Exploring Expansions of the Potential and Dipole Surfaces Used For Vibrational Perturbation Theory

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Abstract

A scheme for evaluating expansions of the potential and dipole moment surfaces for vibrational perturbation theory is described. The approach is based on numerical differentiation of the Hessian in the coordinates of interest. It is shown that performing these calculations in internal coordinates generates expansions that are transferable among isotopologues of the molecule of interest. Additionally, reexpressing the expansion of the potential in terms of functions of the internal coordinates, e.g. cosines of angles or exponential functions of the bond length displacements, provides expansions that can be used for higher-order perturbation theory calculations. The approach is explored and results discussed for water, HOD, ammonia, isomers of HNO_3 and halogenated methane.

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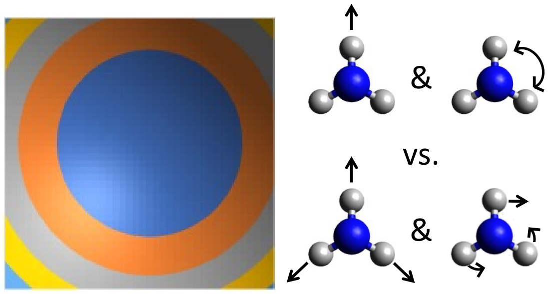

Introduction

Vibrational spectroscopy represents a powerful tool among the available techniques that are used to probe molecular structure, bond strengths and the nature of intermolecular interactions.[1,2] The insights obtained from the analysis of the spectrum of a molecule of interest rely heavily on the harmonic description of molecular vibrations. Within this treatment, the Hamiltonian is expanded through second order in a chosen set of coordinates (typically displacements of the Cartesian coordinates of the atoms), and a set of normal mode coordinates is constructed from linear combinations of the underlying coordinates. The linear transformation between the underlying coordinates and the normal mode coordinates satisfies the requirement that the quadratic expansion of the Hamiltonian in normal mode coordinates is separable. In other words,[3]

$$H = \sum_{j=1}^{3N-6} \frac{\hbar\omega_j}{2}\left(p_j^2 + q_j^2\right) \tag{1}$$

where the system of interest contains N atoms, q_j represents one of the normal mode coordinates, p_j is its conjugate momentum while ω_j provides the associated harmonic frequency. Expressed in this way, p_j and q_j are both dimensionless. A common way to extend approximate approaches beyond the harmonic treatment of molecular vibrations is to use the Hamiltonian in Eq. 1 as the starting point for a perturbative expansion of the energies and wave functions.

At second order, vibrational perturbation theory (VPT2) requires a quartic expansion of the Hamiltonian. While one can write down the kinetic energy contributions to the Hamiltonian analytically,[2–5] the potential energy introduces additional challenges. Often the coefficients in the quartic expansion of the potential were fit to reproduce spectroscopic information.[6,7] In the 1990's accurate electronic structure calculations became more computationally tractable, facilitating the evaluation of the potentials using high-level electronic structure calculations.[8–10] At that time, codes were developed by Harding and Ermler (`SURVIB`)[11] and by Allen (`INTDER`),[12] which automated the expansion of the potential based on evaluations of the electronic energies over a grid of geometries of the molecule of interest.

Vibrational perturbation theory has gained significant traction in the computational chemistry community over the past several decades leading to the development of numerous implementations of the approach.[13–20] This is due to several important advances in the field of theoretical spectroscopy. A key advance is the development of analytical expressions that allow for the evaluation of both energies and transition moments from terms in the expansion of the Hamiltonian in the normal modes that are formed from linear combinations of the displacements of the atoms in Cartesian coordinates.[21–25] While Watson developed expressions for the kinetic contributions to the Hamiltonian in terms of the equilibrium structure and the masses of the atoms which can be differentiated with respect to the normal mode coordinates,[4] the expansion of the potential in terms of these coordinates provides a larger challenge as the number of terms needed to construct a quartic expansion of the potential grows steeply with the size of the system.

Many electronic structure codes have implemented efficient evaluations of the first and second derivatives of the electronic energy, and the first derivatives of the dipole moment in order to perform geometry optimizations and harmonic analyses. With this in hand, the evaluation of the necessary third derivatives of the potential and second derivatives of the dipole moment can be readily achieved by a simple finite difference scheme in which the Hessian and dipole derivatives are evaluated when one of the normal mode coordinates is displaced by a small amount.[18,26] Likewise the fourth derivatives of the potential that involve only three of the normal mode coordinates and third derivatives of the dipole moment that involve two normal mode coordinates can be obtained by the same finite difference scheme. In the absence of degeneracies, fourth derivatives of the potential that involve four different normal mode coordinates will not contribute to the energies evaluated at second order in perturbation theory. Likewise, the third derivative of the dipole moment with respect to three normal mode coordinates will also not contribute to the intensities of transitions to states with one or two quanta of excitation. Through this simplification, the information needed to construct a quartic expansion of the potential and a cubic expansion of the dipole moment can be obtained by performing $2 \times (3N - 6)$ harmonic calculations. These calculations are typically performed in the normal mode coordinates that are based on displacements of the

Cartesian coordinates of the atoms.[27,28]

While the approach outlined above represents a significant savings and numerical stability over evaluating the terms in the expansions of the potential and dipole surfaces numerically, it still relies on the stability of the finite difference schemes. This can introduce challenges especially for low-frequency large amplitude bending vibrations when the normal mode coordinates are generated from linear combinations of displacements of Cartesian coordinates. Additionally, since the expansions are performed in normal mode coordinates, they are not transferable when isotopic substitutions are made as the definition of the normal mode coordiantes depends on the masses of the atoms. Finally when there are degeneracies or near degeneracies, fourth derivatives involving four different normal mode coordinates may become important. This is particularly notable in the potential expansion for methane, where the fourth derivatives of the potential with respect to the four CH stretches is roughly equal to the fourth derivative with respect to a single CH stretch normal mode.[9]

Due to the simplicity of the evaluation of quartic force fields relative to obtaining global potential surfaces and the fact that second order pertrubation theory requires only a quartic expansion of the potential, such potentials have played an important role in studies of vibrational spectra. Examination of the quartic potentials, when expressed in terms of displacements of bond lengths and angles, shows that the largest quartic terms are often those that involve displacements of single coordinates, in particular the XH bond lengths. This observation led to the development of harmonically coupled anharmonic oscillator models by Halonen, Child and co-workers,[29,30] and such models have been shown to provide accurate descriptions of the XH stretch region of vibrational spectra.

These observations led us to explore how well such quartic expansions of the potential in internal coordinates (e.g. bond lengths, angles and dihedral angles) would perform in vibrational perturbation theory. In particular, we are interested in the differences between the results obtained from VPT2 calculations when the restricted quartic expansion of the potential surface and the restricted cubic expansion of the dipole surface are expanded in displacements of the internal coordinates rather than the normal mode coordinates that are constructed from linear combinations of the internal coordinates. We will also explore the possibility of extrapolating the internal coordinate expansions of the potential to higher orders. Specifically, Lee and co-workers[31] have re-expressed quartic expansions of the potential as expansions of functions of the internal coordinates, e.g. cosines of angles or functions of the bond distances, which provide more appropriate asymptotic behavior than expansions in the displacements of the underlying internal coordinates. Expansions of this type would allow for the application of higher order perturbation theory using the approaches used to obtain quartic expansions of the potential descibed above. Such an approach was utilized in studies by Sibert[32–34] and co-workers and by Fortenberry and co-workers for VCI calculations.[35,36]

Theory

As noted above, the focus of the present study is to explore the use of expansions of the potential either in internal coordinates or linear combinations of these coordinates as part of a perturbation theory calculations. The advantages of using internal coordinates for calculations of vibrational energies and wave functions has long been recognized. While the calculated energies will be independent of the coordinate choice so long as the calculation is converged, the choice of coordinates can have a significant impact on the convergence behavior of the calculations. It can also impact the interpretation of the results – for example the origin of intensities for transitions that are expected to be dark in the zero-order linear dipole/harmonic oscillator description of vibrational spectroscopy.[20,37]

All of the calculations in this study were performed using the PyVibPT*n* program package[20,38] developed in our group, and in all cases the VPT calculations will be performed in the normal mode coordinates that are constructed as linear combinations of the displacements of internal coordinates. We use the deperturb and diagonalize approach to handle resonances (sometimes referred to as generalized VPT or GVPT).[16,17,39,40] In our implementation of this approach, states are considered to be in resonance with the state of interest if the contribution to the perturbative expansion to the wave function exceeds 0.3.[41] The electronic structure calculations were performed at the MP2/aug-cc-pVTZ level of theory/basis, as implemented in Gaussian 16.[27]

To obtain the quartic force fields, we initially performed a geometry optimization and normal mode analysis within an electronic structure calculation. This generates the second derivatives of the electronic energies and the first derivatives of the dipole moment with respect to the Cartesian coordinates. These derivatives are reexpressed in terms of the chosen set of internal coordinates, and a FG analysis is performed to obtain the normal mode coordinates as linear combinations of the displacements of these internal coordinates.[2,3] We also use the diagonal elements of the F and G matrices to obtain local mode frequencies, where

$$\omega_i = \sqrt{F_{ii}G_{ii}} \tag{2}$$

The size of the displacements used for the numerical differentiation of the Hessian is selected so that the energies of the displaced geometries, when evaluated at the harmonic level, is 6.5 cm^{-1}. This approach is similar to that taken by Barone and co-workers.[18] By representing the potential as a restricted quartic expansion in the internal coordinates or the normal mode coordinates that are based on displacements of internal coordinates, as opposed to expanding the potential in the normal mode coordinates based on Cartesian coordinates as has been done previously, the energies of the displaced geometries are found to be closer to the targeted 6.5 cm^{-1} value. This improved behavior is particularly notable for large amplitude low-frequency vibrations.

More specifically, when the coordinates are defined to be dimensionless, e.g.

$$q_i = \sqrt{\frac{\omega_i}{G_{ii}\hbar}}\,\Delta r_i \tag{3}$$

where r_i is used to represent a generic internal coordinate and G_{ii} represents the element of the Wilson $G-$matrix for this coordinate,[3] the displacement of the q's are evaluated using

$$\delta_i = \pm\sqrt{\frac{2\Delta E}{\hbar\omega_i}} \tag{4}$$

Harmonic calculations are then performed by displacing each of the coordinates by $\pm\delta_i$, and evaluating the gradient, Hessian and dipole derivatives in terms of the Cartesian coordinates. To obtain derivatives of the potential and dipole surface with respect to internal coordinates, the displaced structures are rotated to an Eckart frame,[42] and the chain rule is employed to obtain the corresponding derivatives with respect to internal coordinates. For the internal coordinate expansions, derivatives of the Hessian and dipole derivatives with respect to individual internal coordinates are evaluated numerically. For the normal mode coordinate expansions the calculated Hessians and dipole derivatives are rotated to the normal mode representation before the numerical differentiation is performed.

Quartic expansions obtained in this way provide the inputs needed for second order vibrational perturbation theory. To allow for extensions to higher order perturbation theory, we follow the work of Halonen,[7] Lee,[31] Ermler and Harding,[11] and others and reexpress the quartic expansion of the potential in terms of the internal coordinates as an expansion in so-called Morse coordinates for bond length displacements

$$y_i = \left[1 - \exp\left(\alpha \Delta r_i\right)\right]/\alpha \tag{5}$$

or displacements of the cosine of an angle for valence angles

$$\Delta z_j = \cos\theta_j - \cos\theta_{j,e} \tag{6}$$

Such expansions are commonly used for basis set calculations, and have been used in previous perturbation theory studies.[43] Following earlier studies,[31] the α-parameter in the definition of the Morse coordinates is determined so that the diagonal cubic term in the expansion of the potential in Morse coordiantes is zero. Specifically,

$$\alpha_i = -\frac{F_{3,i}}{3F_{2,i}} \tag{7}$$

where

$$F_{n,i} = \frac{\partial^n V}{\partial r_i^n} \tag{8}$$

To extrapolate the quartic expansion of the potential in terms of internal coordinates to higher order, the potential is first expressed as a quartic expansion in the Morse coordinates and Δz. Then the rewritten expansion is expanded in terms of the initial Δr and $\Delta\theta$ coordinates up to $(n+2)$th order for a VPTn calculation. This expansion will be identical to the initial expansion through fourth order, and provides a way to extrapolate the potential to higher order with minimal additional expense. An analogous approach is taken to extrapolate the dipole surface to $(n+1)$th order.

Results and Discussion

Water

We begin by considering H_2O and HOD. In some senses water represents a trivial case as all of the terms in the expansion of the potential are captured by numerically differentiating the Hessian with respect to each of the three internal coordinates. On the other hand, the cubic expansion of the dipole surface is missing the term that involves the mixed derivative with respect to all three internal coordinates. We expect that the missing term should be small compared to the other cubic terms in the expansion of the dipole surface. To explore the role of this missing term when the dipole surface is expanded in internal and normal mode coordinates, this additional term was evaluated numerically, and VPT2 calculations for HOH and HOD were performed with and without this term included.

We find that the inclusion of the mixed third derivative of the dipole moment with respect to the three internal coordinates in the dipole expansion leads to changes in the calculated intensities of at most 0.02 km mol^{-1} or 0.001 to 0.4 % when the $\Delta v = 1$ transitions are calculated at second order. By symmetry, this term will not contribute to the intensities of transitions to states with two quanta of excitation at second order in perturbation theory. Typically, the intensities of transitions to states with one quantum of excitation are dominated by the linear terms in the expansion of the dipole moment surface, so this mixed third derivative of the dipole moment surface is expected to represent a small contribution to an already small correction to what would be obtained had a linear expansion of the dipole moment been used.

While the intensities are relatively insensitive to how the expansion of the dipole surface is performed, the calculated intensities can be sensitive to the resonances that are included in the calculation. For example, HOD shows a notable 2:1 resonance between the HOD bend and the OD stretch, and inclusion of this resonance will lead to the intensity borrowing that one expects for a Fermi resonance. It is not unusual to find that the intensities show a greater sensitivity to the choice of resonances than the frequencies. We have recently explored algorithms for identifying resonances for vibrational perturbation theory based on the coefficients in the expansion of the wave function, and the influence of the choice of resonances on the calculated spectrum is an area that merits greater attention.[17,41]

While in general the intensities are found to be relatively insensitive to the form of the expansions of the potential and dipole surfaces, the frequencies show a much larger sensitivity, particularly when perturbation theory is taken beyond second order. In Tables 1 and 2 we report the energies and intensities of states of HOH and HOD with up to two quanta evaluated using the harmonic approximation, VPT2 and VPT4 using a fourth and sixth order expansion of the potential and kinetic energies. Just as VPT2 requires a quartic expansion of the Hamiltonian, VPT4 requires a sixth order expansion. These calculations allow us to consider the importance of the fifth and sixth order terms in the expansion of the Hamiltonian for the VPT4 calculations when the Hamiltonian is expanded in internal coordinates. The results of VPT2 calculations for these two molecules are provided in the Tables S9 - S11. For these calculations we utilize the deperturb and diagonalize approach,[16,17,39,44] where states are considered to be nearly degenerate when their contribution to the wave function at any order exceeds 0.3. For HOH this criterion identifies the 2:2 Darling-Dennison resonance between the two OH stretches, while for HOD it identifies a 2:1 Fermi resonance between the HOD bend and the OD stretch.

As is seen in the results reported in Tables 1 and 2, the changes in energies between second and fourth order perturbation theory are quite large when the expansion of the Hamiltonian is truncated at fourth order, while the VPT4 calculation that was based on a sixth order expansion of the Hamiltonian provides much smaller corrections. For states with one or two quanta of excitation, we expect that second order perturbation theory should provide reliable results, so corrections at fourth order are anticipated to be small. This is what has been seen in prior perturbation theory studies of water, which were performed up to VPT8.[32]

The origin of the problem with using truncated expansions in internal coordinates can be seen in the analysis of the Morse oscillator, which is described in Ref. 20. Specifically, while the values of the energies of the Morse oscillator are correctly captured at VPT2 and do not change at higher orders in perturbation theory, if the expansion of the Morse potential is trucated at fourth order, there will sizable errors in the calculated energies. This can be circumvented by reexpressing the expansion of the potential and dipole moments in Morse variables, as described above. While such an expansion will likely deviate somewhat from the full sixth order expansion of the potential, the two expansions are identical through fourth order, and such higher order terms can be challenging to obtain numerically both due to the large number of terms and challenges with instability of numerical differentiation.

Ammonia

We next turn our attention to ammonia. In addition to providing another small molecule of fundamental interest, studying ammonia allows us to explore the role of coordinate choice on the accuracy of the results of the VPT2 calculation. Unlike displacements of Cartesian coordinates, for which there is no ambiguity in the choice of coordinates, the choice of internal coordinates is not unique, and the convergence behavior of VPT calculations can depend on the choice of internal coordinates used for the study.[43]

For the calculations of ammonia, we use two sets of coordinates. Both sets of coordinates include the three NH bond lengths, and two of the HNH angles. The first set of coordinates, referred to as $z-$matrix coordinates in the following discussion, includes the angle between one of the NH bonds and the plane containing the nitrogen atom and the remaining two hydrogen atoms. The specific definition is given by the $z-$matrix, which is provided in Table S2. The second coordinate set uses the third HNH angle and will be referred to as the $\theta-$coordinates. The $z-$matrix coordinates have the advantage that they fully describe all possible geometries of ammonia. On the other hand the three HNH angles are not treated equivalently. This can lead to a loss of symmetry in the potential as not all of the quartic terms are evaluated. This loss of symmetry will not be a problem for the $\theta-$coordinates. On the other hand, the three angles are linearly dependent in planar geometries.

The energies obtained from the VPT2 calculations, performed using expansions of the potential based on these two coordinate sets as well as expansions of the potential based on normal mode coordinates developed from displacements of these two sets of coordinates are reported in Table 3. The corresponding comparison of the intensities are provided in Table S12. We focus on transitions to states with one or two quanta of excitation in the NH stretch and the HNH bend. Overall the agreement among the four calculations is very good. The largest differences are smaller than 2.5 cm^{-1} for states with energies up to 7000 cm^{-1} above the ground state energy. Likewise, the intensities obtained from the four calculations are in good agreement. Closer examination of the energies and intensities of the degenerate levels, e.g. those with $E-$symmetry, shows that the expansions based on the $\theta-$coordinate do a better job of capturing the underlying symmetry of the molecule than the expansions performed in the $z-$matrix coordinates. This is reflected by the nearly-zero values for most of the entries in the rows labeled as *splitting* in Tables 3 and S12. The exception is found in the energies of the states with one quantum in each of the doubly degenerate vibrations, ($v_a + v_b$, E). For these states, the calculations based on the normal mode expansions of the potential show 1.8 and 2.7 cm^{-1} splittings. This non-zero value of the splitting reflects the omission of the term that is proportional to $q_{a,1}q_{a,2}q_{b,1}q_{b,2}$ from the quartic expansion of the potential. When the expansion of the potential is performed in the internal coordinates and rotated to the normal mode coordinates this term is found to be 1.6 cm^{-1}. As noted in the introduction, the collective nature of the normal mode coordinates can result in non-negligible quartic terms in the potential that involve four different coordinates. Such terms, though, reflect contributions from terms in the expansion involving three or fewer coordinates when the expansion is performed in internal coordinates.

Interestingly, when the potential is expanded in the $z-$matrix coordinates, the erroneous splitting is even larger when the VPT2 calculation is based on the internal coordinate expansion of the potential than when the potential is expanded in the normal mode coordinates directly. This reflects the loss of symmetry in the potential as the three HNH angles are not equivalent. When the $\theta-$coordinates are used for the internal coordinate expansion of the potential, all of the splittings become numerically zero, as they should be.

If we use the quartic expansion of the potential in the internal coordinates to generate a sixth order expansion, as described above, and use this potential in a VPT4 calculation, the problems with the $z-$matrix coordinate expansion become more pronounced. As is seen in the results provided in Table S13, the differences between the energies evaluated at VPT2 and VPT4 when the potential is expanded in the $\theta-$coordiantes are generally smaller than 5 cm^{-1}. This is consistent with the energy differences for HOH and HOD, based on the energies reported in Tables 1 and 2. The three exceptions are found in the states with two quanta in the NH stretches that have A_1 symmetry and the overtone in the umbrella mode. The 20 cm^{-1} shifts in the energies of the states with two quanta in the NH stretching vibrations reflects the inclusion of the 2:2 Darling-Dennison resonance in the VPT4 calculation, which was not identified in the VPT2 calculation. When this resonance is introduced in the VPT2 calculation, the differences between the energies for these states evaluated using VPT2 and VPT4 are reduced to less than 5 cm^{-1}. The poorer convergence for the overtone in the umbrella vibration reflects the low-barrier to planarity for this molecule. At the MP2/aug-cc-pVTZ level of theory/basis used for this study, the barrier to planarity is 1770 cm^{-1}. This is smaller than the energy of the state with two quanta of excitation in the umbrella vibration, as calculated using VPT2. As a result, this vibration is not expected to be well-described by vibrational perturbation theory. This is also the reason the states with excitation in the umbrella vibration are not reported in Tables 3 and S12.

Based on the above analysis, we find that using the internal coordinate expansion of the potential for vibrational perturbation theory calculations provides results that are very close to those obtained when the potential is expanded in the normal mode coordinates. We also find that using coordinates that reflect the symmetry of the molecule, e.g. including all three of the HNH bending angles in NH_3, can provide an expansion of the potential that better reflects the symmetry of the molecule being investigated. Before concluding this discussion, we note that similar sensitivity of the results of high-order perturbation theory was identified in an early study of the out-of-plane bending vibration formladehyde.[34]

Other molecules

We also applied VPT2 to several molecules consisting of five atoms as well as H_2CO. Formaldehyde was chosen due to the fact that four of the modes have frequencies ranging from 1200 to 1700 cm^{-1}, which is roughly half the 2800 cm $^{-1}$ frequency of the CH stretches. This leads to a large number of nearly degenerate states. For this reason, for the perturbation theory calculations on formaldehyde we use the value of[43,45]

$$N_t = 2(n_s + n_a) + n_{\text{CO}} + n_{\text{oop}} + n_{\text{wag}} + n_{\text{rock}} \tag{9}$$

to determine which states are expected to be nearly degenerate. Here n_s and n_a represent the number of quanta in the symmetric and antisymmetric CH stretching vibrations, while the remaining four quantum numbers provide the number of quanta in the CO stretch and the three bending vibrations. For all other molecules, nearly degenerate states are identified based on the size of their contribution to the wave function of the state of interest, as described above. The halogenated methane molecules were chosen to explore how well the $z-$matrix coordinates perform for tetrahedral molecules. Finally we include three isomers of nitric acid. The two isomers of peroxynitrous acid (HOONO) are differentiated by the torsion angles. In tp-HOONO, the OONO is in a trans geometry, while the OH bond is perpendicular to the plane containing the heavy atoms. in cc-HOONO, both HOON and OONO are in cis-geometries, forming a ring structure with an intramolecular hydrogen bond. The existence of the intramolecular hydrogen bond in cc-HOONO leads to the expectation that the terms in the expansion of the potential that involve three or four internal coordinates will be larger than those in the tp-HOONO, which does not contain a hydrogen bond.

A summary of the results obtained by performing VPT2 calculations on these molecules when the potential is expanded in internal and normal mode coordinates is provided in Table 4. The results are characterized by the mean absolute difference (MAD) between the energies obtained from the two calculations as well as the magnitude of the largest difference between these energies (maximum). Complete lists of the VPT2 results are provided in the Supporting Information. The results in Table 4 are separately reported for states with one and two quantum of excitation. They are further divided between states with two quanta of excitation in a single vibration and ones where two vibrations each have one quantum of excitation.

With the exception of CH_3F, the mean absolute differences are smaller than 1 cm^{-1} and the largest differences are smaller than 5 cm^{-1}. The larger differences for CH_3F reflects the challenges in capturing the symmetry when z-matrix coordinates are used. When the symmetry is reduced in CH_2F_2 and CH_2FCl the differences between the calculations based on the two potential expansions are smaller and are comparable to those found for the isomers of nitric acid. Of the three isomers of nitric acid, cc-HOONO shows the largest sensitivity to how the potential is expanded. This is attributed to the intramolecular hydrogen bond. When we look at the results for tp-HOONO, which has similar vibrational frequencies but no intramolecular hydrogen bond, the differences between the results obtained using the two expansions of the potential are reduced significantly.

Conclusions

In this work, we presented an alternative approach for obtaining the quartic expansions of the potentials used in vibrational perturbation theory calculations. We show that expanding the potential in terms of internal coordinates provides energies and intensities at second order that are in good agreement with those obtained when an expansion of the potential in normal mode coordinates is used. In cases where the molecules have high symmetry, care needs to be taken to ensure that the internal coordinates that are used to expand the potential capture this symmetry.

The use of internal coordinate expansions of the potential has several advantages over using expansions in normal mode coordinates. First, the expansion coordinates do not depend on the masses of the atoms, making these potentials transferable among isotopologues. Also such internal coordinate expansions can be extrapolated to higher order, through a change in variables from displacements of distances and angles to displacements of Morse-coordinates or the cosines of the angles. This provides a straightforward way to obtain the higher order expansions of the potential, which are needed to extend the perturbation theory to higher orders, without requiring additional electronic structure calculations. Finally if a restricted quartic expansion of the potential is to be used in which only terms in the expansion that involve at most three vibrational coordinates are included, one expects that the omitted terms in the internal coordinate expansion will be smaller than those in the normal mode coordinate expansion. This can become important when near degeneracies are considered as was demonstrated for NH_3.

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Supporting Information Available

Summary of VPT results for all of the molecules listed in Table 4; $z-$matrices used for the VPT calculations; Optimized geometries for molecules listed in 4.

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Table 1: Results of Vibrational Perturbation Theory Calculations of Water

			Harmonic		Anharmonic - 2nd[b]		Anharmonic - 4th [c]		Anharmonic - 6th[d]	
State[a]			Energy	Intensity	Energy	Intensity	Energy	Intensity	Energy	Intensity
n_b	n_s	n_a	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))
0	0	1	3947.70	75.46	3767.79	72.22	3824.83	73.31	3767.62	72.09
0	1	0	3821.87	5.56	3654.26	4.34	3709.25	4.41	3653.77	4.31
1	0	0	1628.38	71.68	1578.09	72.40	1581.02	72.54	1575.67	72.46
0	0	2	7895.40	0.00	7466.09	0.09	7625.73	0.03	7466.77	0.07
0	2	0	7643.75	0.00	7204.04	0.26	7399.94	0.33	7201.00	0.30
2	0	0	3256.75	0.00	3124.46	0.61	3130.32	0.61	3114.73	0.60
0	1	1	7769.57	0.00	7267.08	2.26	7506.67	2.33	7263.89	2.32
1	0	1	5576.07	0.00	5325.67	3.96	5391.84	4.01	5324.55	4.07
1	1	0	5450.25	0.00	5215.39	0.06	5278.89	0.06	5212.72	0.06

[a] States are labeled by the number of quanta in the HOH (b)end, (s)ymmetric OH stretch and (a)symmetric OH stretch.

[b] Results of VPT2.

[c] Results of VPT4 based on a quartic expansion of the Hamiltonian.

[d] Results of VPT4 based on a sixth order expansion of the Hamiltonian.

Table 2: Results of Vibrational Perturbation Theory Calculations of HOD

			Harmonic		Anharmonic - 2nd[b]		Anharmonic - 4th [c]		Anharmonic - 6th[d]	
	State[a]		Energy	Intensity	Energy	Intensity	Energy	Intensity	Energy	Intensity
n_b	n_{OD}	n_{OH}	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))	(/cm^{-1})	(/(km mol^{-1}))
0	0	1	3887.72	45.28	3712.84	41.79	3769.36	42.43	3712.87	41.87
0	1	0	2820.84	19.75	2722.43	15.10	2740.59	11.12	2721.16	13.88
1	0	0	1427.37	60.82	1388.25	61.26	1390.33	61.36	1386.64	61.30
0	0	2	7775.44	0.00	7268.10	1.20	7510.85	1.23	7267.68	1.22
0	2	0	5641.68	0.00	5362.36	0.56	5461.47	0.60	5372.08	0.49
2	0	0	2854.75	0.00	2757.85	4.87	2765.54	8.72	2752.58	5.80
0	1	1	6708.56	0.00	6422.52	0.20	6516.85	0.11	6437.76	0.11
1	0	1	5315.09	0.00	5079.24	1.68	5144.63	1.70	5078.91	1.64
1	1	0	4248.21	0.00	4091.61	1.90	4142.73	1.72	4117.47	1.52

[a] States are labeled by the number of quanta in the HOD (b)end, the (OD) stretch and the (OH) stretch.

[b] Results of VPT2.

[c] Results of VPT4 based on a quartic expansion of the Hamiltonian.

[d] Results of VPT4 based on a sixth order expansion of the Hamiltonian.

Table 3: Energies (in cm^{-1}) Obtained from VPT2 Calculations of NH$_3$

	Coordinates[a]			
state[b,c]	q/z	r/z	q/θ	r/θ
v_a	3483.97	3483.93	3484.00	3483.96
splitting[d]	0.02	0.09	0.02	0.01
v_a	3360.27	3360.36	3360.29	3360.26
v_b	1621.40	1621.43	1621.39	1621.37
splitting[d]	0.02	0.29	0.00	0.00
v_u	959.28	959.43	959.01	959.08
$2v_a, A_1$	6856.70	6856.47	6856.77	6856.62
$2v_a, E$	6931.03	6930.87	6931.08	6930.96
splitting[d]	0.07	0.09	-0.10	0.03
$2v_s$	6669.39	6669.55	6669.44	6669.37
$2v_b$,E	3232.22	3231.89	3232.22	3232.17
splitting[d]	0.01	0.23	0.01	0.00
$2v_b, A_1$	3209.30	3209.07	3209.30	3209.25
$v_a + v_s$	6728.88	6728.85	6728.96	6728.85
splitting[d]	0.11	0.02	0.08	0.02
$v_a + v_b, A_1$	5100.67	5099.53	5099.83	5100.54
$v_a + v_b, E$	5089.69	5089.60	5087.46	5088.49
splitting[d]	1.82	2.33	2.72	0.00
$v_a + v_b, A_2$	5084.13	5084.79	5085.04	5083.67
$v_s + v_b$	4978.10	4977.78	4978.10	4978.56
splitting[d]	0.02	0.97	0.00	0.00

[a] Potential is expanded in either internal (r) or normal mode (q) coordinates in which the angles are defined based on the $z-$matrix (z) or treating all three HNH angles equivalently (θ).

[b] States are labeled by the number of quanta in the HNH (b)end, the (s)ymmetric NH stretch, (a)symmetric NH stretch and the umbrella vibration.

[c] Symmetry labels under C_{3v} are included when there are multiple excited states with the same assignment and different symmetries.

[d] Energy difference between pairs of states that should be degenerate.

Table 4: Maximum and Mean Absolute Difference (MAD) (in cm^{-1}) Between VPT2 Energies Calculated When the Potential is Expanded in Internal and Normal Mode Coordinates.

	$v = 1^a$		$v = 2^b$		$v = 1$ and $v' = 1^c$	
Molecule	MAD	maximum	MAD	maximum	MAD	maximum
H_2CO^d	0.12	0.35	0.30	1.62	0.54	2.90
NH_3 $(z)^e$	0.12	0.24	0.29	0.65	0.44	1.33
NH_3 $(\theta)^e$	0.04	0.07	0.12	0.25	0.56	1.69
CH_3F	1.00	3.30	1.99	7.16	1.83	7.19
CH_2F_2	0.35	0.79	1.16	4.11	0.89	4.60
CCH_2FCl	0.43	0.91	0.91	2.70	0.93	4.04
HNO_3	0.36	1.54	0.88	4.18	0.59	2.62
cc-HOONO	0.90	1.82	1.70	3.65	1.65	4.20
tp-HOONO	0.11	0.34	0.20	0.69	0.23	0.67

[a] States with one quantum of excitation.

[b] States with two quanta of excitation in a single mode.

[c] States with one quantum of excitation in two modes.

[d] Energies calculated using resonance conditions based on the global quantum number, N_t, defined in Eq 9.

[e] Energies calculated for NH_3 when the angles are defined based on the $z-$matrix (z) or treating all three HNH angles equivalently (θ).