Stretching Vibrational Energy Levels of $^{1}H_{2}{}^{16}O$ Determined via the HCAO Method

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Introduction

Following the harmonically-coupled anharmonic oscillator (HCAO) approximation,[1] the stretching vibrational eigenstates of $^{1}H_{2}{}^{16}O$ will be determined. Using a local mode model, these eigenstates will be evaluated in the basis given by the direct product of Morse states of each O-H stretch. The code written for this project and figures comparing energy levels are hosted on GitHub at

github.com/Rhuel67/Chem584_MiniProject

Task I

Determination of Parameters

The parameters ω_e, ω_x, α, r_e, β and g were determined through a geometry optimization and normal mode frequency determination using Gaussian[2] with basis set 6-311+G(2d,p). Various levels of theory were tested. Of those tested, the B3LYP functional provided the lowest ground state energy, but the parameters determined with the coupled cluster method

with singles, doubles, and triples produced the most accurate energy levels. The parameters determined with CCSDT theory are shown in Table 1.

Table 1: Key parameters for the stretching states of $^1H_2{}^{16}O$ determined with CCSDT using the basis set 6-311+G(2d,p).

Parameter	SI	Atomic Units
ω_e	$7.291\,026 \times 10^{14}\,\mathrm{s}^{-1}$	$1.763\,613 \times 10^{-2}$ Hartree
ω_x	$1.537\,183 \times 10^{13}\,\mathrm{s}^{-1}$	$3.718\,266 \times 10^{-4}$ Hartree
α	$2.142\,341 \times 10^{10}\,\mathrm{m}^{-1}$	$1.133\,678\,\mathrm{a}_0^{-1}$
r_e	$9.63 \times 10^{-11}\,\mathrm{m}$	$1.81\,\mathrm{a}_0$
β	$104.631°$	
g	$-9.510\,204 \times 10^{-24}\,\mathrm{kg}^{-1}$	$-8.663\,215 \times 10^{-6}\,\mathrm{m}_\mathrm{e}^{-1}$

Task II

Constructing a Suitable Basis

Following the local mode model, the two O-H stretches of $^1H_2{}^{16}O$ will be considered as two coupled Morse oscillators.[3] Due to the symmetry of the water molecule, the two Morse oscillators must be considered indistinguishable. Therefore, a combined vibrational state is either symmetric or antisymmetric with respect to exchange. Then, if one oscillator occupies $|n_1\rangle$ and the other $|n_2\rangle$ with $n_1 \neq n_2$, the combined state is given by either

$$|n_1 n_2, +\rangle \equiv |n_2 n_1, +\rangle \equiv \frac{1}{\sqrt{2}}\Big(|n_1\rangle\,|n_2\rangle + |n_2\rangle\,|n_1\rangle \Big)$$

for the symmetric state, or

$$|n_1 n_2, -\rangle \equiv -\,|n_2 n_1, -\rangle \equiv \frac{1}{\sqrt{2}}\Big(|n_1\rangle\,|n_2\rangle - |n_2\rangle\,|n_1\rangle \Big)$$

for the antisymmetric state. To ensure normalization, the case with $n_1 = n_2$ must be treated separately:

$$|n_1 n_1, +\rangle \equiv |n_1\rangle\,|n_1\rangle$$

It is immediately apparent that an antisymmetric state in which $n_1 = n_2$ is physically impossible. If a value $\sigma = \pm 1$ is assigned to each state such that symmetric states have $\sigma = +1$ and antisymmetric states have $\sigma = -1$, the inner product between two general states, $\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle$, can be evaluated. For $m_1 \neq m_2$ and $n_1 \neq n_2$,

$$\begin{aligned}
\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle &= \frac{1}{2}\Big(\langle n_1| \langle n_2| + \sigma_l \langle n_2| \langle n_1| \Big)\Big(|n_1\rangle |n_2\rangle + \sigma_r |n_2\rangle |n_1\rangle \Big) \\
&= \frac{1}{2}\Big(\delta_{m_1 n_1}\delta_{m_2 n_2} + \sigma_r \delta_{m_1 n_2}\delta_{m_2 n_1} + \sigma_l \delta_{m_2 n_1}\delta_{m_1 n_2} + \sigma_l\sigma_r \delta_{m_1 n_1}\delta_{m_2 n_2}\Big) \\
&= \frac{1}{2}\Big[(1+\sigma_l\sigma_r)\delta_{m_1 n_1}\delta_{m_2 n_2} + (\sigma_r + \sigma_l)\delta_{m_1 n_2}\delta_{m_2 n_1}\Big]
\end{aligned}$$

Since σ_l and σ_r can only take values ± 1, $(1 + \sigma_l\sigma_r) = 2\delta_{\sigma_l \sigma_r}$ and $(\sigma_r + \sigma_l) = \sigma_r(1 + \sigma_l/\sigma_r) = 2\sigma_r \delta_{\sigma_l \sigma_r}$. So,

$$\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle = \delta_{\sigma_l \sigma_r}\big(\delta_{m_1 n_1}\delta_{m_2 n_2} + \sigma_r \delta_{m_1 n_2}\delta_{m_2 n_1}\big) \text{ for } m_1 \neq m_2 \text{ and } n_1 \neq n_2 \qquad (1)$$

Since $\langle n_1 n_2, \pm| = \pm \langle n_1 n_2, \pm|$, if the restriction is placed that $n_1 > n_2$, then $\delta_{m_1 n_2}\delta_{m_2 n_1} = 0$, so (1) implies that all $\big\{|n_1 n_2, \pm\rangle : n_2 < n_1\big\}$ are orthonormal.

For the case with $m_1 = m_2$ and $n_1 \neq n_2$,

$$\begin{aligned}
\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle &= \langle m_1 m_1, + | n_1 n_2, \pm_r \rangle \\
&= \frac{1}{\sqrt{2}} \langle m_1| \langle m_1| \Big(|n_1\rangle |n_2\rangle + \sigma_r |n_2\rangle |n_1\rangle \Big) \\
&= \frac{1}{\sqrt{2}}\Big(\delta_{m_1 n_1}\delta_{m_1 n_2} + \sigma_r \delta_{m_1 n_2}\delta_{m_1 n_1}\Big) \\
&= \frac{1+\sigma_r}{\sqrt{2}}\delta_{m_1 n_1}\delta_{m_1 n_2} \\
&= 0 \qquad (\text{since } n_1 \neq n_2)
\end{aligned}$$

For $m_1 \neq m_2$ and $n_1 = n_2$,

$$\begin{aligned}
\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle &= \langle m_1 m_2, \pm_l | n_1 n_1, + \rangle \\
&= \frac{1}{\sqrt{2}} \Big(\langle m_1 | \langle m_2 | + \sigma_l \langle m_2 | \langle m_1 | \Big) | n_1 \rangle | n_1 \rangle \\
&= \frac{1}{\sqrt{2}} \Big(\delta_{m_1 n_1} \delta_{m_2 n_1} + \sigma_l \delta_{m_2 n_1} \delta_{m_1 n_1} \Big) \\
&= \frac{1 + \sigma_r}{\sqrt{2}} \delta_{m_1 n_1} \delta_{m_2 n_1} \\
&= 0 \qquad (\text{since } m_1 \neq m_2)
\end{aligned}$$

For $m_1 = m_2$ and $n_2 = n_1$,

$$\begin{aligned}
\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle &= \langle m_1 m_1, + | n_1 n_1, + \rangle \\
&= \Big(\langle m_1 | \langle m_1 | \Big) \Big(| n_1 \rangle | n_1 \rangle \Big) \\
&= \delta_{m_1 n_1}
\end{aligned}$$

In summary:

$$\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle = \begin{cases} \delta_{\sigma_l \sigma_r} \big(\delta_{m_1 n_1} \delta_{m_2 n_2} + \sigma_r \delta_{m_1 n_2} \delta_{m_2 n_1} \big) & m_1 \neq m_2 \text{ and } n_1 \neq n_2 \\ 0 & m_1 = m_2 \text{ and } n_1 \neq n_2 \\ 0 & m_1 \neq m_2 \text{ and } n_1 = n_2 \\ \delta_{m_1 n_1} & m_1 = m_2 \text{ and } n_1 = n_2 \end{cases} \tag{2}$$

If the restriction $n_1 \leq n_2$ is imposed, then (2) is reduced to (3):

$$\langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle = \delta_{\sigma_l \sigma_r} \delta_{m_1 n_1} \delta_{m_2 n_2} \tag{3}$$

From (3), it is clear that $\big\{ | n_1 n_2, \pm \rangle : n_2 < n_1 \big\}$ forms an orthonormal basis. Though less compact than (3), (2) will prove useful when evaluating inner products between states acted

on by raising and lowering operators.

Evaluation of Hamiltonian Matrix Elements

The Hamiltonian of this two-oscillator system is modeled by

$$\hat{H}_{2D} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

where the zero-order Hamiltonian, $\hat{H}^{(0)}$, is the non-interacting term, i.e. the sum of the Hamiltonians of each independent oscillator:

$$\hat{H}^{(0)} = \hat{H}_1^{\text{Morse}} + \hat{H}_2^{\text{Morse}}$$

These Morse oscillator Hamiltonians only act on their respective oscillator, so $\hat{H}^{(0)}$ acts on the combined state to yield

$$\begin{aligned}
\hat{H}^{(0)} |n_1 n_2, \pm\rangle &= \frac{1}{\sqrt{2}} \Big(\hat{H}_1^{\text{Morse}} + \hat{H}_2^{\text{Morse}} \Big) \Big(|n_1\rangle |n_2\rangle \pm |n_2\rangle |n_1\rangle \Big) \\
&= \frac{1}{\sqrt{2}} \Big(\varepsilon_{n_1}^M |n_1\rangle |n_2\rangle \pm \varepsilon_{n_2}^M |n_2\rangle |n_1\rangle + \varepsilon_{n_2}^M |n_1\rangle |n_2\rangle \pm \varepsilon_{n_1}^M |n_2\rangle |n_1\rangle \Big) \\
&= \Big(\varepsilon_{n_1}^M + \varepsilon_{n_2}^M \Big) |n_1 n_2, \pm\rangle \, .
\end{aligned}$$

The matrix elements of $\hat{H}^{(0)}$ in the $\big\{ |n_1 n_2, \pm\rangle \big\}$ basis are then given by

$$\mathbf{H}^{(0)}_{m_1 m_2 \sigma_l, n_1 n_2 \sigma_r} \equiv \langle m_1 m_2, \pm_l | \hat{H}^{(0)} | n_1 n_2, \pm_r \rangle = \Big(\varepsilon_{n_1}^M + \varepsilon_{n_2}^M \Big) \langle m_1 m_2, \pm_l | n_1 n_2, \pm_r \rangle \, .$$

In evaluating these inner products, the assumption that $n_1 \leq n_2$ can be strictly imposed, so (3) can be used to reduce the expression to

$$\mathbf{H}^{(0)}_{m_1 m_2 \sigma_l, n_1 n_2 \sigma_r} = \Big(\varepsilon_{n_1}^M + \varepsilon_{n_2}^M \Big) \delta_{\sigma_l \sigma_r} \delta_{m_1 n_1} \delta_{m_2 n_2} . \tag{4}$$

The coupling Hamiltonian, $\hat{H}^{(1)}$, is given by

$$\hat{H}^{(1)} = g\hat{p}_1\hat{p}_2 + f(\hat{r}_1 - r_e)(\hat{r}_2 - r_e).$$

Following the HCAO approximation,[1] the matrix elements of $\hat{H}^{(1)}$ in the basis $\left\{|n_1 n_2, \pm\rangle\right\}$ will be approximated using the basis $\left\{|n_1 n_2, \pm\rangle_H\right\}$. This basis is constructed identically to the previous, but the harmonic oscillator basis states (which will be represented as $|n\rangle_H$) are used instead of the Morse states. In this basis, the coupling Hamiltonian can be expressed in terms of the harmonic oscillator raising and lowering operators ($\hat{a}^\dagger$ and $\hat{a}$) as

$$\hat{H}^{(1)} = c_{\hat{S}}\hat{S} + c_{\hat{A}}\hat{A}, \tag{5}$$

with

$$\hat{S} \equiv \hat{a}_1^\dagger\hat{a}_2^\dagger + \hat{a}_1\hat{a}_2,\ \ \hat{A} \equiv \hat{a}_1^\dagger\hat{a}_2 + \hat{a}_1\hat{a}_2^\dagger$$

$$c_{\hat{S}} \equiv \frac{f}{2\mu\omega_e} - \frac{g\mu\omega_e}{2},\ \ c_{\hat{A}} \equiv \frac{f}{2\mu\omega_e} + \frac{g\mu\omega_e}{2}.$$

The action of $\hat{S}$ on the combined harmonic oscillator basis states is then given by

$$\begin{aligned}\hat{S}\,|n_1 n_2, \pm\rangle_H = &\sqrt{(n_1+1)(n_2+1)}\,|(n_1+1)(n_2+1), \pm\rangle_H \\ &+ \sqrt{n_1 n_2}\,|(n_1-1)(n_2-1), \pm\rangle_H\end{aligned}$$

The action of $\hat{A}$ must be treated in three cases. First, if $n_1 = n_2 = n$:

$$\begin{aligned}\hat{A}\,|nn, +\rangle_H &= |n+1\rangle_H\,|n-1\rangle_H\,\sqrt{(n+1)n} \\ &\quad + |n-1\rangle_H\,|n+1\rangle_H\,\sqrt{n(n+1)} \\ &= |(n+1)(n-1), +\rangle_H\,\sqrt{2n(n+1)}.\end{aligned}$$

Second, if $n_1 = n+1$ and $n_2 = n-1$:

$$\begin{aligned}
\hat{A}\,|(n+1)(n-1),\pm\rangle_H &= \frac{1}{\sqrt{2}}(\hat{a}_1^\dagger \hat{a}_2 + \hat{a}_1 \hat{a}_2^\dagger)\Big(|n+1\rangle_H\,|n-1\rangle_H \pm |n-1\rangle_H\,|n+1\rangle_H\Big) \\
&= \frac{1}{\sqrt{2}}\Big(|n+2\rangle_H\,|n-2\rangle_H\,\sqrt{(n+2)(n-1)} \pm |n\rangle_H\,|n\rangle_H\,\sqrt{n(n+1)} \\
&+ |n\rangle_H\,|n\rangle_H\,\sqrt{(n+1)n} \pm |n-2\rangle_H\,|n+2\rangle_H\,\sqrt{(n-1)(n+2)}\Big) \\
&= |nn,+\rangle_H\,\delta_{\sigma,+1}\sqrt{2n(n+1)} + |(n+2)(n-2),\pm\rangle_H\,\sqrt{(n-1)(n+2)}
\end{aligned}$$

Third, all other cases:

$$\begin{aligned}
\hat{A}\,|n_1 n_2,\pm\rangle_H &= |(n_1+1)(n_2-1),\pm\rangle_H\,\sqrt{(n_1+1)n_2} \\
&+ |(n_1-1)(n_2+1),\pm\rangle_H\,\sqrt{n_1(n_2+1)}.
\end{aligned}$$

The matrix elements of $\hat{S}$ are then

$$\begin{aligned}
\mathbf{S}_{m_1 m_2 \sigma_l, n_1 n_2 \sigma_r} &\equiv \langle m_1 m_2,\pm|\hat{S}|n_1 n_2,\pm\rangle_H \\
&= \delta_{\sigma_l \sigma_r}\Big(\delta_{m_1 n_1+1}\delta_{m_2 n_2+1}\sqrt{(n_1+1)(n_2+1)} \\
&\quad + \delta_{m_1 n_1-1}\delta_{m_2 n_2-1}\sqrt{n_1 n_2}\Big).
\end{aligned}$$

For $\hat{A}$, with $n_1 = n_2 = n$:

$$\begin{aligned}
\mathbf{A}_{m_1 m_2 \sigma_l, nn\sigma_r} &\equiv \langle m_1 m_2,\pm|\hat{H}|nn,\pm\rangle_H \\
&= \langle m_1 m_2,\pm|(n+1)(n-1),+\rangle_H\,\sqrt{2n(n+1)}.
\end{aligned}$$

For $\hat{A}$, with $n_1 = n + 1$ and $n_2 = n - 1$:

$$\begin{aligned}\mathbf{A}_{m_1 m_2 \sigma_l,(n+1)(n-1)\sigma_r} &\equiv \langle m_1 m_2, \pm|\hat{A}|(n+1)(n-1), \pm\rangle_H \\ &= \langle m_1 m_2, \pm|nn, +\rangle_H \, \delta_{\sigma,+1}\sqrt{2n(n+1)} \\ &+ \langle m_1 m_2, \pm|(n+2)(n-2), \pm\rangle_H \, \sqrt{(n-1)(n+2)}.\end{aligned}$$

For $\hat{A}$, in all other cases:

$$\begin{aligned}\mathbf{A}_{m_1 m_2 \sigma_l, n_1 n_2 \sigma_r} &\equiv \langle m_1 m_2, \pm|\hat{A}|m_1 m_2, \pm\rangle_H \\ &= \langle m_1 m_2, \pm|(n_1+1)(n_2-1), \pm\rangle_H \, \sqrt{(n_1+1)n_2} \\ &+ \langle m_1 m_2, \pm|(n_1-1)(n_2+1), \pm\rangle_H \, \sqrt{n_1(n_2+1)}\end{aligned}$$

Evaluation of Eigenstates

Fortunately, neither $\hat{H}^{(0)}$ nor $\hat{H}^{(1)}$ couple states with different symmetries, since they both have a factor $\delta_{\sigma_l \sigma_r}$. This is also true for the total Hamiltonian $\hat{H}_{2D} = \hat{H}^{(0)} + \hat{H}^{(1)}$, so each eigenstate of $\hat{H}_{2D}$ must occupy either the subspace of symmetric states or the subspace of antisymmetric states. The eigenvalue problem ahead can then be solved separately in each of these subspaces. The eigenstates of $\hat{H}_{2D}$ were determined using Python's NumPy library. The resulting eigenvalues are compared to experimental values[4] in Table 2. Full eigenvectors are displayed in Table 5 (at the end of this document).

As shown in Table 2, the transition energies calculated using the HCAO method resemble the experimental values remarkably well. The vast majority of energies differ from experiment by less than 0.5%. The model performs best for states with greatest contributions from states of the form $|n_1 0, \pm\rangle$. As shown in Table 5, such states are well approximated by one of the basis states of the uncoupled system, implying they are subject to little coupling. The model performs poorly on states like (2, 2, +), which have large contributions from multiple uncoupled basis states. This likely indicates that the model for the coupling of states was

not very accurate. This likely due to the use of HCAO method, in which the energy of the coupling is evaluated as if the Morse oscillators are harmonic.

Table 2: Comparison of transition energies (in cm^{-1}) determined via the HCAO method and experimental values.[4]

Label	Calculated	Experimental	Error
(1,0,+)	3658.21	3657.05	0.032%
(1,0,-)	3756.71	3755.93	0.021%
(2,0,+)	7205.40	7201.54	0.054%
(2,0,-)	7251.71	7249.82	0.026%
(1,1,+)	7461.23	7445.05	0.217%
(3,0,+)	10604.35	10599.69	0.044%
(3,0,-)	10616.26	10613.35	0.027%
(2,1,+)	10889.06	10868.88	0.186%
(2,1,-)	11074.15	11032.41	0.378%
(4,0,+)	13829.79	13828.28	0.011%
(4,0,-)	13831.49	13830.94	0.004%
(3,1,+)	14249.75	14221.16	0.201%
(3,1,-)	14359.27	14318.81	0.283%
(2,2,+)	14614.62	14537.50	0.530%
(5,0,+)	16886.47	16898.40	0.071%
(5,0,-)	16886.64	16898.84	0.072%
(4,1,+)	17497.40	17458.35	0.224%
(4,1,-)	17537.92	17495.53	0.242%
(3,2,+)	17816.00	17748.11	0.383%
(6,0,+)	19778.70	19781.00	0.012%
(6,0,-)	19778.72	19781.10	0.012%
(5,1,+)	20576.34	20533.60	0.208%
(5,1,-)	20584.27	20543.14	0.200%
(7,0,+)	22507.49	22529.30	0.097%
(7,0,-)	22507.49	22529.44	0.097%
(8,0,-)	25072.83	25120.28	0.189%

Task III

Refinement Scheme

Since all of the $\mathbf{H}_{2D}$ is Hermitian and its eigenvalues are unique, the differentials of those eigenvalues can be evaluated trivially:

$$\begin{aligned}
\mathbf{H}_{2D}\mathbf{v} &= E_i\mathbf{v} \\
\partial\mathbf{H}_{2D}\mathbf{v} + \mathbf{H}_{2D}\partial\mathbf{v} &= \partial E_i\mathbf{v} + E_i\partial\mathbf{v} \\
\mathbf{v}^\mathbf{T}\partial\mathbf{H}_{2D}\mathbf{v} + \mathbf{v}^\mathbf{T}\mathbf{H}_{2D}\partial\mathbf{v} &= \partial E_i\mathbf{v}^\mathbf{T}\mathbf{v} + E_i\mathbf{v}^\mathbf{T}\partial\mathbf{v} \\
\mathbf{v}^\mathbf{T}\partial\mathbf{H}_{2D}\mathbf{v} + E_i\mathbf{v}^\mathbf{T}\partial\mathbf{v} &= \partial E_i\mathbf{v}^\mathbf{T}\mathbf{v} + E_i\mathbf{v}^\mathbf{T}\partial\mathbf{v} \\
\partial E_i &= \mathbf{v}^\mathbf{T}\partial\mathbf{H}_{2D}\mathbf{v} \qquad (6)
\end{aligned}$$

The gradient of each of these eigenvalues with respect to the vector of parameters D_e, g, and f can then be evaluated using its corresponding eigenvector and the gradient of the matrix $\mathbf{H}_{2D}$. Then, the gradient of some cost function depending on these eigenvalues can be minimized via a gradient-based optimization method.

This optimization was carried out with weighted square residual cost function (weighted least squares):

$$c(D_e, g, f) = \frac{1}{2}\sum_{(n_1,n_2,\pm)} w_{(n_1,n_2,\pm)}\left(E^{\text{Exp}}_{(n_1,n_2,\pm)} - E^{\text{Calc}}_{(n_1,n_2,\pm)}(D_e, g, f)\right)^2$$

$$w_{(n_1,n_2,\pm)} = (n_1 + n_2)^{-2}$$

The cost function was minimized by simple gradient descent with a step size of $-0.001\nabla c(D_e, g, f)$. After 100 steps, the magnitude of the gradient was reduced by 99.817%, but the cost function was only reduced by 5.907%. The optimized parameters are shown in Table 3. The transition energies determined using the HCAO method with these optimized parameters are compared to the experimental values in Table 4.

Table 3: Comparison of initial parameters and those fit to experimental data by gradient descent.

Parameter	Initial value	Optimized value
D_e	$2.091\,252 \times 10^{-1}$ Hartree	$2.091\,249 \times 10^{-1}$ Hartree
g	$-8.663\,215 \times 10^{-6}\,\mathrm{m_e^{-1}}$	$-7.580\,083 \times 10^{-6}\,\mathrm{m_e^{-1}}$
f	$-5.631\,139 \times 10^{-3}$ Hartree	$-5.631\,134 \times 10^{-3}$ Hartree
α	$1.133\,678\,\mathrm{a_0^{-1}}$	$1.133\,678\,\mathrm{a_0^{-1}}$

As shown in Table 3, D_e and f were not significantly changed during the fitting. g, on the other hand, was decreased by about 12.5%. Though the cost function was decreased by the fitting, not all of the energy levels had decreased error. In particular, energy levels with low $n_1 + n_2$ generally increased in error. The weighting of the cost function was designed to mitigate this, but was not fully successful.

References

(1) Child, M. S.; Lawton, R. T. Local and normal vibrational states: a harmonically coupled anharmonic-oscillator model. *71*, 273–285, Publisher: The Royal Society of Chemistry.

(2) Frisch, M. J. et al. Gaussian˜16 Revision C.01. 2016; Gaussian Inc. Wallingford CT.

(3) Morse, P. M. Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels. *34*, 57–64, Publisher: American Physical Society.

(4) Tennyson, J.; Zobov, N. F.; Williamson, R.; Polyansky, O. L.; Bernath, P. F. Experimental Energy Levels of the Water Molecule. *30*, 735–831.

Table 4: Comparison of transition energies (in cm^{-1}) determined via the HCAO method with refined parameters and experimental values.[4]

Label	Calculated	Experimental	Error
(1,0,+)	3661.84	3657.05	0.131%
(1,0,-)	3753.09	3755.93	0.075%
(2,0,+)	7210.91	7201.54	0.130%
(2,0,-)	7251.72	7249.82	0.026%
(1,1,+)	7455.75	7445.05	0.144%
(3,0,+)	10608.67	10599.69	0.085%
(3,0,-)	10618.31	10613.35	0.047%
(2,1,+)	10892.02	10868.88	0.213%
(2,1,-)	11064.90	11032.41	0.294%
(4,0,+)	13832.87	13828.28	0.033%
(4,0,-)	13834.13	13830.94	0.023%
(3,1,+)	14258.60	14221.16	0.263%
(3,1,-)	14356.68	14318.81	0.264%
(2,2,+)	14602.78	14537.50	0.449%
(5,0,+)	16889.18	16898.40	0.055%
(5,0,-)	16889.29	16898.84	0.057%
(4,1,+)	17506.34	17458.35	0.275%
(4,1,-)	17539.87	17495.53	0.253%
(3,2,+)	17815.34	17748.11	0.379%
(6,0,+)	19781.28	19781.00	0.001%
(6,0,-)	19781.29	19781.10	0.001%
(5,1,+)	20582.02	20533.60	0.236%
(5,1,-)	20587.97	20543.14	0.218%
(7,0,+)	22509.93	22529.30	0.086%
(7,0,-)	22509.94	22529.44	0.087%
(8,0,-)	25075.22	25120.28	0.179%

Table 5: Calculated stretching states of $^1H_2{}^{16}O$. Basis states with contribution less than 10^{-5} are ommited.

n_1	n_2	σ	E (cm^{-1})	Eigenfunction
0	0	+	0.000	$1.00000\,\|00,+\rangle - 0.00117\,\|11,+\rangle - 0.00002\,\|20,+\rangle$
1	0	+	3658.210	$-1.00000\,\|10,+\rangle + 0.00171\,\|21,+\rangle + 0.00002\,\|30,+\rangle$
1	0	-	3756.711	$1.00000\,\|00,-\rangle - 0.00117\,\|11,-\rangle - 0.00002\,\|20,-\rangle$
2	0	+	7205.399	$-0.90498\,\|20,+\rangle - 0.42545\,\|11,+\rangle + 0.00194\,\|31,+\rangle + 0.00106\,\|22,+\rangle - 0.00051\,\|00,+\rangle + 0.00003\,\|40,+\rangle$
2	0	-	7251.707	$-1.00000\,\|10,-\rangle + 0.00171\,\|21,-\rangle + 0.00002\,\|30,-\rangle$
1	1	+	7461.228	$-0.90498\,\|11,+\rangle + 0.42545\,\|20,+\rangle + 0.00222\,\|22,+\rangle - 0.00106\,\|00,+\rangle - 0.00088\,\|31,+\rangle - 0.00001\,\|40,+\rangle$
3	0	+	10604.351	$0.94883\,\|30,+\rangle + 0.31578\,\|21,+\rangle - 0.00240\,\|41,+\rangle - 0.00099\,\|32,+\rangle + 0.00056\,\|10,+\rangle - 0.00004\,\|50,+\rangle$
3	0	-	10616.255	$-0.90498\,\|20,-\rangle - 0.42545\,\|11,-\rangle + 0.00194\,\|31,-\rangle + 0.00106\,\|22,-\rangle - 0.00051\,\|00,-\rangle + 0.00003\,\|40,-\rangle$
2	1	+	10889.055	$0.94883\,\|21,+\rangle - 0.31578\,\|30,+\rangle - 0.00294\,\|32,+\rangle + 0.00161\,\|10,+\rangle + 0.00076\,\|41,+\rangle + 0.00001\,\|50,+\rangle$
2	1	-	11074.153	$-0.90498\,\|11,-\rangle + 0.42545\,\|20,-\rangle + 0.00222\,\|22,-\rangle - 0.00106\,\|00,-\rangle - 0.00088\,\|31,-\rangle - 0.00001\,\|40,-\rangle$
4	0	+	13829.793	$0.97715\,\|40,+\rangle + 0.20602\,\|31,+\rangle + 0.05218\,\|22,+\rangle - 0.00282\,\|51,+\rangle - 0.00076\,\|42,+\rangle + 0.00047\,\|20,+\rangle - 0.00021\,\|33,+\rangle + 0.00013\,\|11,+\rangle - 0.00006\,\|60,+\rangle$
4	0	-	13831.488	$0.94883\,\|30,-\rangle + 0.31578\,\|21,-\rangle - 0.00240\,\|41,-\rangle - 0.00099\,\|32,-\rangle + 0.00056\,\|10,-\rangle - 0.00004\,\|50,-\rangle$
3	1	+	14249.753	$0.81290\,\|31,+\rangle + 0.54675\,\|22,+\rangle - 0.20059\,\|40,+\rangle - 0.00298\,\|42,+\rangle - 0.00214\,\|33,+\rangle + 0.00173\,\|20,+\rangle + 0.00137\,\|11,+\rangle + 0.00054\,\|51,+\rangle + 0.00001\,\|60,+\rangle$
3	1	-	14359.271	$0.94883\,\|21,-\rangle - 0.31578\,\|30,-\rangle - 0.00294\,\|32,-\rangle + 0.00161\,\|10,-\rangle + 0.00076\,\|41,-\rangle + 0.00001\,\|50,-\rangle$
2	2	+	14614.624	$0.83565\,\|22,+\rangle - 0.54473\,\|31,+\rangle + 0.07023\,\|40,+\rangle - 0.00321\,\|33,+\rangle + 0.00204\,\|11,+\rangle + 0.00194\,\|42,+\rangle - 0.00114\,\|20,+\rangle - 0.00018\,\|51,+\rangle$
5	0	+	16886.472	$-0.98552\,\|50,+\rangle - 0.16730\,\|41,+\rangle - 0.02741\,\|32,+\rangle + 0.00319\,\|61,+\rangle + 0.00071\,\|52,+\rangle - 0.00046\,\|30,+\rangle + 0.00013\,\|43,+\rangle - 0.00009\,\|21,+\rangle + 0.00007\,\|70,+\rangle$
5	0	-	16886.635	$0.97715\,\|40,-\rangle + 0.20602\,\|31,-\rangle + 0.05218\,\|22,-\rangle - 0.00282\,\|51,-\rangle - 0.00076\,\|42,-\rangle + 0.00047\,\|20,-\rangle - 0.00021\,\|33,-\rangle + 0.00013\,\|11,-\rangle - 0.00006\,\|60,-\rangle$
4	1	+	17497.401	$-0.85327\,\|41,+\rangle - 0.49673\,\|32,+\rangle + 0.15867\,\|50,+\rangle + 0.00358\,\|52,+\rangle + 0.00231\,\|43,+\rangle - 0.00214\,\|30,+\rangle - 0.00157\,\|21,+\rangle - 0.00046\,\|61,+\rangle - 0.00001\,\|70,+\rangle$

4	1	-	17537.924	$0.81290\,\|31,-\rangle + 0.54675\,\|22,-\rangle - 0.20059\,\|40,-\rangle - 0.00298\,\|42,-\rangle - 0.00214\,\|33,-\rangle + 0.00173\,\|20,-\rangle + 0.00137\,\|11,-\rangle + 0.00054\,\|51,-\rangle + 0.00001\,\|60,-\rangle$
3	2	+	17816.001	$0.86746\,\|32,+\rangle - 0.49389\,\|41,+\rangle + 0.05972\,\|50,+\rangle - 0.00398\,\|43,+\rangle + 0.00267\,\|21,+\rangle + 0.00202\,\|52,+\rangle - 0.00123\,\|30,+\rangle - 0.00016\,\|61,+\rangle$
3	2	-	18070.818	$0.83565\,\|22,-\rangle - 0.54473\,\|31,-\rangle + 0.07023\,\|40,-\rangle - 0.00321\,\|33,-\rangle + 0.00204\,\|11,-\rangle + 0.00194\,\|42,-\rangle - 0.00114\,\|20,-\rangle - 0.00018\,\|51,-\rangle$
6	0	+	19778.787	$0.98906\,\|60,+\rangle + 0.14639\,\|51,+\rangle + 0.01775\,\|42,+\rangle + 0.00288\,\|33,+\rangle + 0.00048\,\|40,+\rangle + 0.00007\,\|31,+\rangle + 0.00001\,\|22,+\rangle$
6	0	-	19778.799	$0.86746\,\|32,-\rangle - 0.49389\,\|41,-\rangle + 0.05972\,\|50,-\rangle - 0.00398\,\|43,-\rangle + 0.00267\,\|21,-\rangle + 0.00202\,\|52,-\rangle - 0.00123\,\|30,-\rangle - 0.00016\,\|61,-\rangle$
5	1	+	20576.484	$0.92702\,\|51,+\rangle + 0.32703\,\|42,+\rangle - 0.14341\,\|60,+\rangle + 0.11449\,\|33,+\rangle + 0.00266\,\|40,+\rangle + 0.00124\,\|31,+\rangle + 0.00046\,\|22,+\rangle$
5	1	-	20584.413	$-0.85327\,\|41,-\rangle - 0.49673\,\|32,-\rangle + 0.15867\,\|50,-\rangle + 0.00358\,\|52,-\rangle + 0.00231\,\|43,-\rangle - 0.00214\,\|30,-\rangle - 0.00157\,\|21,-\rangle - 0.00046\,\|61,-\rangle - 0.00001\,\|70,-\rangle$
4	2	+	20973.133	$-0.72880\,\|42,+\rangle - 0.60111\,\|33,+\rangle + 0.32617\,\|51,+\rangle - 0.03345\,\|60,+\rangle - 0.00266\,\|31,+\rangle - 0.00236\,\|22,+\rangle + 0.00093\,\|40,+\rangle$
4	2	-	21148.628	$-0.98552\,\|50,-\rangle - 0.16730\,\|41,-\rangle - 0.02741\,\|32,-\rangle + 0.00319\,\|61,-\rangle + 0.00071\,\|52,-\rangle - 0.00046\,\|30,-\rangle + 0.00013\,\|43,-\rangle - 0.00009\,\|21,-\rangle + 0.00007\,\|70,-\rangle$
3	3	+	21449.098	$-0.79091\,\|33,+\rangle + 0.60131\,\|42,+\rangle - 0.11317\,\|51,+\rangle + 0.00826\,\|60,+\rangle - 0.00303\,\|22,+\rangle + 0.00216\,\|31,+\rangle - 0.00032\,\|40,+\rangle$
7	0	+	22507.489	$0.99116\,\|70,+\rangle + 0.13194\,\|61,+\rangle + 0.01382\,\|52,+\rangle + 0.00148\,\|43,+\rangle + 0.00050\,\|50,+\rangle + 0.00007\,\|41,+\rangle$
7	0	-	22507.490	$0.98906\,\|60,-\rangle + 0.14639\,\|51,-\rangle + 0.01775\,\|42,-\rangle + 0.00288\,\|33,-\rangle + 0.00048\,\|40,-\rangle + 0.00007\,\|31,-\rangle + 0.00001\,\|22,-\rangle$
6	1	+	23476.257	$-0.95575\,\|61,+\rangle - 0.25641\,\|52,+\rangle + 0.13090\,\|70,+\rangle - 0.06036\,\|43,+\rangle - 0.00308\,\|50,+\rangle - 0.00113\,\|41,+\rangle - 0.00029\,\|32,+\rangle$
6	1	-	23477.206	$0.92702\,\|51,-\rangle + 0.32703\,\|42,-\rangle - 0.14341\,\|60,-\rangle + 0.11449\,\|33,-\rangle + 0.00266\,\|40,-\rangle + 0.00124\,\|31,-\rangle + 0.00046\,\|22,-\rangle$

5	2	+	24054.361	$0.75039\,\|52,+\rangle\ +\ 0.61651\,\|43,+\rangle\ -\ 0.23749\,\|61,+\rangle\ +$ $0.02023\,\|70,+\rangle\ +\ 0.00313\,\|41,+\rangle\ +\ 0.00287\,\|32,+\rangle\ -$ $0.00076\,\|50,+\rangle$
5	2	-	24136.929	$-0.72880\,\|42,-\rangle\ -\ 0.60111\,\|33,-\rangle\ +\ 0.32617\,\|51,-\rangle\ -$ $0.03345\,\|60,-\rangle\ -\ 0.00266\,\|31,-\rangle\ -\ 0.00236\,\|22,-\rangle\ +$ $0.00093\,\|40,-\rangle$
4	3	+	24434.519	$-0.78502\,\|43,+\rangle\ +\ 0.60906\,\|52,+\rangle\ -\ 0.11277\,\|61,+\rangle\ +$ $0.00769\,\|70,+\rangle\ -\ 0.00359\,\|32,+\rangle\ +\ 0.00252\,\|41,+\rangle\ -$ $0.00036\,\|50,+\rangle$
4	3	-	24745.003	$-0.79091\,\|33,-\rangle\ +\ 0.60131\,\|42,-\rangle\ -\ 0.11317\,\|51,-\rangle\ +$ $0.00826\,\|60,-\rangle\ -\ 0.00303\,\|22,-\rangle\ +\ 0.00216\,\|31,-\rangle\ -$ $0.00032\,\|40,-\rangle$