta\theta^2 p_\theta + (1/24)f_{\theta\theta\theta\theta}\theta^4 \quad (4)$$

$$H_2 = g_{r\theta}^{(e)}(p_1 + p_2)p_\theta + a^{-1}f_{r\theta}(y_1 + y_2)\theta \quad (5)$$

$$H_3 = (1/2)a^{-1}\left(\frac{\partial g_{\theta\theta}}{\partial r}\right)_e (y_1 + y_2)p_\theta^2 +$$

$$(1/2)\left(\frac{\partial g_{r\theta}}{\partial\theta}\right)_e (p_1 + p_2)(p_\theta\theta + \theta p_\theta) + (1/2)a^{-1}f_{r\theta\theta}(y_1 + y_2)\theta^2$$

$$(6)$$

$$H_4 = (1/4)\left[a^{-2}\left(\frac{\partial^2 g_{\theta\theta}}{\partial r^2}\right)_e + a^{-1}\left(\frac{\partial g_{\theta\theta}}{\partial r}\right)_e\right](y_1^2 + y_2^2)p_\theta^2 +$$

$$(1/4)(a^{-2}f_{rr\theta\theta} + a^{-1}f_{r\theta\theta})(y_1^2 + y_2^2)\theta^2 \quad (7)$$

and

$$H_5 = (1/2)(a^{-2}f_{rr\theta} + a^{-1}f_{r\theta})(y_1^2 + y_2^2)\theta + \left(\frac{\partial g_{rr}}{\partial\theta}\right)_e p_1 p_2\theta +$$

$$a^{-1}\left(\frac{\partial g_{r\theta}}{\partial r'}\right)_e (y_2 p_1 + y_1 p_2)p_\theta + a^{-2}f_{rr'\theta}y_1 y_2\theta \quad (8)$$

$p_j = -i\hbar(\partial/\partial r_j)$ ($j = 1$ or 2) and $p_\theta = -i\hbar(\partial/\partial\theta)$ are momenta conjugate to r_j and θ, respectively. H_0 and H_1 contain the pure stretching and bending terms, respectively. H_2 contains bilinear coupling terms between the stretches and the bend, H_3 is the Fermi resonance operator, H_4 is a quartic coupling operator between the stretches and the bend, and H_5 contains some additional cubic coupling terms. Except for the potential energy terms in T_1 and T_2, the Hamiltonian is identical with the one given in ref 2 where more details can be found. The **g** matrix elements, their equilibrium values, and their derivatives are also given in ref 2. The coefficients of the Hamiltonian are written such that the usual spectroscopic quantities as force constants possess their usual meanings.

The eigenvalues of the Hamiltonian given in eqs 2–8 are obtained variationally with a basis whose functions are products of

TABLE II: Potential Energy Parameters for Water[a]

parameter	this work	HC[b]	J[c]	anh ff[d]	ab initio[e]
D_e/aJ	0.8514 (170)	0.9997 (44)			
a/Å⁻¹	2.2259 (210)	2.0531 (45)			
T_1/aJ	0[g]				
T_2/aJ	0.0557 (110)				
f_{rr}/aJ Å⁻²	8.437[f]	8.428[f]	8.43938 (19)	8.454 (1)	8.4430 (16)
f_{rrr}/aJ Å⁻³	−56.34[f]	−51.91[f]	−55.40 (33)	−58.2 (23)	−58.81 (6)
f_{rrrr}/aJ Å⁻⁴	325.42[f]	248.7[f]	306.0 (47)	367 (50)	368 (18)
$f_{\theta\theta}$/aJ	0.71758 (280)	0.6990 (12)	0.70700 (12)	0.697 (1)	0.7286 (3)
$f_{\theta\theta\theta}$/aJ	−0.6538 (310)	−0.9186 (94)	−0.7332 (70)	−0.9 (1)	−0.6882 (28)
$f_{\theta\theta\theta\theta}$/aJ	−1.098 (120)	−0.1[h]	−0.238 (19)	−0.1 (2)	−0.68 (22)
$f_{rr'}$/aJ Å⁻²	−0.08531 (580)	−0.101[h]	−0.10515 (16)	−0.101 (1)	−0.1000 (11)
$f_{rrr'}$/aJ Å⁻³	−0.3963 (890)	0.645 (69)	−0.318 (20)	−0.8 (3)	−0.079 (17)
$f_{r\theta}$/aJ Å⁻¹	0.3644 (120)	0.219[h]	0.30641 (23)	0.219 (2)	0.2631 (3)
$f_{r\theta\theta}$/aJ Å⁻¹	−0.2910 (460)	−0.314 (14)	−0.3383 (62)	−0.2 (1)	−0.3079 (19)
$f_{rr'\theta}$/aJ Å⁻²	0[g]	1.341 (73)	−0.252 (55)	0.4 (2)	−0.084 (18)
$f_{rr'\theta}$/aJ Å⁻²	−0.3163 (550)	0.414 (52)	−0.447 (25)	−0.6 (2)	−0.505 (15)
$f_{rr\theta\theta}$/aJ Å⁻²	−0.212 (410)	−2[h]	−0.950 (51)	−2 (1)	−0.28 (88)

[a] Uncertainties given in parentheses are one standard error (this work) or as quoted in references. The surface of this work is obtained with the equilibrium structure R_e = 0.9575 Å, φ_e = 104.51° (ref 44). The surfaces from the quoted references contain more parameters than given in this table. [b] From Halonen and Carrington (ref 2). [c] From Jensen (ref 21). [d] From the anharmonic force field calculation of Mills (ref 19). [e] From ref 41. [f] Calculated from D_e, a, and T_2 using eqs 15. [g] Constrained value in the least-squares calculation. [h] Constrained to the value from ref 19.

harmonic oscillator wave functions for the bend and the Morse oscillator eigenfunctions for the stretches. The Morse oscillator eigenfunctions are symmetrized as described in previous papers.[2,12] Analytical matrix elements are employed in all cases.[9,13-15] This can be achieved by setting the Morse basis functions to be consistent with the Morse parameter a and the Morse dissociation energy D_e. All matrix elements needed in this work are given in Table I.

The rotational motion is included in the model by introducing perturbation theory in the rectilinear normal-coordinate representation.[4-6] For the present purposes the significant effects to be considered are both vibrational dependence of rotational constants and Coriolis and α resonances between rotational states of close-lying vibrational states.[16] The vibration–rotation operators which are responsible for these effects can be obtained by expanding the general vibration–rotation Hamiltonian expressed in terms of dimensionless normal coordinates $q_r = (4\pi^2 c\omega_r/h)^{1/2}Q_r$, their conjugate momentum operators $p_r = -i(\partial/\partial q_r)$ (where r = 1, 2, and 3 for the symmetric stretch, bend, and the antisymmetric stretch), and in terms of molecule-fixed Cartesian components $\hat{J}_x$, $\hat{J}_y$, and $\hat{J}_z$ of the total angular momentum $\hat{\mathbf{J}}$.[4-6] Q_r is the usual rth normal coordinate and ω_r is the corresponding harmonic wavenumber.[9] When the molecular axes are chosen to be principal axes such that the z axis is the C_2 axis and the y axis is perpendicular to the molecular plane, the operator responsible for vibrational dependence of the rotational constants becomes (r = 1, 2, or 3; ξ = x, y, or z)

$$H_{22}/hc = -(1/2)\sum_r\sum_\xi \alpha_r^{(\xi)}(p_r^2 + q_r^2)\hat{J}_\xi^2 \tag{9}$$

the Coriolis operator connecting rotational states of stretching vibrational states is

$$H_{21}/hc = -2B_e^{(y)}\zeta_{13}^{(y)}[(\omega_3/\omega_1)^{1/2}q_1p_3 - (\omega_1/\omega_3)^{1/2}p_1q_3]\hat{J}_y \tag{10}$$

and the α resonance operator between the rotational states of stretching states is

$$H_{22}^{(a)}/hc = \tfrac{1}{2}\alpha_{13}^{(xz)}(q_1q_3 + p_1p_3)(\hat{J}_z\hat{J}_x + \hat{J}_x\hat{J}_z) \tag{11}$$

When harmonic oscillator formulas are employed, the H_{22} operators given in eq 9 give rise to the usual expression for rotational constants as follows[4,17]

$$B^{(\xi)} = B_e^{(\xi)} - \alpha_1^{(\xi)}(v_1 + \tfrac{1}{2}) - \alpha_2^{(\xi)}(v_2 + \tfrac{1}{2}) - \alpha_3^{(\xi)}(v_3 + \tfrac{1}{2}) \tag{12}$$

where $B_e^{(\xi)}$ is the equilibrium rotational constant associated with the axis ξ and v_1, v_2, and v_3 are customary normal-mode quantum numbers for the symmetric stretch, bend, and the antisymmetric stretch. In principle, eq 12 should be a power series but the higher order terms are often small and they are neglected in this paper. In the present application we are dealing only with fundamentals in obtaining information about the vibration–rotation parameters $\alpha_r^{(\xi)}$, $\zeta_{13}^{(y)}$, and $\alpha_{13}^{(xz)}$. Due to the large separation of stretching and bending fundamentals the Coriolis and α interactions between the rotational states of stretching and bending levels are treated with perturbation theory when theoretical expressions are derived for the spectroscopic parameters.

The Coriolis coupling coefficient $\zeta_{13}^{(y)}$ is a function of equilibrium structure and harmonic part of the potential energy surface of the molecule in question.[3] The α parameters depend on both the quadratic and the cubic force field. The standard theoretical expression for the $\alpha_r^{(\xi)}$ constants takes the form[4]

$$\alpha_r^{(\xi)} = -\frac{2(B_e^{(\xi)})^2}{\omega_r}\left\{\sum_\epsilon \frac{3(a_r^{(\epsilon\xi)})^2}{4I_\epsilon^{(e)}} + \tfrac{1}{2}\sum_s (\zeta_{rs}^{(\xi)})^2\left[\frac{(\omega_r + \omega_s)^2}{\omega_s(\omega_r - \omega_s)} - \frac{(\omega_r - \omega_s)^2}{\omega_s(\omega_r + \omega_s)}\right] + \pi(c/h)^{1/2}\sum_s \phi_{rrs}\, a_s^{(\xi\xi)}\omega_r/\omega_s^{3/2}\right\} \tag{13}$$

and for the $\alpha_{13}^{(xz)}$ constant[5]

$$\alpha_{13}^{(xz)} = \frac{4B_e^{(x)}B_e^{(z)}a_3^{(xz)}}{(\omega_1\omega_3)^{1/2}}\left[(3/8)(a_1^{(xx)}/I_x^{(e)} + a_1^{(zz)}/I_z^{(e)}) + \pi(c/h)^{1/2}\phi_{133}\frac{\omega_1^{1/2}\omega_3}{\omega_3^2 - (\omega_1 - \omega_3)^2}\right] \tag{14}$$

where $I_\epsilon^{(e)} = I_{\epsilon\epsilon}^{(e)}$ is the equilibrium moment of inertia around the ϵ (=x, y, or z) axis, ω_r is the harmonic wavenumber of the rth mode, $a_r^{(\epsilon\xi)} = (\partial I_{\epsilon\xi}/\partial Q_r)_e$, and $\phi_{rrs} = (\partial^3 V/\partial q_r^2\, \partial q_s)_e$ is a cubic force constant in the dimensionless rectilinear normal-coordinate representation. The $a_r^{(\epsilon\xi)}$ and ω_r parameters can be calculated from the structure and the harmonic part of the potential energy function.[9,16] The transformation from the curvilinear internal coordinate force constants f to the force constants ϕ in the dimensionless rectilinear normal-coordinate representation is performed with the L tensor formalism as described in detail in the past.[18,19]

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TABLE III: Potential Energy Parameters for Hydrogen Sulfide[a]

parameter	this work	HC[b]	anh ff[c]	ab initio[d]
D_e/aJ	0.69445 (450)	0.7722 (17)		
a/Å^{-1}	1.75637 (570)	1.6656 (21)		
T_1/aJ	0[e]			
T_2/aJ	0.05177 (360)			
f_{rr}/aJ Å^{-2}	4.285[f]	4.284[f]	4.284 (2)	4.299
f_{rrr}/aJ Å^{-3}	-22.58[f]	-21.406[f]	-23.4 (3)	-22.5
f_{rrrr}/aJ Å^{-4}	104.34[f]	83.19[f]	120 (6)	103.4
$f_{\theta\theta}$/aJ	0.76269 (340)	0.75866 (65)	0.758 (5)	0.765
$f_{\theta\theta\theta}$/aJ	-0.2221 (110)	-0.1[g]	-0.1 (1)	-0.28
$f_{\theta\theta\theta\theta}$/aJ	-0.770 (280)	-0.9[g]	-0.9 (1)	-0.04
$f_{rr'}$/aJ Å^{-2}	-0.02014 (200)	-0.01864 (94)	-0.015 (5)	-0.014
$f_{rrr'}$/aJ Å^{-3}	0[e]		-0.1 (1)	-0.02
$f_{r\theta}$/aJ Å^{-1}	0.12075 (320)	0.054[g]	0.054 (30)	0.076
$f_{r\theta\theta}$/aJ Å^{-1}	-0.2668 (230)	-0.2268 (69)	-0.2 (1)	-0.35
$f_{rr\theta}$/aJ Å^{-2}	0[e]		-0.4 (1)	-0.04
$f_{rr'\theta}$/aJ Å^{-2}	-0.2074 (120)		-0.2 (1)	-0.19
$f_{rr\theta\theta}$/aJ Å^{-2}	-1.251 (200)	-1.6[g]	-1.6 (7)	-0.46

[a] Uncertainties given in parentheses are one standard error (this work) or as quoted in references. The surface of this work is obtained with the equilibrium structure R_e = 1.3356 Å, φ_e = 92.12° (ref 44). The surfaces taken from the quoted references contain more parameters than given in this table. [b] From Halonen and Carrington (ref 2). [c] From the anharmonic force field calculation of Mills (ref 19). [d] From ref 42. [e] Constrained value in the least squares calculation. [f] Calculated from D_e, a, and T_2 using eqs 15. [g] Constrained to the value from ref 19.

TABLE IV: Potential Energy Parameters for Hydrogen Selenide[a]

parameter	this work	HC[b]	anh ff[c]	ab initio[d]
D_e/aJ	0.63112 (520)	0.7059 (13)		
a/Å^{-1}	1.66570 (690)	1.5752 (17)		
T_1/aJ	0[e]			
T_2/aJ	0.04835 (400)			
f_{rr}/aJ Å^{-2}	3.501[f]	3.503[f]	3.507 (10)	3.485
f_{rrr}/aJ Å^{-3}	-17.50[f]	-16.556[f]	-16.7 (3)	-17.390
f_{rrrr}/aJ Å^{-4}	76.95[f]	60.85[f]	63 (5)	75.761
$f_{\theta\theta}$/aJ	0.69959 (190)	0.71741 (59)	0.710 (10)	0.760
$f_{\theta\theta\theta}$/aJ	-0.1609 (150)	-0.7[g]	-0.70 (4)	-0.315
$f_{\theta\theta\theta\theta}$/aJ	0[e]	-0.09[g]	-0.09 (3)	-1.074
$f_{rr'}$/aJ Å^{-2}	-0.02168 (200)	-0.02268 (75)	-0.024 (10)	-0.013
$f_{rrr'}$/aJ Å^{-3}	0[e]		0.00 (1)	-0.019
$f_{r\theta}$/aJ Å^{-1}	0.07999 (850)	0.130[g]	0.130 (50)	0.075
$f_{r\theta\theta}$/aJ Å^{-1}	-0.2745 (280)	-0.1901 (85)	-0.2 (1)	-0.355
$f_{rr\theta}$/aJ Å^{-2}	-0.0677 (440)		-0.3 (1)	-0.110
$f_{rr'\theta}$/aJ Å^{-2}	-0.3321 (120)		0.1 (1)	-0.220
$f_{rr\theta\theta}$/aJ Å^{-2}	-0.756 (220)	-1.8[g]	-1.8 (6)	-0.646

[a] Uncertainties given in parentheses are one standard error (this work) or as quoted in references. The surface of this work is obtained with the equilibrium structure R_e = 1.460 Å, φ_e = 90.57° (ref 44). The surfaces from the quoted references contain more parameters than given in this table. [b] From Halonen and Carrington (ref 2). [c] From the anharmonic force field calculation of Mills (ref 19). [d] From ref 43. [e] Constrained value in the least-squares calculation. [f] Calculated from D_e, a, and T_2 using eqs 15. [g] Constrained to the value from ref 19.

Potential energy parameters are optimized with the nonlinear least-squares method.[14] The experimental data set included in these calculations consists of vibrational term values, Coriolis coupling coefficients, and α constants.

Application of the Model to H_2O, H_2S, and H_2Se

We have started the least-squares optimizations of the potential energy parameters from the surfaces obtained before with a model where only vibrational term value data were included.[2] One object of our calculations is to find out how well the model and the experimental data set available are able to determine potential energy surfaces. For this reason we have decided either to optimize the potential energy parameters freely or to constrain them to zero. No constraints are made to ab initio values or to values of surfaces from other empirical methods. Vibrational term values, α constants, and Coriolis coupling coefficients of five different isotopic species of water ($H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, $D_2^{16}O$, and $T_2^{16}O$), five of hydrogen sulfide ($H_2^{32}S$, $H_2^{33}S$, $H_2^{34}S$, $D_2^{32}S$, and $D_2^{34}S$), and

TABLE V: Observed and Calculated Vibrational Term Values (cm^{-1}) for Water[a]

normal $v_1v_2v_3$	local $mn^{\pm}v$	$H_2^{16}O$ obsd	o – c	$H_2^{17}O$ obsd	o – c	$H_2^{18}O$ obsd	o – c
010	00+1	1594.75	0.52	1591.32	0.63	1588.28	0.77
020	00+2	3151.64	1.46	3144.98	1.18	3139.05	1.85
100	10+0	3657.05	-2.75	3653.15	-3.12	3649.69	-3.44
001	10-0	3755.93	2.92	3748.32	2.94	3741.57	2.97
030	00+3	4666.78	0.98			4648.46	1.47
110	10+1	5234.99	0.91	5227.75	0.61	5221.25	0.45
011	10-1	5331.27	-1.53	5320.26	-1.34	5310.46	-1.14
040	00+4	6134.03	-3.34				
120	10+2	6775.10	7.48			6755.51	7.07
021	10-2	6871.52	-3.74			6844.60	-3.17
200	20+0	7201.54	-6.48			7185.90	-7.55
101	20-0	7249.82	0.39	7238.73	0.03	7228.90	-0.24
002	11+0	7445.07	4.02			7418.72	3.84
130	10+3	8273.98	14.91				
031	10-3	8373.85	-5.43				
210	20+1	8761.58	-2.42				
111	20-1	8807.00	-2.92				
012	11+1	9000.14[b]	-4.15				
041	10-4	9833.58	-8.22			9795.33	-7.43
220	20+2	10284.4	7.73			10256.58	6.36
121	20-2	10328.72	-0.89			10295.63	-1.02
022	11+2	10524.3	-5.50				
300	30+0	10599.66	-6.29			10573.92	-7.13
201	30-0	10613.41	-1.28			10585.28	-2.43
102	21+0	10868.86	-0.10			10839.96	-1.73
003	21-0	11032.40	4.88			10993.68	4.86
131	20-3	11813.19	4.04				
310	30+1	12139.2	-7.79				
211	30-1	12151.26	-6.31				
112	21+1	12407.64	-1.56				
013	21-1	12565.00	-9.93				
221	30-2	13652.65	-1.35				
400	40+0	13828.3[b]	1.09				
301	40-0	13830.92	1.17				
122	21+2	13910.8[b]	1.85				
023	21-2	14066.19[b]	-19.03				
202	31+0	14221.14	-6.08				
103	31-0	14318.80	7.08				
004	22+0	14536.87[b]	5.06				
231	30-3	15119.03	8.10				
410	40+1	15344.50	1.34				
311	40-1	15347.95	-8.77				
212	31+1	15742.79	-3.66				
113	31-1	15832.76	-6.22				
420	40+2	16821.63	7.71				
321	40-2	16825.23	4.86				
500	50+0	16898.42	0.21				
401	50-0	16898.83	0.73				
222	31+2	17227.7[b]	11.40				
123	31-2	17312.54[b]	-7.92				
302	41+0	17458.20	-2.05				
203	41-0	17495.52	8.57				
104	32+0	17748.07[b]	7.11				
331	40-3	18265.82[b]	12.09				
510	50+1	18392.97[b]	-11.34				
411	50-1	18393.31[b]	-10.22				
213	41-1	18989.96[b]	-5.68				

normal $v_1v_2v_3$	local $mn^{\pm}v$	$D_2^{16}O$ obsd	o – c	$T_2^{16}O$ obsd	o – e
010	00+1	1178.38	-0.99	995.37	-2.05
020	00+2	2336.84	-1.17		
100	10+0	2671.65	2.40	2237.15	5.47
001	10-0	2787.72	2.85	2366.61	2.70
011	10-1	3956.21	-0.81		
021	10-2	5105.44	-3.25		
200	20+0	5291.60	3.15		
101	20-0	5373.98	4.66		
210	20+1	6452.91	4.33		
111	20-1	6533.24	0.94		
300	30+0	7853.0[c]	2.78		
201	30-0	7899.80	5.12		
112	21+1	9205.86	4.37		
013	21-1	9376.05	4.90		

[a] Many of the quantum labels given are only qualitative due to strong Fermi and local-mode resonances. o – c denotes observed minus calculated value. Experimental data are taken from ref 2 (where references to original experimental work are found) and from refs 20 and 22. [b] Not included in the fit due to convergence difficulties in the least-squares calculation. [c] Uncertain data. Not included in the fit.

TABLE VI: Observed and Calculated Vibrational Term Values (cm⁻¹) for Hydrogen Sulfide[a]

normal $v_1v_2v_3$	local $mn^{\pm}v$	H₂³²S obsd	o − c	H₂³³S obsd	o − c	H₂³⁴S obsd	o − c
010	00⁺1	1182.57	0.05	1182.02	0.07	1181.50	0.08
020	00⁺2	2353.97	−0.14	2352.87	−0.11	2351.84	−0.09
100	10⁺0	2614.41	−0.13	2613.35	−0.18	2612.36	−0.21
001	10⁻0	2628.46	0.16	2627.25	0.14	2626.12	0.14
110	10⁺1	3779.17	2.13				
011	10⁻1	3789.28	−0.36				
021	10⁻2	4939.23	−0.75				
200	20⁺0	5145.12	0.15				
101	20⁻0	5147.36	−0.17				
210	20⁺1	6288.15	1.38			6283.01	1.29
111	20⁻1	6289.17	0.26			6283.96	0.22
012	11⁺1	6388.73[b]	5.04				
300	30⁺0	7576.3	0.48				
201	30⁻0	7576.3	0.19				
102	21⁺0	7751.9	−2.69				
003	21⁻0	7779.2	1.56				
211	30⁻1	8697.3	−0.12				
301	40⁻0	9911.05	2.01				
202	31⁺0	10188.25	−1.09				
103	31⁻0	10194.48	−0.62				
311	40⁻1	11008.78	−1.93				

normal $v_1v_2v_3$	local $mn^{\pm}v$	D₂³²S obsd	o − c	D₂³⁴S obsd	o − c
010	00⁺1	855.40	−0.48	853.99	−0.43
100	10⁺0	1896.43	0.87		
001	10⁻0	1910.18	0.13		
110	10⁺1	2742.77	1.55		
011	10⁻1	2754.44	−0.57		
111	20⁻1	4592.32	0.72		

[a] Many of the quantum labels are only qualitative due to Fermi and local-mode resonances. o − c denotes observed minus calculated value. Experimental data are taken from ref 2 (where the references to original experimental work are found) and from ref 22–27. [b] Not included in the fit.

TABLE VII: Observed and Calculated Vibrational Term Values (cm⁻¹) for Hydrogen Selenide[a]

normal $v_1v_2v_3$	local $mn^{\pm}v$	H₂⁸⁰Se obsd	o − c	D₂⁸⁰Se obsd	o − c
010	00⁺1	1034.17	1.25	741.42	1.49
020	00⁺2	2059.97	−1.43		
100	10⁺0	2344.36	0.05	1686.70	−0.09
001	10⁻0	2357.66	0.90	1697.36	0.39
110	10⁺1	3361.72	2.11		
011	10⁻1	3371.81	−0.12		
200	20⁺0	4615.33	0.55		
101	20⁻0	4617.40	−0.00		
210	20⁺1	5612.73	0.18		
111	20⁻1	5613.72	−1.24		
300	30⁺0	6798.15	0.35		
201	30⁻0	6798.23	0.09		
102	21⁺0	6953.6	−1.07		
301	40⁻0	8894.6	0.01		

[a] Many of the quantum labels given are qualitative due to Fermi and local-mode interaction. Experimental data are taken from ref 2 where the references to original experimental work are found. o − c denotes observed minus calculated value.

TABLE VIII: Observed and Calculated α and Coriolis Constants for Water[a]

	H₂¹⁶O obsd	o − c	ref	H₂¹⁷O obsd	o − c	ref
$\alpha_1^{(A)}$	0.7584	0.0193	31	0.7602	0.0190	32
$\alpha_2^{(A)}$	−3.248	−0.648	30		[−2.581]	
$\alpha_3^{(A)}$	1.233	0.157	31	1.213	0.152	32
$\alpha_1^{(B)}$	0.2168	0.0236	31	0.2165	0.0258	32
$\alpha_2^{(B)}$	−0.1660	0.0181	30		[−0.1827]	
$\alpha_3^{(B)}$	0.0903	−0.0103	31	0.0930	−0.0084	32
$\alpha_1^{(C)}$	0.1732	−0.0053	31	0.1762	−0.0035	32
$\alpha_2^{(C)}$	0.1486	0.0079	30		[0.1399]	
$\alpha_3^{(C)}$	0.1396	0.0124	31	0.1381	0.0130	32
$\alpha_{13}^{(AB)}$	−0.638	0.013	31	−0.619	0.030	32
$\zeta_{13}^{(C)}$		[−0.043]			[−0.047]	

	H₂¹⁸O obsd	o − c	ref	D₂¹⁶O obsd	o − c	ref
$\alpha_1^{(A)}$	0.7622	0.0192	32	0.2398	−0.0028	33
$\alpha_2^{(A)}$		[−2.563]		−1.215	−0.178	34
$\alpha_3^{(A)}$	1.198	0.151	32	0.5329	0.0531	33
$\alpha_1^{(B)}$	0.2144	0.0259	32	0.0927	0.0095	33
$\alpha_2^{(B)}$		[−0.1814]		−0.0657	0.0078	34
$\alpha_3^{(B)}$	0.0941	−0.0080	32	0.0278	−0.0034	33
$\alpha_1^{(C)}$	0.1770	−0.0040	32	0.0653[b]	0.0018[b]	33
$\alpha_2^{(C)}$		[0.1392]		0.0555	0.0021	34
$\alpha_3^{(C)}$	0.1375	0.0144	32	0.0527[b]	0.0025[b]	33
$\alpha_{13}^{(AB)}$	−0.597	0.050	32	−0.263	−0.019	33
$\zeta_{13}^{(C)}$		[−0.050]		0.053[c]	0.035	33

[a] The α constants are in cm⁻¹ and the Coriolis coupling coefficients are dimensionless. References are for observed data. The ground-state rotational constants needed to calculate α constants are taken from refs 28, 29, and 33. o − c denotes observed minus calculated value. Numbers in square brackets are calculated values. [b] Coriolis contribution due to a term in $\zeta_{13}^{(C)}$ have been excluded both from the observed and the calculated values (see eq 10 and the text). [c] Not included in the fit.

two of hydrogen selenide (H₂⁸⁰Se and D₂⁸⁰Se) are included as data in the potential parameter optimization.[2,20–40] The experimental α and Coriolis constants are obtained from the analyses of fundamental bands. In the case of D₂¹⁶O, H₂³²S, H₂³³S, H₂³⁴S, D₂³²S, D₂³⁴S, and H₂⁸⁰Se very small Coriolis resonance contributions [first term in ($\zeta_{13}^{(C)}$)² of eq 13] due to close-lying stretching vibrational

states are left out in calculating $\alpha_1^{(C)}$ and $\alpha_3^{(C)}$ constants (in all molecules included in this work A = x, B = z, and C = y when I_A is the smallest and I_C is the largest moment of inertia). In these cases the analyses of the stretching vibrational bands already include Coriolis interaction between rotational states of stretching states and thus the experimental constants $\alpha_1^{(C)}$ and $\alpha_3^{(C)}$ do not contain this contribution. The basis set sizes included in these calculations are such that all Morse basis functions ($|mn\rangle$ = $|m\rangle|n\rangle$) and all harmonic oscillator basis functions ($|v\rangle$) are included as follows: $m + n \leq 9$ and $v \leq 9$ for H₂¹⁶O; $m + n \leq 7$ and $v \leq 9$ for H₂¹⁸O; $m + n \leq 6$ and $v \leq 6$ for H₂¹⁷O and D₂¹⁶O;

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TABLE IX: Observed and Calculated α and Coriolis Constants for Hydrogen Sulfide[a]

	$H_2{}^{32}S$			$H_2{}^{33}S$			$H_2{}^{34}S$		
	obsd	o − c	ref	obsd	o − c	ref	obsd	o − c	ref
$\alpha_1^{(A)}$	0.1596	0.0019	24	0.1595	0.0017	24	0.1594	0.0015	24
$\alpha_2^{(A)}$	−0.3618	−0.0160	25	−0.362	−0.0168	25	−0.3615	−0.0169	25
$\alpha_3^{(A)}$	0.2178	−0.0013	24	[0.2183]			0.2157	−0.0019	24
$\alpha_1^{(B)}$	0.1237	0.0012	24	0.1236	0.0014	24	0.1234	0.0016	24
$\alpha_2^{(B)}$	−0.2063	−0.0086	25	−0.205	−0.0075	25	−0.2058	−0.0086	25
$\alpha_3^{(B)}$	0.0789	−0.0005	24	[0.0796]			0.0797	−0.0000	24
$\alpha_1^{(C)\,b}$	0.0698	0.0006	24	0.0697	0.0006	24	0.0697	0.0006	24
$\alpha_2^{(C)}$	0.0619	0.0023	25	0.061	0.0015	25	0.0615	0.0021	25
$\alpha_3^{(C)\,b}$	0.0544	0.0008	24	[0.0535]			0.0543	0.0008	24
$\alpha_{13}^{(AB)}$	−0.296	−0.021	24	[−0.275]			−0.292	−0.018	24
$\zeta_{13}^{(C)}$	−0.009[c]	0.006	24	[−0.016]			[−0.017]		

	$D_2{}^{32}S$			$D_2{}^{34}S$		
	obsd	o − c	ref	obsd	o − c	ref
$\alpha_1^{(A)}$	0.0554	0.0010	27		[0.0546]	
$\alpha_2^{(A)}$	−0.1333	−0.0041	27	−0.1325	−0.0041	27
$\alpha_3^{(A)}$	0.0862	−0.0010	27		[0.0860]	
$\alpha_1^{(B)}$	0.0479	0.0000	27		[0.0474]	
$\alpha_2^{(B)}$	−0.0740	−0.0011	27	−0.0737	−0.0012	27
$\alpha_3^{(B)}$	0.0260	−0.0002	27		[0.0265]	
$\alpha_1^{(C)\,b}$	0.0276	0.0021	27		[0.0254]	
$\alpha_2^{(C)}$	0.0227	0.0008	27	0.0226	0.0008	27
$\alpha_3^{(C)\,b}$	0.0175	−0.0021	27		[0.0195]	
$\alpha_{13}^{(AB)}$	−0.115	−0.013	27		[−0.101]	
$\zeta_{13}^{(C)}$	0.017[c]	−0.004	27		[0.017]	

[a] The α constants are in cm^{-1} and the Coriolis coupling coefficients are dimensionless. References are for observed data. The ground-state rotational constants needed to calculate α constants are taken from refs 35 and 36. o − c denotes observed minus calculated value. Numbers in square brackets are calculated values. [b] Coriolis contribution due to a term in $\zeta_{13}^{(C)}$ have been excluded both from the observed and the calculated values (see eq 10 and the text). [c] Not included in the fit.

TABLE X: Observed and Calculated α and Coriolis Parameters for Hydrogen Selenide[a]

	$H_2{}^{80}Se$			$D_2{}^{80}Se$		
	obsd	o − c	ref	obsd	o − c	ref
$\alpha_1^{(A)}$	0.113	0.002	38	0.043	0.004	40
$\alpha_2^{(A)}$	−0.249	−0.011	39	−0.092	−0.006	40
$\alpha_3^{(A)}$	0.176	0.002	38	0.053	−0.012	40
$\alpha_1^{(B)}$	0.113	0.002	38	0.038	−0.003	40
$\alpha_2^{(B)}$	−0.180	−0.006	39	−0.052	0.010	40
$\alpha_3^{(B)}$	0.058	0.000	38	0.018	−0.002	40
$\alpha_1^{(C)}$	0.055[b]	−0.001[b]	38	0.017	−0.003	40
$\alpha_2^{(C)}$	0.046	0.002	39	0.016	−0.000	40
$\alpha_3^{(C)}$	0.044[b]	−0.001[b]	38	0.017	0.001	40
$\alpha_{13}^{(AB)}$	−0.200	0.020	38	[−0.079]		
$\zeta_{13}^{(C)}$	−0.024	−0.001	38	[−0.009]		

[a] The α constants are in cm^{-1} and the Coriolis coupling coefficients are dimensionless. References are for observed data. The ground-state rotational constants needed to calculate α constants are taken from refs 37–40. o − c denotes observed minus calculated value. Numbers in square brackets are calculated values. [b] Coriolis contribution due to a term in $\zeta_{13}^{(C)}$ have been excluded both from the observed and the calculated values (see eq 10 and the text).

$m + n \leq 7$ and $v \leq 6$ for $H_2{}^{32}S$ and $H_2{}^{80}Se$; $m + n \leq 5$ and $v \leq 6$ for $H_2{}^{34}S$; $m + n \leq 4$ and $v \leq 6$ for $T_2{}^{16}O$ and $H_2{}^{33}S$; $m + n \leq 5$ and $v \leq 4$ for $D_2{}^{32}S$; and $m + n \leq 4$ and $v \leq 4$ for $D_2{}^{34}S$ and $D_2{}^{80}Se$. The Morse basis functions for the stretches are chosen to be consistent with the Morse dissociation energy D_e and the Morse parameter a. In water the harmonic wavenumbers of the harmonic oscillator basis functions are chosen to be slightly smaller than the corresponding values of $f_{\theta\theta}$: $\omega = 1400$ cm^{-1} in $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$; $\omega = 1100$ cm^{-1} in $D_2{}^{16}O$; and $\omega = 950$ cm^{-1} in $T_2{}^{16}O$. This ensures a slightly better convergence. In hydrogen sulfide and hydrogen selenide a good convergence is achieved by employing harmonic oscillator basis functions which are consistent with the bending force constant $f_{\theta\theta}$.

Tables II, III, and IV contain potential energy parameters of water, hydrogen sulfide, and hydrogen selenide determined in this work and comparisons with both ab initio and other empirical surfaces.[2,19,21,41-43] The force constants given are the usual derivatives of the potential energy function with respect to the curvilinear internal coordinates. The molecular structures needed in our calculations are also given in these tables.[44] Except for $T_1, f_{rr\theta}$ in H_2O and H_2S, f_{rrr} in H_2S and H_2Se, and $T_1, f_{\theta\theta\theta\theta}$ in H_2Se all potential energy parameters of the Hamiltonian in eqs 2–8 are optimized freely with the least-squares method. When $f_{rr\theta}$ or f_{rrr} is constrained to zero the whole potential energy term which contains the coefficient is constrained to zero. It was found that the inclusion of the term in T_1 resulted in convergence difficulties and that the other coefficients constrained to zero are small and insignificantly determined if included in the optimization. Tables II–IV also contain the quadratic, cubic, and quartic diagonal stretching force constants calculated from a, D_e, T_1, and T_2 with relations ($i = 1$ or 2)

$$f_{rr} = \left(\frac{\partial^2 V}{\partial r_i^2}\right)_e = 2a^2 D_e$$

$$f_{rrr} = \left(\frac{\partial^3 V}{\partial r_i^3}\right)_e = -6a^3(D_e - T_1)$$

$$f_{rrrr} = \left(\frac{\partial^4 V}{\partial r_i^4}\right)_e = a^4(14D_e - 36T_1 + 24T_2) \tag{15}$$

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The fits to vibrational term values are given in Tables V–VII and the fits to the rotational data are in Tables VIII–X. Uncertainties of 1 cm^{-1} are used for all vibrational term values included in the fits. Uncertainties used for the vibrationally diagonal α constants are as follows: 2% of the absolute value of the constant for water, 1% for hydrogen sulfide and $H_2{}^{80}Se$, and 20% for $D_2{}^{80}Se$. An uncertainty of 5% was attached to all vibrationally off-diagonal α constants and uncertainty of 10% to Coriolis coupling coefficients included in the fits. These estimates represent only relative uncertainties. The corresponding weights in the least-squares calculations are taken as $1/u^2$, where u is the uncertainty. Only in the case of hydrogen selenide are Coriolis coupling coefficients included in the fit. In the transformation from internal coordinate force constants to dimensionless normal-coordinate force constants needed to calculate α constants, the cubic force constants $f_{rr\theta}$ of water and hydrogen sulfide and the cubic force constant $f_{rr'}$ of hydrogen sulfide and hydrogen selenide, which are constrained to zero in calculating the vibrational term values, are obtained from potential energy terms in $f_{r\theta}$ and $f_{rr'}$, respectively, by expanding the Morse y variables. The inclusion of these force constants made only a minor contribution to the calculated α constants. Rms deviations obtained for vibrational term values and vibrationally diagonal α constants are as follows: 4.63 cm^{-1} and 0.0091 cm^{-1} for water, 0.94 cm^{-1} and 0.0017 cm^{-1} for hydrogen sulfide, and 0.92 and 0.0018 cm^{-1} for hydrogen selenide.

In water some mainly high wavenumber levels are left out from the fit due to convergence difficulties caused by the finite difference method adopted in the least-squares calculation.[14] In the water fit the high bending levels are not reproduced by the model as well as the other data. This can be expected due to the importance of the neglected V' term of the vibrational Hamiltonian in the case of near linear configurations of water.[2] In hydrogen sulfide and hydrogen selenide the barrier from the equilibrium bent to the linear configuration is much higher than in water. Consequently our model works much better for H_2S and H_2Se as is observed from Tables VI and VII. In any case one should be aware that an approximation has been made in neglecting the V' term. In ref 45, where a different coordinate system is used, it is found that the V'-like term is important and it even affects the two stretching fundamentals by a significant amount and in opposite directions. In ref 2 the importance of V' in water is checked by expanding it in a Taylor series. It is found that its effect should be relatively small.

Ab initio and previously determined empirical potential energy surfaces are compared in Tables II–IV with our results. In general the different surfaces are in excellent agreement with our surfaces. This is pleasing because apart from the study by Halonen and Carrington[2] the methods used in previous studies differ a lot from ours. In the anharmonic force field calculations for H_2O, H_2S,

and H_2Se both vibrational and rotational data are analyzed with perturbation theory.[19] In the study of water surface by Jensen a MORBID Hamiltonian is employed in a model which is more exact than ours.[21] A comparison of our results with those of Halonen and Carrington[2] shows nicely how essential it is to include rotational data in the analysis. In this work we are able to remove many of the constraints made before. Also in our work the stretching parts of the surfaces are much better in agreement with ab initio surfaces than in the previous calculations. In the case of water Jensen[21] is able to obtain better results than we are but in order to achieve this 19 ajustable potential energy parameters have been included compared with 12 in this work. The MORBID model is also much more complicated than ours, it is computationally heavy, and it might be difficult to extend it to larger molecules.

Conclusion

We have shown that the simple model presented in this paper produces reliable potential energy surfaces. The strength of our approach is its simplicity when compared with other more exact methods to model rovibrational energy levels of polyatomic molecules[21,46] (see also refs 18, 45, 47–56 and references therein for other methods to solve rovibrational energy levels of bent triatomic molecules). The various terms in the vibrational Hamiltonian adopted possess clear physical interpretations. Analytic formulas can be used in setting up Hamiltonian matrices. This makes calculations relatively fast and it enables one to optimize potential energy parameters with the nonlinear least-squares method. The perturbation theory modeling of rotational motion is standard and well-known. We believe that this mixture of perturbation theory and variational calculations would be useful in extending these models to larger molecules.

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