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Degenerate perturbation theory corrections for the vibrational self-consistent field approximation: Method and applications

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A new algorithm for computing anharmonic vibrational states for polyatomic molecules is proposed. The algorithm starts with the vibrational self-consistent field (VSCF) method and uses degenerate perturbation theory to correct for effects of correlation between different vibrational modes. The algorithm is developed in a version that computes the anharmonic vibrational spectroscopy directly from potential energy surface points calculated by using *ab initio* codes. The method is applied to several molecules where near degeneracies occur for excited vibrational states, including HOOH, HSSH, and HOOOH. The method yields results in very good accordance with experiments and generally provides improvements over nondegenerate perturbation corrections for VSCF. © 2002 American Institute of Physics. [DOI: 10.1063/1.1494978]

I. INTRODUCTION

Anharmonic calculations of vibrational spectroscopy are often required for the interpretation of experimental data, even for fundamental and other low-lying excitations. Such calculations are a challenge for large polyatomic systems. Harmonic vibrational frequencies are readily computable for virtually all empirical force fields and for semiempirical and *ab initio* electronic structure programs. The harmonic approximation, which utilizes local expansion of potential energy truncated at second order, is generally in substantial error, making assignment of experimental vibrational spectra difficult. Empirical correction is introduced, e.g., by Hehre *et al.*,¹ to correct such errors in the *ab initio* frequencies, and the use of empirical correction has become a standard practice in the electronic structure calculations. General applicability of the empirical correction is, however, questionable.

Methods for calculating anharmonic vibrational spectroscopy have been vigorously pursued. Only for very small molecules are numerically exact calculations of the spectroscopy feasible. For large systems, approximation methods are necessary. Such applications must deal adequately with the anharmonic coupling between different vibrational modes. The approach taken in the present work is based on the vibrational self-consistent field (VSCF) approximation,²⁻⁵ which assumes separability of the wave functions in suitable

modes, such as the normal modes for low-lying transitions. VSCF includes coupling effects between different modes through certain average potentials, but does not account for correlation effects, i.e., the nonseparability of the true vibrational functions. Extensions to VSCF were proposed⁶⁻⁹ that allow for such correlation effects that are generally of great importance. An extension that proved computationally very efficient for large system is correlation-corrected VSCF (CC-VSCF),^{7,8} which employs nondegenerate perturbation theory, typically up to second order. In addition to this development, VSCF and CC-VSCF methods have been interfaced with *ab initio* and semiempirical electronic structure theory codes.^{10,11} The potential energy surface points needed by VSCF and CC-VSCF were calculated directly from these programs. A similar direct approach has also been reported by other groups.^{12,13}

The VSCF method based on empirical potentials has been successfully applied to $(\text{H}_2\text{O})_n$ and $\text{Cl}^-(\text{H}_2\text{O})_n$, where $n = 1, 2, 3$,⁷ Ar₁₃,⁷ oligomeric peptides¹⁴ and even to bovine pancreatic trypsin inhibitor protein hydrated with 196 water molecules, giving rise to 3435 coupled modes.^{15,16} The *ab initio* electronic structure calculation-based VSCF and CC-VSCF has been applied to $(\text{H}_2\text{O})_n$, where $n = 1, 2, 3$,^{11,17} $\text{Cl}^-(\text{H}_2\text{O})$,^{11,17} methanol-H₂O,¹⁷ glycine,¹⁸ glycine-H₂O,¹⁹ $(\text{HCl})_n(\text{NH}_3)_n$ and $(\text{HCl})_n(\text{H}_2\text{O})_n$, where $n = 1, 2$,²⁰ rare gas containing molecules,^{21,22} CH₃NH₂,²³ and N-methylacetamide.²⁴ Furthermore, the VSCF method has been applied to an extended system using several different boundary conditions to examine I₂ in an Ar matrix.²⁵

The one-electron as well as many-electron bases of

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the electronic structure theory have been examined for suitability in solving the anharmonic vibrational problem. The closed-shell second-order Møller-Plesset perturbation theory²⁶ (MP2) and density functional theory (DFT), particularly the Becke three-parameter, Lee-Yang-Parr functional (B3LYP),^{27,28} both with triple-zeta+ polarization (TZP) basis,²⁹ have been found^{10,11} to be quite robust.

In the present article, we propose a new method utilizing degenerate perturbation theory based on the VSCF wave functions. The CC-VSCF method, based on nondegenerate perturbation theory, can suffer from the near-degeneracy problem, resulting in an unphysically large correction to the energy. The objectives in development of the new method are twofold: good agreement with experimental results must be obtained while keeping the computations efficient. By utilizing degenerate perturbation theory, near degeneracy is handled correctly, and at the same time, the computation is relatively efficient in comparison to the configuration mixing method, such as VSCF-CI (configuration interaction).⁶

The present work is organized as follows. Theoretical descriptions of the degenerate as well as the nondegenerate perturbation theory based on the VSCF wave functions are presented in Sec. II. Section III gives examples of systems to check the consistency of the degenerate perturbation theory. Section III also presents the results of calculations where the near degeneracy is seen in the CC-VSCF method. Finally, Sec. IV gives concluding remarks.

II. THEORETICAL APPROACH

The VSCF and CC-VSCF theory and algorithm given below have been extensively explored; therefore, only a brief description that is pertinent to the present work is presented. Further details are found in Refs. 5, 7, and 8.

A. Vibrational self-consistent field

The vibrational Schrödinger equation, for nonrotating molecules in the Born-Oppenheimer approximation, is to a good approximation given as

$$\left[-\frac{1}{2} \sum_{j=1}^N \frac{\partial^2}{\partial Q_j^2} + V(Q_1, \dots, Q_N) \right] \Psi_n(Q_1, \dots, Q_N) = E_n \Psi_n(Q_1, \dots, Q_N), \quad (1)$$

where Q_j is the j th mass-weighted normal coordinate. Equation (1) neglects vibrational-rotational coupling,^{30,31} which in some cases can play an important role, even for $J=0$ states. Extension of the method below for such cases may be feasible, but will not be considered here, and for the system and states considered here the issue is of secondary importance.

In the VSCF method the total wave function is approximated by the product of single-mode wave functions $\psi_j(Q_j)$ for the mode j :

$$\Psi_n(Q_1, \dots, Q_N) = \prod_{j=1}^N \psi_j^{(n)}(Q_j). \quad (2)$$

By substituting Eq. (2) into Eq. (1) and integrating over ψ_l , where $l \neq j$, one can arrive at a set of single-mode VSCF equations,

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial Q_j^2} + \bar{V}_j^{(n)}(Q_j) \right] \psi_j^{(n)}(Q_j) = \epsilon_j^{(n)} \psi_j^{(n)}(Q_j), \quad (3)$$

where $\bar{V}_j^{(n)}(Q_j)$ is the effective potential of the n th state for mode Q_j and is given by

$$\bar{V}_j^{(n)}(Q_j) = \left\langle \prod_{l \neq j}^N \psi_l^{(n)}(Q_l) \left| V(Q_1, Q_2, \dots, Q_N) \right| \prod_{l \neq j}^N \psi_l^{(n)}(Q_l) \right\rangle. \quad (4)$$

The integral above depends on $\psi_l^{(n)}$; therefore, the single-mode vibrational Schrödinger equation must be solved in an iteratively self-consistent manner. The effective potential $\bar{V}_j^{(n)}$ can be interpreted as the potential energy of the j th mode interacting with the average field of all other modes. There is no explicit mode correlation built into the VSCF equation.

The total energy of the system is expressed as a trace of single-mode energy $\epsilon_j^{(n)}$:

$$E_n^{\text{VSCF}} = \sum_{j=1}^N \epsilon_j^{(n)} - (N-1) \times \left\langle \prod_{j=1}^N \psi_j^{(n)}(Q_j) \left| V(Q_1, \dots, Q_N) \right| \prod_{j=1}^N \psi_j^{(n)}(Q_j) \right\rangle. \quad (5)$$

The second term on the right-hand side is due to the double counting of the off-diagonal interaction potentials in the Hamiltonian.

B. Correlation-corrected VSCF

The effect of correlation between different modes as a correction to VSCF can be obtained by means of Rayleigh-Schrödinger perturbation theory treatment. The second-order perturbation theory, known as Møller-Plesset perturbation partitioning,^{26,32,33} has been known to be reliable and computationally less demanding than methods such as the CI method. The perturbation correction to the VSCF is also reliable and can be computed with efficiency.

The full Hamiltonian of the system is given by $H = H^0 + \Delta V$ and in terms of the VSCF equation

$$V(Q_1, \dots, Q_N) = \sum_{j=1}^N \bar{V}_j^{(n)}(Q_j) + \Delta V(Q_1, \dots, Q_N), \quad (6)$$

where the true potential is a sum of VSCF separable potentials, $\bar{V}_j^{(n)}(Q_j)$, and a small perturbation. In order to obtain second-order energy expression of the n th state, the energy and wave functions are expanded as a power series in the ordering parameter, λ :

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots, \quad (7)$$

$$\Psi_n = \Psi_n^0 + \lambda \Psi_n^1 + \lambda^2 \Psi_n^2 + \dots. \quad (8)$$

The superscripted number is used for the order of the perturbation expansion, and the subscripted number represents a

state label. By substituting above equations into $H\Psi_n = E_n\Psi_n$, where $H = H_n^0 + \lambda\Delta V$, and collecting terms in the powers of λ in the usual way, one can arrive at the second-order energy contribution expression

$$E_n^2 = \sum_{m \neq n} \frac{\langle \Psi_n^0 | \Delta V | \Psi_m^0 \rangle \langle \Psi_m^0 | \Delta V | \Psi_n^0 \rangle}{E_n^0 - E_m^0}, \quad (9)$$

where Ψ_n^0 and Ψ_m^0 are the product wave functions of Eq. (2). The perturbation energy expression above assumes that the zeroth-order energies are well separated.

C. Degenerate perturbation theory VSCF

The second-order energy expression in the perturbation expansion can lead to an unphysically large energy correction due to the small energy difference in the denominator of Eq. (9). In such case, Eq. (9) is no longer appropriate for obtaining the second-order energy correction to VSCF. Degenerate perturbation theory³⁴ (DPT) can be used to correctly handle near degeneracy.

Consider a case where $(H^0 - E)\Psi_k^0 = 0$ and different values of k give the degenerate eigenvalues E . The task is to obtain an appropriate linear combination of the wave functions Ψ_k^0 to lift the degeneracy at first order. Since the term that is zeroth order in λ of Eq. (8) now contains a linear combination of Ψ_k^0 , the power series expansion of Ψ_n is now given as

$$\Psi_n = c_1\Psi_1^0 + \dots + c_k\Psi_k^0 + \lambda\Psi_n^1 + \lambda^2\Psi_n^2 + \dots, \quad (10)$$

where k spans only in the degenerate space. Substitution of $c_k\Psi_k^0$ into the first-order energy expression $\langle \Psi_k^0 | H^1 | \Psi_k^0 \rangle = E_k^1$ results in a set of simultaneous linear equations of order k . In terms of VSCF wave functions, we have

$$[\Delta V - E_k^1]\Phi_{n'} = 0, \quad (11)$$

where $\Phi_{n'} = \sum_{j=1}^k c_j\Psi_j^0$ and n' denotes that the states n are expanded in the linear combination. The nontrivial solution can be sought by diagonalizing the Hamiltonian matrix of order k to lift degeneracy at the first order in energy. This is equivalent to solving the CI problem in the space that spans the degenerate subspace k . The eigenvalues obtained this way are referred to as DPT1-VSCF.

The second-order energy contribution is obtained in the same way as the nondegenerate case. The second-order energy is given by

$$E_n^2 = \sum_{m \neq n'} \frac{\langle \Phi_{n'} | \Delta V | \Psi_m^0 \rangle \langle \Psi_m^0 | \Delta V | \Phi_{n'} \rangle}{E_n^0 - E_m^0}, \quad (12)$$

where the sum runs over all m except for the degenerate space n' . The difference between the equations above and Eq. (9) is that $\Phi_{n'}$ contains the linear combinations that spans the degenerate space.

The results obtained by using the second-order energy correction through the degenerate perturbation theory is referred to as DPT2-VSCF in the following discussion. The degenerate space chosen for the present study is to include excitation of a single mode to first excited level for all degrees of freedom. The choice is justified by the fact that there is no systematic way at present to choose such a configura-

tion space *a priori*. Based on the results of this choice and those considered in future studies, selection of the degenerate configurations should become clearer.

D. Pairwise approximation to mode coupling and grid representation

The potential energy term in Eq. (4) can be represented in several ways. One way is to expand the potential energy in a Taylor series. In this approach, higher-order derivatives of energy with respect to nuclear coordinates must be available through either analytical or numerical differentiation. The empirical force-field-based direct computation of VSCF and CC-VSCF energies has been carried out¹⁴ with this expansion by including all cubic and parts of quartic force constants, obtained with the numerical differentiation of the Hessian. Such expansions become computationally very costly as the size of the system increases, especially if high-order terms in the expansion are required.

The approach chosen for the present study is to express $V(Q_1, \dots, Q_N)$ in terms of a pairwise potential in grid form,

$$V(Q_1, \dots, Q_N) = \sum_i V_i(Q_i) + \sum_{i \neq j} V_{ij}(Q_i, Q_j). \quad (13)$$

The first term on the right-hand side of Eq. (13) is the diagonal potential and the second represents the pair coupling potential. In terms of the full potential in normal coordinates,

$$V_j(Q_j) = V(Q_1=0, \dots, Q_j, \dots, Q_N=0), \quad (14)$$

$$V_{ij}(Q_i, Q_j) = V(0, \dots, Q_i, \dots, Q_j, \dots, 0) - V_i(Q_i) - V_j(Q_j). \quad (15)$$

An advantage in choosing the pairwise potential in grid points is the fact that all anharmonic contributions in the diagonal potential are included, while in the Taylor series expansion method, the order to which the potential is truncated determines the highest contribution in the diagonal potential. Moreover, the Taylor series expansion approach scales more poorly with the size of the system than the grid method. In this study, a 16-point grid is used for each normal coordinate. This requires $16n + 16^2[n(n-1)/2]$ single-point energy calculations, where n is the number of normal modes. The one-dimensional Schrödinger equations in Eq. (3) are solved by using the collocation method described by Yang and Peet.^{7,35}

E. Electronic structure calculations

In the previous articles,^{10,11} the calculated fundamental transitions were compared with experiments utilizing the MP2 (Ref. 26) or density functional (Refs. 27 and 28) electronic structure methods. In certain cases, such as glycine conformers,¹⁸ the double-zeta+ polarization³⁶ (DZP) basis set is sufficient. In order to obtain greater accuracy in the calculated frequencies, the basis set chosen for this study is the TZP basis of Dunning²⁹ along with MP2 for the many-electron basis, as described in another study.¹⁰ In addition, convergence of fundamental frequencies on one-electron as well as many-electron bases has also been examined for

TABLE I. Comparison of fundamental vibrational frequencies (cm^{-1}) of H_2O .

Mode	Harmonic	VSCF	CC-VSCF	DPT1-VSCF	DPT2-VSCF	Expt. ^a
1	4015	3835	3797	3835	3794	3756
2	3877	3760	3699	3760	3696	3652
3	1603	1554	1548	1553	1548	1595

^aReferences 38 and 39.

H_2O .¹¹ This study also compares several vibrational methods and gives estimates of errors resulting from different approximations used in the VSCF and CC-VSCF methods adopted for the present study. The DPT-VSCF methods have been incorporated in the GAMESS electronic structure program,³⁷ and all calculations reported here were performed with GAMESS.

III. RESULTS AND DISCUSSION

In order to assess the performance of DPT2-VSCF, a few examples are shown below to compare it with other methods and with experimental data. More specifically, H_2O and NH_3 are used as a consistency check for the DPT2-VSCF method against CC-VSCF, where VSCF is corrected for correlation between modes by nondegenerate perturbation theory. Then the results are presented for HOOH, HSSH, and HOOOH. All calculations in DPT1-VSCF utilize the degenerate space that includes the ground level and excitation of a single mode to first excited level for all degrees of freedom.

A. H_2O

Table I shows the comparison of the calculated fundamental frequencies using the harmonic approximation, VSCF, CC-VSCF, DPT1-VSCF, and DPT2-VSCF methods to the experimental frequencies for H_2O . At the MP2/TZP level of theory, the errors in the fundamental frequencies using DPT2-VSCF calculated compared to the experiment are consistently smaller than those calculated with the CC-VSCF method. For a strongly bound system such as H_2O , the DPT2-VSCF frequencies are expected to be in close agreement with the CC-VSCF results. This is due to the fact that DPT1-VSCF results are very close to the results obtained with the VSCF method, which indicates that there is virtually no mixing of configurations.

TABLE II. Comparison of calculated fundamental vibrational frequencies (cm^{-1}) of NH_3 .

Mode	Harmonic	VSCF	CC-VSCF	DPT1-VSCF	DPT2-VSCF	Expt. ^a
1	3713	3547	3498	3548	3495	3444,3444
2	3713	3511	3467	3510	3461	3444,3444
3	3553	3455	3381	3455	3376	3336,3337
4	1689	1629	1625	1629	1625	1626,1627
5	1689	1631	1627	1631	1627	1626,1627
6	1055	928	899	925	898	932,968

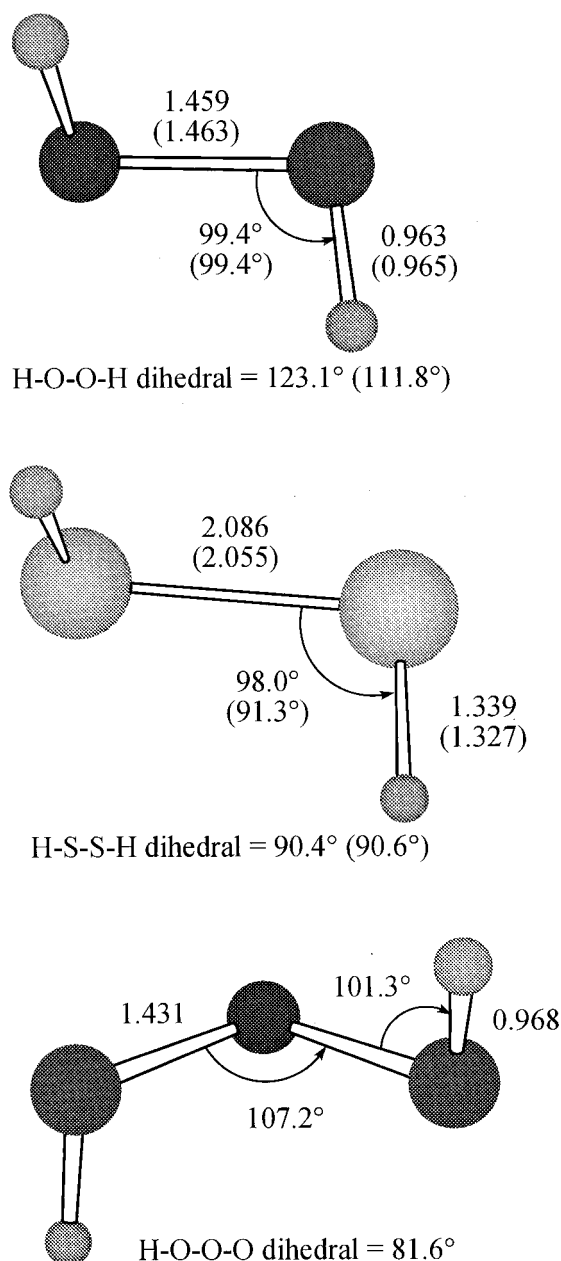
^aReferences 38 and 39. The values shown are symmetric and antisymmetric combinations of the inversion doublets.

FIG. 1. Calculated geometries of HOOH, HSSH, and HOOOH. The geometries are obtained at the MP2/TZP level of theory. The bond length and bond angles are in Å and degrees, respectively. The values in parentheses are the experimental values; see Ref. 40 for HOOH and see Ref. 42 for HSSH.

B. NH_3

The fundamental frequencies calculated for NH_3 are shown in Table II. As expected from the strongly bound NH_3 , the frequencies calculated using the DPT2-VSCF and CC-VSCF methods are similar, as were found for H_2O . The maximum deviation in the calculated values between DPT2-VSCF and CC-VSCF is only 6 cm^{-1} . The errors in comparison to the experimental results are somewhat larger than that in the H_2O case, which is likely to originate from lack of convergence in the computed potential.

At the harmonic level pairs of modes, such as modes 1 and 2 and modes 4 and 5 in NH_3 , are exactly degenerate. Beyond the harmonic approximation such modes generally

TABLE III. Comparison of calculated fundamental vibrational frequencies (cm^{-1}) of HOOH.

Mode	Description	Harmonic	VSCF	CC-VSCF	DPT1-VSCF	DPT2-VSCF	Expt. ^a	Theory ^b
1	sym OH str	3854	3627	3585	3615	3611	3605	3606
2	antisym OH str	3853	3606	3572	3622	3622	3605	3606
3	sym OH bend	1443	1398	1386	1398	1386	1394	1400,1406
4	antisym OH bend	1277	1238	1210	1238	1210	1265,1285	1246,1268
5	O–O str	916	885	879	885	879	866,878	851,862
6	torsion	341	374	273	361	276	254,371	260,380

^aReferences 38 and 39. The values shown are symmetric and antisymmetric combinations of the torsional doublets.

^bReference 41. Six-dimensional variational calculations. The two values of each mode are torsional tunneling values.

become only nearly degenerate. Depending on the system, this may be due to the potential function in the anharmonic region, which may not be symmetric for the two modes, or the nondegeneracy may arise at the VSCF level due to numerical reasons: Degeneracy is not imposed on the VSCF equations, even when the potential function is symmetric also in the anharmonic region. The modes are treated separately, and due to somewhat different errors in the modes, different frequencies may arise.

The experimental frequencies in Table II include inversion doublet transitions, which arise from the double-well interactions. The average of the mode-6 inversion doublet frequencies should give a reasonable zeroth-order transition energy. Then the error in the mode-6 frequency calculated with DPT2-VSCF is within 50 cm^{-1} , which is about a 5% error in comparison to the experimental frequency. Again, the VSCF and DPT1-VSCF results are close to each other, and therefore one can also expect the results from the CC-VSCF and DPT2-VSCF methods to be in close agreement.

C. HOOH

Figure 1 shows the geometric parameters obtained at the MP2/TZP level of electronic structure theory. The structure calculated is one of the two chiral conformations with a C_2 symmetry. The calculated geometries are in good accordance with the experimental geometries, except for the dihedral angle, where it is off by 10° . This is due to lack of including a set of diffuse functions.⁴⁰

Table III shows the calculated fundamental frequencies in comparison with the experiment. The results obtained with CC-VSCF and DPT2-VSCF do not differ greatly. The largest deviation between the two methods is in modes 1 and 2, where the differences are 26 and 50 cm^{-1} , respectively. The results of DPT1-VSCF show configurational mixing between

modes 1 and 2, while the mode-1 state has 13% mixing with mode 2 and the mode-2 state has 20% mixing of mode 1. The rest of the modes are nearly identical in the two methods.

The DPT2-VSCF results are in good agreement with the experimental frequencies. Along with the experimental frequencies, a theoretical work of Kuhn *et al.*,⁴¹ which agrees well with the experiments, is also shown in the table. This theoretical work employs over 13 000 single-point *ab initio* energy calculations, fitted to an analytical potential for vibrational variational calculations. Their results reproduce experimental results at nearly spectroscopic accuracy. Although the present work cannot handle tunneling situations, our approach only needs fewer than 4000 single-point energy evaluations, which are fed directly into VSCF, and subsequent determination of correlation energy. Since our approach cannot handle tunneling, the experimental frequencies are averaged over the torsional tunneling pairs, shown in Table III. The average deviation of the DPT2-VSCF method from the experimental values, using the tunneling average, is only 23 cm^{-1} . The largest two deviations are in modes 4 and 6. There is virtually no configurational mixing in either of the states according to the DPT1-VSCF results. The experimental torsional tunneling splitting is over 100 cm^{-1} in mode 6. This makes the determination of the mode-6 fundamental frequency difficult.

D. HSSH

The calculated geometric parameters are shown in Fig. 1. They are in good agreement with the experimental geometry.⁴² As in HOOH, the calculated structure is one of the two chiral conformations with a C_2 symmetry. The ex-

TABLE IV. Comparison of calculated fundamental vibrational frequencies (cm^{-1}) of HSSH.

Mode	Description	Harmonic	VSCF	CC-VSCF	DPT1-VSCF	DPT2-VSCF	Expt. ^a
1	SH sym str	2748	2620	2598	2621	2601	2556
2	SH antisym str	2746	2650	2629	2650	2632	2559
3	SH sym bend	923	909	901	909	901	883
4	SH antisym bend	920	904	897	904	897	886
5	SS str	530	521	520	523	530	510
6	torsion	437	428	400	423	433	417

^aReference 39; also see Ref. 43.

TABLE V. Comparison of calculated fundamental vibrational frequencies (cm^{-1}) of HOOOH.

Mode	Description	Harmonic	VSCF	CC-VSCF	DPT1-VSCF	DPT2-VSCF	Expt. ^a
1	sym OH str	3794	3584	3536	3581	3547	3530
2	antisym OH str	3790	3502	3447	3506	3463	3530
3	sym HOO bend	1381	1339	1317	1339	1317	1347
4	antisym HOO bend	1373	1331	1312	1331	1313	1359
5	sym OO str	901	884	872	884	873	821
6	antisym OO str	812	782	776	782	776	776
7	OOO bend	535	550	327	496	531	509
8	antisym tor rot	418	517	442	516	445	387
9	sym torsional rot	369	483	295	365	393	346

^aReference 44, HOOOH in the Ar matrix.

perimental dihedral angles for HSSH and HOOH differ by 20° . The dihedral angle in HSSH is 91° , reflecting the bond angle of sulfur.

The calculated fundamental frequencies are compared with the experiment in Table IV. The differences between CC-VSCF and DPT2-VSCF are again quite small. The largest difference between the two methods is 33 cm^{-1} for mode 6, where configurational mixing is observed. The mode-5 configuration mixes into the mode-6 state, which amounts to 45% in the CI expansion, and it reflects the largest deviation.

Unlike HOOH, the torsional splitting of HSSH is in the MHz range;⁴³ therefore, direct comparison with the experimental frequencies should be possible. The largest deviation, 73 cm^{-1} , for the DPT2-VSCF result in comparison with the experiment is in mode 2. However, the configurational mixing in the mode-2 state is minimal; only 1% of mode-1 configuration mixes according to the expansion coefficient in DPT1-VSCF. On average, the difference between the DPT2-VSCF results and experiment is 30 cm^{-1} .

E. HOOOH

In a recent article, Engdahl and Nelander⁴⁴ reported a positive identification of HOOOH in an Ar matrix. To our knowledge, this is the only experimental study of this molecule to date. The authors measured vibrational frequencies by which they identified the molecule. Their own calculations were carried out at the harmonic levels only. The calculated geometry, shown in Fig. 1 is in good agreement with the available *ab initio* calculations.⁴⁵ The calculated structure of HOOOH also possesses two chiral C_2 symmetry conformers.

The calculated fundamental frequencies are compared in Table V. The results obtained with CC-VSCF and DPT2-VSCF are in relatively good agreement with each other, except for modes 7 and 9. The mode-7 frequencies calculated with CC-VSCF and DPT2-VSCF differ by 204 cm^{-1} , and the mode-9 frequencies differ by 98 cm^{-1} . In these two modes, there is considerable configurational mixing, where 28% of the mode-9 configuration mixes in the mode-7 state, and the mode-7 configuration mixes by 48% into the mode-9 state. In addition, there is small mixing observed for mode 1 where 2% comes from mode 2, and for the mode-2 state 3% comes from mode 1. This is reflected by small differences between calculated frequencies for CC-VSCF and DPT2-VSCF.

The results obtained by DPT2-VSCF have the smaller deviation from experiment. Although there is large difference between the CC-VSCF and DPT2-VSCF results in mode 9, the errors in CC-VSCF and DPT2-VSCF, when comparing with experiment, are nearly equal, 51 and 47 cm^{-1} , respectively. The overall deviation of the DPT2-VSCF results from the experimental frequencies is only 38 cm^{-1} , while the CC-VSCF results deviate by 56 cm^{-1} .

IV. CONCLUSION

A new anharmonic spectroscopy algorithm for calculating the fundamental vibrational frequencies for polyatomic molecules is proposed. The method utilizes the degenerate perturbation theory to correct the VSCF approximation for correlation effects between different modes. The version of algorithm presented here computes the anharmonic vibrational states directly from *ab initio* codes, where the points on the potential energy surfaces are evaluated using the electronic structure calculations. In cases where vibrational near degeneracy causes appreciable correlation between different modes, and therefore gives rise to significant mixing of different VSCF states, the DPT2-VSCF method agrees better with experimental data than the CC-VSCF method, which corrects VSCF by nondegenerate perturbation theory. DPT1-VSCF gives valuable information on the mixing of VSCF states.

The degenerate perturbation theory method agrees very well with the available experimental results for the fundamental transitions of HOOH, HSSH, and HOOOH. The DPT2-VSCF frequencies, in comparison to the experiments, are within 31 cm^{-1} for the three molecules discussed in the present work. In the cases studied here, the improvement provided by DPT2-VSCF over CC-VSCF is definitely of a magnitude significant to analysis of experiments.

DPT1 and DPT2-VSCF are computationally only slightly more costly than CC-VSCF. Thus the new algorithm should be applicable to relatively large molecules. We estimate that with computational resources available at the present time, the DPT2-VSCF calculations that include treatment of all modes and the pairwise coupling between them should be feasible for molecules having up to 15–20 atoms.

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