Anharmonic Vibrational Spectroscopy of Hydrogen-Bonded Systems Directly Computed from ab Initio Potential Surfaces: $(H_2O)_n$, $n = 2, 3$; $Cl^-(H_2O)_n$, $n = 1, 2$; $H^+(H_2O)_n$, $n = 1, 2$; H_2O-CH_3OH

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Vibrational energy levels and infrared absorption intensities of several neutral and ionic hydrogen-bonded clusters are computed directly from ab initio potential energy surfaces, and the results are compared with experiment. The electronic structure method used to compute the potential surfaces is MP2, with Dunning's triple-ζ + polarization basis set. The calculation of the vibrational states from the potential surface points is carried out using the correlation corrected vibrational self-consistent field (CC-VSCF) method. This method includes anharmonicity and the coupling between different vibrational modes. The combined electronic structure/vibrational algorithm thus provides first-principles calculations of vibrational spectroscopy at a fairly accurate anharmonic level and can be useful for testing the accuracy of electronic structure methods by comparing with experimental vibrational spectroscopy. Systems treated here are $(H_2O)_n$, $n = 2, 3$; $Cl^-(H_2O)_n$, $n = 1, 2$; $H^+(H_2O)_n$, $n = 1, 2$; and H_2O-CH_3OH. In the cases of $(H_2O)_3$ and H_2O-CH_3OH, over 13 000 potential surface points are computed. For each system treated, all the fundamental transitions are computed, but the experimental data for comparison is mostly available for the OH stretches or other stiff modes only. The results show very good agreement between the calculated and experimental frequencies for all systems. The typical deviation for OH stretching modes is on the order of 50 cm^{-1}, indicating that the ab initio potential surfaces are of good accuracy. This is very encouraging for further pursuing MP2 calculations of potential energy surfaces of hydrogen-bonded systems.

Introduction

The use of electronic structure theory to compute vibrational spectra of molecular systems has become an important tool for interpretation of experimental IR spectra. Most electronic structure calculations obtain harmonic vibrational frequencies by diagonalizing the matrix of second derivatives of energy with respect to nuclear coordinates. This is done routinely by the majority of electronic structure packages, by either analytic or numerical evaluation of second derivatives. However, vibrational frequencies obtained this way can be spectroscopically very inaccurate: they differ substantially from experimental frequencies, with the deviation depending on the vibrational mode (e.g., the calculated harmonic frequencies for OH stretching modes typically deviate from experiment by 200−300 cm^{-1}). There are two main sources for this inaccuracy: one is the use of electronic structure approximations to obtain potential surfaces and their derivatives (limited level of ab initio theory and incomplete basis sets); the second (and most important one) is the use of the harmonic approximation, that is, the neglect of anharmonic effects and mode−mode couplings.

The most widely used tool for correcting these deficiencies at the present time is scaling factors. Several scaling factors have been suggested for harmonic frequencies obtained at different levels of ab initio, DFT, and semiempirical methods.[1] Such approaches are inherently empirical, and their validity is, at least in general, questionable.

Among the theoretically based methods used for correcting the harmonic approximation are the vibrational self-consistent field (VSCF) method and its correlation-corrected extensions.[2−8] Though based on the separability approximation, VSCF was shown to give a substantial improvement over the harmonic level and to bring the calculated frequencies into much closer agreement with experiment. The main advantage of the method is its applicability to very large systems. For example, it has been successfully applied for peptide−water complexes[9] and for the protein BPTI with hydration water molecules.[10,11] The VSCF method and its extensions have been also applied to water clusters using empirical potentials[12] and have proved successful for these highly anharmonic hydrogen-bonded systems.

There are several approaches in the literature that employ ab initio methods to obtain potentials for the use with the vibrational SCF method. One of them involves the use of ab initio points to obtain fitted analytical potential surfaces.[13,14] Fitting analytical potential surfaces is a very difficult task and is extremely challenging for systems larger than 3−4 atoms. Another approach is to express the potential as a series expansion, which includes higher order (cubic and quartic) terms.[10,15] However, previous calculations which employed this approach with empirical potentials showed that for strongly anharmonic systems, e.g., hydrogen-bonded systems, the quartic force field is inadequate.[12] Besides, the calculation of fourth-order derivatives of ab initio potentials is very expensive and is not feasible for large molecules.

In our work, we use an alternative approach, employing a grid representation of the potential, as described in more detail in the next section. Potential points on grids are calculated directly from an ab initio electronic structure program. Only a minimal amount of fitting is involved (in the form of polynomial

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interpolation). Anharmonic vibrational spectra are obtained as a direct application of ab initio electronic structure code. In this work, GAMESS[16] electronic structure package is used to obtain potentials on grids and to perform VSCF calculations.

The greatest advantage of using ab initio potential surfaces directly, is generality and applicability to any chemical system of the moderate size of up to 12−15 atoms. There is no need to develop an analytic form of the potential function. The VSCF program is built into the electronic structure package, and anharmonic frequencies can be obtained in the output of the program in addition to harmonic ones. Transitions other than fundamental (overtone and combination excitations) can be also obtained, as well as the corresponding IR intensities.

This ab initio VSCF method was introduced in our previous paper[17] and applied to H_2O, $(H_2O)_2$ and $Cl^-(H_2O)$ systems. It was concluded that the inaccuracies in potential energy surfaces due to electronic structure approximations are much higher than those of the VSCF method (at least for the stiff intramolecular vibrations). This opens a possibility for the use of the combined ab initio/VSCF method to test the quality of potential energy surfaces obtained from different levels of electronic structure. Such an application is of great importance in our view, since the calculation of potential energy surfaces is among the main goals of electronic structure theory. Here qualitatively, the combined electronic structure/VSCF algorithm provides the possibility of the assignment of spectroscopic transitions, valid in the regime where the harmonic approximation is inadequate.

In this paper, we extend the method to be applicable for larger systems and apply it to water trimer, complex of Cl^- with two water molecules, protonated water complexes H_3O^+ and $H_2O_5^+$, and complexes of water with methanol. Experimental vibrational spectra are available for these complexes, which makes them a good test of the proposed method. We will assess the quality of the computed potential energy surfaces by comparison with experiment, and comment on some properties of the ab initio potentials for these systems.

Methodology

Here we give a brief outline of the vibrational SCF method and its perturbation theory corrected extension, which was described in detail previously.[2−8,12]

After the equilibrium geometry of the molecular system is obtained, normal-mode analysis is performed using the electronic structure code. This provides harmonic frequencies and normal mode coordinates.

The vibrational Schrödinger equation in mass-weighted normal coordinates $Q_1, ..., Q_N$:

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

where $V(Q_1, ..., Q_N)$ is the full potential and N is the number of vibrational degrees of freedom. The VSCF approximation uses the separability ansatz,

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

which leads to the single-mode VSCF equations

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

where the effective VSCF potential $\bar{V}_j^{(n)}(Q_j)$ for mode Q_j is

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

Equations 3 and 4 are solved self-consistently, giving the set of VSCF single-mode energies and single-mode wave functions. The total VSCF energy is given by

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

After the VSCF solution is obtained, we correct it for correlation effects using second-order perturbation theory:[12]

$$E_n^{\mathrm{MP2}} = E_n^{\mathrm{VSCF}} + \sum_{m\neq n}\frac{\langle\prod_{j=1}^{N}\psi_j^{(n)}(Q_j)|\Delta V|\prod_{j=1}^{N}\psi_j^{(m)}(Q_j)\rangle^2}{E_n^{(0)} - E_m^{(0)}} \quad (6)$$

where ΔV is the difference between the true potential and the separable VSCF potential and can be considered a small perturbation,

$$\Delta V(Q_1, ..., Q_N) = V(Q_1, ..., Q_N) - \sum_{j=1}^{N}\bar{V}_j^{(n)}(Q_j) \quad (7)$$

Approximation 6 assumes no excited-state degeneracies. E_n^{VSCF} is the total VSCF energy, given by (5), $E_m^{(0)} = \sum_{j=1}^{N}\epsilon_j^{(n),m}$, where $\epsilon_j^{(n),m}$ is the mth SCF energy level of the jth mode, computed from the Hamiltonian $\bar{H}_j^{(n)}(Q_j)$.

The main computational difficulty of the above scheme is the evaluation of multidimensional integrals in eqs 4−6, which contain full potential $V(Q_1, ..., Q_N)$. To overcome this difficulty, the potential V is simplified as follows:[12]

$$V(Q_1, ..., Q_N) = \sum_{j}^{N}V_j^{\mathrm{diag}}(Q_j) + \sum_{i}\sum_{i<j}V_{ij}^{\mathrm{coup}}(Q_i,Q_j) \quad (8)$$

where $V_j^{\mathrm{diag}}(Q_j) = V(0, ..., Q_j, ..., 0)$ are the "diagonal", single-mode terms and $V_{ij}^{\mathrm{coup}}(Q_i,Q_j) = V(0, ..., Q_j, ..., Q_i, ..., 0)$ are the pairwise mode−mode coupling terms.

Thus, couplings between three and more normal modes are neglected. This approximation of pairwise interactions was shown to work reasonably well for water clusters studied with empirical potentials,[12] as well as for the applications tested in our previous paper.[17] Obviously, the pairwise interaction model is an assumption that in principle should be tested in each application.

With the pairwise approximation, the calculation of effective VSCF potentials [eq 4] involves only one-dimensional integrals of the form

$$V_j^{\mathrm{coup},(n)}(Q_j) \equiv \langle\psi_i(Q_i)|V_{ij}^{\mathrm{coup}}(Q_i,Q_j)|\psi_i(Q_i)\rangle \quad (9)$$

The calculation of the total VSCF energies, and also of the correlation-corrected energies [eqs 5 and 6] require up to two-dimensional integrals. The computation of these integrals is done numerically using a grid representation of single-mode and pair-coupling potentials. The single-mode VSCF equations (3) are also solved numerically using the collocation method of Yang and Peet.[18] The grid points for each normal mode coordinate Q_i are chosen equidistantly on an interval $[-Q_m, Q_m]$, where Q_m is proportional to $1/\sqrt{\omega_i}$(ω_i $-$ harmonic frequency for mode i). In the previous paper,[17] it was shown that 16 point grids are sufficient in accuracy for use with the collocation method.

Although the pairwise mode coupling approximation was originally introduced to simplify the integration, in the present context it has a more important computational benefit, which is to reduce the number of points at which the ab initio potential surface needs to be evaluated. Inclusion of a limited number of triple-mode or higher order coupling potentials is feasible, but only provided the number of such terms is limited, otherwise the number of ab initio points to be evaluated will be too large.

In this paper, we perform ab initio calculations of energy points on 8-point grids for diagonal potentials and 8 × 8 point grids for pair-coupling potentials. Then, we interpolate these potentials into 16 and 16 × 16 point grids using polynomial interpolation. Comparison of results for $(H_2O)_2$ and $Cl^-(H_2O)$ with calculated and interpolated 16-point grids shows that the resulting VSCF frequencies differ by typically around 5 cm^{-1}, with the deviation in the worst case equal to 17 cm^{-1}. These deviations are within the accuracy of our method, which is on the order of about 50 cm^{-1}.

Energy points on grids are calculated in the present paper at the MP2 level of electronic structure theory[19] using Dunning's triple-ζ basis set with polarization (TZP).[20] This level of theory was found to give satisfactory results for the applications performed previously.[17] It was shown that the potential surfaces obtained at this level of ab initio theory and used with the correlation-corrected VSCF method give fundamental vibrational frequencies which differ from experimental ones by up to 50 cm^{-1}, while the harmonic frequencies are often off by several hundreds of cm^{-1}. It was found[17] that using smaller, double-ζ + polarization (DZP),[21] basis set for calculation of potential energy surfaces gives somewhat larger errors in the resulting vibrational frequencies (up to 70−80 cm^{-1}). Larger, correlation-consistent (cc) basis sets give potential energy surfaces of better quality, but are not feasible for the systems studied here. Also, a level of ab initio theory higher than MP2 has to be used with larger cc-basis sets for a consistent improvement of potential surface quality.

The number of ab initio single-point energy calculations needed for diagonal and pair coupling potentials on grids is equal to

$$N_{\text{points}} = N_{\text{mode}} N_{\text{grid}} + \frac{N_{\text{mode}}(N_{\text{mode}} - 1)}{2} N_{\text{grid}}^{\ 2}$$

where N_{mode} is the number of normal modes of the system and N_{grid} is the number of grid points in one dimension. For each of the largest systems studied in this paper (water trimer and methanol−water complexes), the number of points calculated with ab initio (using pairwise approximation and 8-point grids) was 13 608. This required about 1 month of the CPU time on a R10000 SGI computer. Note that including higher body interactions at the level of triples would require calculation of an additional $N_{\text{grid}}^{\ 3}(N_{\text{mode}}(N_{\text{mode}} - 1)(N_{\text{mode}} - 2))/(2 \times 3)$ number of potential points, 680 960 for the above molecular systems. Such calculations are not feasible at the present time. However, the effect of three-body couplings can be tested for smaller 3−4 atomic systems. The results of such a test for water molecule are presented in Table 1. Addition of three-body coupling improved the strongest stretching frequency by 30 cm^{-1} bringing it closer (within 20 cm^{-1}) to experiment, while the other two frequencies practically did not change. This test shows that three-body coupling effects are not negligible and can be quite significant, but can be ignored for the purposes of our study that does not aim at the spectroscopic accuracy.

TABLE 1: Effect of Three-Body Interaction on the Calculated Fundamental Excitation Frequencies of H_2O Molecule

	ab initio vibrational frequencies, cm^{-1}			
mode	harmonic	CC-VSCF(2)[a]	CC-VSCF(3)[a]	experiment, cm^{-1}
1	3994	3798	3768	3756
2	3854	3700	3696	3652
3	1615	1548	1543	1595

[a] CC-VSCF(2) calculation includes only pair-coupling terms; CC-VSCF(3) includes also three-body coupling. All potentials are calculated at the MP2/TZP level of ab initio theory.

The outline of the calculations is as follows. The geometrical parameters for all hydrogen-bonded compounds studied in this paper were obtained by optimization at the MP2/TZP level of ab initio theory, using analytic gradients. Then, second derivatives were calculated numerically using double differencing, and harmonic vibrational analysis was performed. Afterward, diagonal and mode−mode pair coupling potentials were computed, and VSCF and correlation-corrected VSCF (CC-VSCF) calculations were performed. Finally, IR intensities were calculated using dipole moments estimated along normal modes and VSCF wave functions for the ground and excited vibrational states:

$$I_i = \frac{8\pi^3 N_A}{3hc}\omega_i(\langle\psi_i^{(0)}(Q_i)|\mu_x(Q_i)|\psi_i^{(1)}(Q_i)\rangle^2 + \langle\psi_i^{(0)}(Q_i)|\mu_y(Q_i)|\psi_i^{(1)}(Q_i)\rangle^2 + \langle\psi_i^{(0)}(Q_i)|\mu_z(Q_i)|\psi_i^{(1)}(Q_i)\rangle^2)$$

where $\mu_x(Q_i)$, $\mu_y(Q_i)$, and $\mu_z(Q_i)$ are the dipole moment components, calculated along normal coordinate Q_i; ω_i is the VSCF vibrational frequency for the normal mode i; and $\psi_i^{(0)}$ and $\psi_i^{(1)}$ are the orthogonal VSCF wave functions for the ground and the first excited (fundamental) vibrational states.

Results and Discussion

Water Clusters: $(H_2O)_2$ and $(H_2O)_3$. Geometrical structures of water dimer and cyclic water trimer are shown in Figure 1. Vibrational frequencies obtained using ab initio vibrational spectroscopy and their comparison with experimental frequencies[22,23] are presented in Tables 2 and 3. Harmonic, VSCF, and correlation-corrected VSCF fundamental frequencies are shown, as well as the IR intensities. It can be seen that anharmonicities are very large for these systems. In particular, OH stretching vibrations are very anharmonic. Accounting for anharmonicities and mode−mode couplings by VSCF and correlation-corrected VSCF methods improves the agreement with experiment over the harmonic level, bringing the error down from 200−300 cm^{-1} to 20−40 cm^{-1}. The resulting frequencies are still far from being spectroscopically accurate but differ from experimental frequencies in a rather consistent way; the stretching frequencies are generally overestimated by 20−40 cm^{-1}, while bending frequencies are underestimated by the same amount. Thus, the VSCF vibrational spectroscopy based on the MP2 electronic

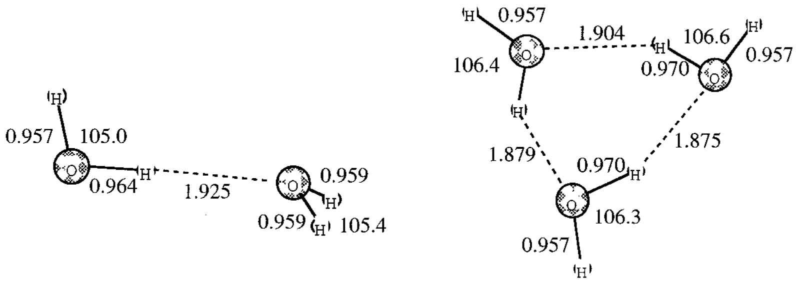

Figure 1. MP2/TZP geometrical parameters of water dimer and trimer.

TABLE 2: Fundamental Excitation Frequencies and IR Intensities for $(H_2O)_2$

	frequency, cm^{-1}					
mode	harmonic	VSCF	CC-VSCF	exptl[a]	intensity, km/mol	description
1	4005	3763	3724	3745	92	accept asym
2	3982	3733	3745	3730	99	donor (free OH)
3	3874	3689	3647	3600	21	accept sym
4	3799	3560	3565	3530	274	donor (bonded OH)
5	1646	1612	1605	1619	94	donor bend
6	1618	1565	1564	1601	108	accept bend
7	674	769	732		207	
8	366	550	521		167	
9	191	451	409		118	
10	179	259	147	150	138	O−O stretch
11	161	414	309		151	
12	142	545	419		27	

[a] Reference 22.

TABLE 3: Fundamental Excitation Frequencies and IR Intensities for $(H_2O)_3$

	frequencies, cm^{-1}				
mode	harmonic	VSCF	CC-VSCF	exptl[a]	intensities, km/mol
1	3976	3714	3725	3703	94
2	3974	3709	3723		99
3	3972	3719	3738		112
4	3726	3469	3429	3400	440
5	3717	3497	3457		483
6	3658	3319	3283	3340	11
7	1671	1633	1623	1632	11
8	1639	1601	1595	1620	121
9	1635	1599	1592	1602	171
10	879	940	927		27
11	737	849	841		553
12	588	755	734		180
13	475	631	596		168
14	374	581	542		56
15	364	514	504		109
16	284	436	434		39
17	233	332	325		4
18	231	346	347		208
19	210	268	264		39
20	192	276	273		82
21	189	263	275		47

[a] Reference 23.

structure potential, is a substantial improvement over the widely used harmonic and scaled harmonic approximations. In fact, the comparison of the calculated frequencies and the experimental ones gives a direct measure of the quality of the MP2 potential energy surface. DFT harmonic frequencies of water clusters[24] are somewhat closer to experiment comparing with the MP2 harmonic frequencies, but this is a result of erroneous underestimation of harmonic frequencies at the DFT level, which in general gives more shallow potential energy surfaces. Underestimated DFT harmonic frequencies cannot be compared with anharmonic experimental results. CC-VSCF results which include anharmonic and mode−mode coupling corrections can provide more insight with regard to assignment of the experimentally measured vibrational frequencies. An example is using theoretical results for the assignment of the experimental frequencies for the water trimer. Xantheas and Dunning[25] have found harmonic frequencies for a number of water clusters using ab initio level of theory similar to the one used in this paper, MP2 with correlation-consistent aug-cc-pVDZ basis sets. However, the frequencies corresponding to OH stretches were overestimated by 200−300 cm^{-1} at the harmonic level, and therefore the authors concluded that the experimental bands of 3400±5 cm^{-1} and 3340−3366 cm^{-1}, assigned to the water trimer, might correspond to larger water clusters. However, anharmonic VSCF corrections bring the values for the OH stretches (which correspond to the OH bonds participating in the hydrogen bonding) down to the 3430−3450 and 3280 cm^{-1} regions, which are in a good agreement with the mentioned experimental bands.

The calculated IR intensities give relatively high values for the OH stretches corresponding to the elongated OH bonds that participate in the hydrogen bonding. The red shift of the hydrogen bonding OH stretch in the water dimer compared with the OH stretch of pure water is 135 cm^{-1} which is in reasonably good agreement with experiment (122 cm^{-1}). The red shifts for the water trimer are much larger, 243, 271, and 417 cm^{-1} (experimental values are 248 and 312 cm^{-1}). Our results for the water tetramer (obtained at a lower, MP2/DZP level of ab initio theory) show that the hydrogen-bonded OH stretches are red-shifted much further, from the 3330−3400 cm^{-1} region for the trimer to the 3100−3200 cm^{-1} region for the tetramer.

The results presented here constitute, to our knowledge, a first quantitative test of the full dimensional ab initio potential energy surfaces for the water dimer and trimer against spectroscopy, beyond the level of the harmonic approximation or of empirical anharmonic scaling prescriptions. The agreement found between the calculated and experimental frequencies, of no worse or better than several tens of cm^{-1} for the stretching modes, indicates that the potential surface in the region probed

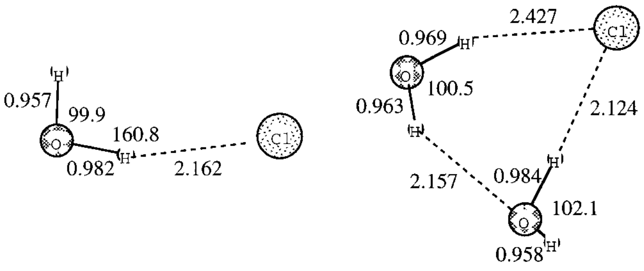

Figure 2. MP2/TZP geometrical parameters of complexes of Cl^- with water molecules.

TABLE 4: Vibrational Frequencies and IR Intensities for $Cl^-(H_2O)$, cm^{-1}

mode	frequencies, cm^{-1} harmonic	VSCF	CC-VSCF	exptl	intensity, km/mol
1	3919	3723	3735	3698,[a] 3690[b]	24
2	3470	3130	3151	3285,[a] 3130[b]	718
3	1693	1662	1633		173
4	782	764	694		185
5	329	392	265		59
6	195	197	194	155,[a] 210[b]	23

[a] Experimental data of M. Okumura et al., ref 27. [b] Experimental data of M. A. Johnson et al., ref 28.

TABLE 5: Vibrational Frequencies and IR Intensities for $Cl^-(H_2O)_2$

mode	frequencies, cm^{-1} harmonic	VSCF	CC-VSCF	exptl	intensity, km/mol
1	3971	3691	3690		35
2	3912	3668	3690	3700,[a] 3686[b]	123
3	3682	3445	3458	3317,[a] 3375[b]	403
4	3440	3149	3165	3245,[a] 3130[b]	785
5	1716	1668	1654		181
6	1679	1628	1611		132
7	843	965	957		238
8	705	860	849		250
9	474	719	702		35
10	438	647	617		85
11	322	580	549		30
12	208	210	205		29
13	163	266	215		42
14	146	412	341		58
15	82	221	109		18

[a] Experimental data of M. Okumura et al., ref 27. [b] Experimental data of M. A. Johnson et al. referenced in 29.

TABLE 6: Fundamental Excitation Frequencies and IR Intensities for H_3O^+

mode	frequency, cm^{-1} harmonic	VSCF	CC−VSCF	exptl	intensity, km/mol	description
1	3764	3582	3509	3519	550	OH stretch
2	3764	3532	3478	3519	558	OH stretch
3	3640	3535	3454	3390	49	OH stretch
4	1705	1631	1621	1626	139	deformation
5	1705	1627	1618	1626	139	deformation
6	813	573	432	526	387	umbrella

is of very good accuracy. In a future study, we will compare ab initio and empirical potential functions against the test of vibrational spectroscopy. However, we note that tentatively it appears from the preliminary results that ab initio predictions for the stretching mode frequencies are better than, or at least as good as, those of state-of-the-art empirical potentials that were tested. It must be kept in mind that so far the potentials were tested only for a few transitions. Our CC-VSCF method was not extended yet to the tunneling spectroscopy of Saykally.[26] It would be highly desirable to have experimental data for other transitions, such as combination modes. Such transitions are readily obtainable by the present CC-VSCF algorithm, and the corresponding data when available will provide a test sensitive to additional regions of the potential surface.

Complexes $Cl^-(H_2O)$ and $Cl^-(H_2O)_2$. Optimized geometries of complexes of Cl^- with one and two water molecules are shown in Figure 2. The calculated vibrational frequencies are listed in Tables 4 and 5 and compared with experimental results of M. Okumura and co-workers[27] and of P. Ayotte and M. A. Johnson (see ref 28 for $Cl^-(H_2O)$ and data for $Cl^-(H_2O)_2$ referenced in the paper of Dorsett, Watts, and Xantheas that studies temperature effects on the infrared spectra of this system[29]). Again, it can be seen from Tables 4 and 5 that anharmonic corrections are very large, and the agreement with experiment is improved considerably at the VSCF and correlation-corrected VSCF levels as compared to harmonic level. This agreement is much better than that obtained by previous higher level ab initio calculations at the harmonic level.[30] The free OH stretching vibrations of $Cl^-(H_2O)$ and $Cl^-(H_2O)_2$, as well as the intermolecular stretch of $Cl^-(H_2O)$, are within 10−40 cm^{-1} agreement with experiment. The errors for the OH stretches elongated by hydrogen bonding are on the order of 100 cm^{-1} comparing with experimental data of M. Okumura.[27] The agreement of our calculated hydrogen bonded OH stretching frequencies with experimental data of M. A. Johnson is better, within 20−35 cm^{-1}(see Tables 4 and 5), possibly due to a lower temperature of the clusters in the experiment.

Complexation with Cl^- leads to a very significant red shift of the hydrogen-bonded OH stretch (over 500 cm^{-1}). Its high intensity shows that it has a strong ionic character. In $Cl^-(H_2O)_2$, one water molecule makes a strong hydrogen bond with Cl^-, and the corresponding OH stretch has frequency and intensity close to those in $Cl^-(H_2O)$. The OH stretches of the second water molecule, which makes hydrogen bonds with both Cl^- and (a much weaker one) with another water molecule, are shifted to the red to a much lesser extent and have lower intensities.

In conclusion, the CC-VSCF vibrational frequencies for complexes of Cl^- with water, though not spectroscopically accurate, are in much closer agreement with experiment than the harmonic ones. CC-VSCF results reflect the red shifts due to hydrogen bonding qualitatively correctly, although the hydrogen bonding effects are somewhat overestimated.

Finally, we note that also for $Cl^-(H_2O)_2$, a study comparing the ab initio potential surfaces against state-of-the-art empirical ones, with spectroscopy as the test, is under way. Preliminary results indicate that the ab initio potential surfaces are at least as good as, or superior to, the best empirical potentials.

H_3O^+ and $H_5O_2^+$ Complexes. Tables 6 and 7 show fundamental vibrational frequencies for protonated water and protonated water dimer. The calculated H_3O^+ vibrational frequencies can be compared with extensive experimental results,[31] while the experimental data for $H_5O_2^+$ is limited.[32] The structures of H_3O^+ and $H_5O_2^+$ ions are shown in Figure 3. Note that these systems have C_{3v} and C_2 symmetry, respectively. The VSCF procedure we use does not preserve symmetry, and therefore, the degenerate vibrational frequencies are not exactly degenerate at the VSCF and CC-VSCF levels. Work is in progress to correct for this flaw by constructing symmetry-adapted VSCF wave functions.

As can be seen from Table 6, the harmonic OH stretching frequencies for H_3O^+ are improved substantially by VSCF and (to a smaller extent) by correlation correction, CC-VSCF. The

TABLE 7: Fundamental Excitation Frequencies and IR Intensities for $H_5O_2^+$

	frequencies, cm^{-1}				
mode	harmonic	VSCF	CC-VSCF	exptl[a]	intensity, km/mol
1	3921	3634	3579	3684	333
2	3920	3632	3577	3684	342
3	3817	3669	3593	3609	10
4	3809	3623	3518	3609	317
5	1803	1802	1853		1564
6	1712	1659	1662		7
7	1552	1494	1494		168
8	1511	1451	1442		328
9	871	1230	1209		2628
10	633	625	599		1
11	497	579	559		29
12	488	568	529		12
13	376	542	494		332
14	228	612	501		414
15	207	428	383		11

[a] Reference 31.

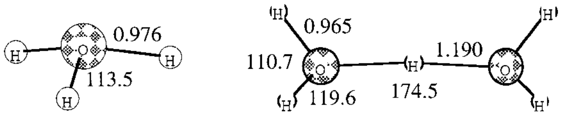

Figure 3. MP2/TZP geometrical parameters of H_3O^+ and $H_5O_2^+$.

bending and umbrella vibrational frequencies are also improved by VSCF, but CC-VSCF "overcorrects" in this case, bringing these frequencies slightly further from experimental values. In general, the agreement with experiment is very good. The OH bonds in H_3O^+ ion are longer than in H_2O molecule, and consequently, the OH stretches of H_3O^+ are further to the red than the OH stretches of H_2O. Note that splittings due to tunneling effects are quite large for the protonated systems, but these effects are not included in our treatment. Despite all these approximations, the results we obtained are in a rather good agreement with experiment.

For $H_5O_2^+$, we found the symmetric C_2 structure to be a global minimum at the MP2/TZP level of ab initio theory and performed vibrational spectroscopy calculation for this structure. Ab initio calculations at higher levels (CCSD(T)/TZ2Pf)[33] showed the presence of two minima, with C_2 and C_s symmetry, which are very close in energy (the C_s structure is only 0.1–0.2 kcal/mol above the C_2). The C_2 minimum has the H atom in the center of the molecule forming equal bonds with the two H_2O molecules, while the C_s structure has the H atom shifted to one of the H_2O molecules, making this structure closer to $H_3O^+(H_2O)$. The potential energy surface of $H_5O_2^+$ was found to be very flat, with the barrier height separating these two minima at only 0.4 kcal/mol.[33] This may affect both experimental and calculated results for vibrational frequencies. The vibrational wave functions in such a case may be delocalized over both structures. In any case, our calculated effective potentials have single well structures, including the one for the normal mode that corresponds to the central H atom motion. However, the latter potential has a rather flat and anharmonic form (shown in Figure 5). Again, it can be seen from Table 7 that VSCF corrects the harmonic values for OH stretches to a great extent, bringing them much closer to experimental values. However, as in the case of H_3O^+, these frequencies are erroneously split by VSCF (especially, symmetric stretches). Also, correlation correction (CC-VSCF) appears to overcorrect the VSCF results in this case too. It seems that the relatively large and incorrect changes that the perturbation theoretic CC-VSCF treatment gives with respect to VSCF for H_3O^+ and $H_5O_2^+$ systems are due to the degeneracies. Clearly, the nondegenerate perturbative corrections to VSCF (described in section II) may not be valid here, and a pseudodegenerate perturbation theory is needed.[34] Note that the frequency of the asymmetric stretch vibration, that corresponds to the central H atom motion (mode number 9), increases by more that 300 cm^{-1} when anharmonic corrections are included. This effect was also observed by Vener and Sauer[35] in their 3D model anharmonic study of $H_5O_2^+$.

Water–Methanol Complexes. Geometrical parameters for water–methanol and methanol–water hydrogen-bonded complexes are shown in Figure 4. The results of vibrational spectroscopy calculation are shown in Tables 8 and 9. These are compared with experimental data measured in solid argon[36] and nitrogen matrixes.[37] The water–methanol complex, where water molecule is a proton donor, is 0.4 kcal/mol lower in energy than the methanol–water conformer at the MP2/TZP level of ab initio theory. This is in a good agreement with higher level ab initio calculations of González, Mó, and Yáñez.[38] Their G2[39] calculations give 0.5 kcal/mol difference between the water–methanol and the methanol–water conformers. Vibrational spectroscopy of these complexes was also studied in the above paper at the harmonic level using the B3LYP/6-31+G(d,p) method. The B3LYP and the MP2 harmonic levels, though reasonably good for bending frequencies, overestimate OH stretching frequencies by 100–300 cm^{-1}. As can be seen from Tables 8 and 9, the stretching frequencies are improved greatly by VSCF, resulting in agreement with experiment within 50 cm^{-1}. Note that the experimental frequencies are shifted due to matrix effects, and this may account partially for the differences between our calculated data and the experiment. The water–methanol bonding OH stretch is red-shifted comparing with the bonding OH stretch of the water dimer by 64 cm^{-1} at the CC-VSCF level (cf. Tables 2 and 8) and suggests that the hydrogen bond in the water–methanol complex is stronger than in the water dimer. The latter is also supported by the comparison of intermolecular O–O stretching frequency, which is higher for the water–methanol complex than for the water dimer (172 vs 147 cm^{-1}).

Comparison of the calculated IR intensities for methanol–water complexes with the available experimental data shows good qualitative agreement. Calculations correctly predict the highest intensity for the OH stretch, which corresponds to the elongated OH bond participating in hydrogen bonding. This indicates that in general the combined information from vibrational frequencies and intensities, improved over the

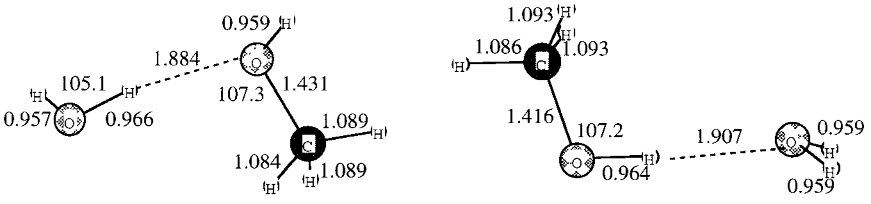

Figure 4. MP2/TZP geometrical parameters for water–methanol and methanol–water complexes.

TABLE 8: Fundamental Excitation Frequencies and IR Intensities for Water−Methanol Complex

	frequencies, cm^{-1}				intensities,km/mol		
mode	harmonic	VSCF	CC-VSCF	exptl[a]	VSCF	exptl[a]	description
1	3975	3742	3792	3704	97	40	H_2O str (free OH)
2	3911	3683	3713	3663	56	17	methanol OH str
3	3760	3530	3501	3539	321	180	H_2O str (bonded OH)
4	3229	3050	3026		28		CH_3 str
5	3172	2975	2935	3018	59	13	CH_3 str
6	3093	2955	2907	2974	54	28	CH_3 str
7	1641	1593	1582	1614	75	45	H_2O bend
8	1552	1539	1539		4		CH_3 bend
9	1540	1531	1532		4		CH_3 bend
10	1532	1503	1500	1466	8		CH_3 bend
11	1390	1371	1366		33		methanol bend
12	1210	1203	1201		2		methanol bend
13	1098	1104	1093	1078	30	4	methanol bend
14	1065	1039	1037	1032	148	100	CO stretch
15	678	827	799		174		
16	402	623	592		92		
17	306	579	546		135		
18	200	195	172		5		OO stretch
19	130	578	575		149		
20	75	279	142		2		
21	55	252	174		27		

[a] Reference 34.

TABLE 9: Fundamental Excitation Frequencies and IR Intensities for Methanol−Water Complex

	frequencies, cm^{-1}				intensities,km/mol		
mode	harmonic	VSCF	CC-VSCF	exptl[a]	VSCF	exptl[a]	description
1	4005	3705	3661	3714	78	44	H_2O asym str
2	3874	3689	3645	3627	4	6	H_2O sym str
3	3812	3572	3595	3536	347	100	meth OH str
4	3194	3020	3007	2982	42	8	CH_3 str
5	3123	2934	2904		71		CH_3 str
6	3061	2930	2891	2835	68	12	CH_3 str
7	1619	1617	1625	1601	77	23	H_2O bend
8	1555	1524	1523	1475	2	1	CH3 bend
9	1536	1515	1516	1464	1	2	CH3 bend
10	1531	1497	1495	1448	12	1	CH3 bend
11	1456	1428	1420	1380	32	7	COH bend
12	1209	1192	1189		1		OCH bend
13	1141	1135	1128	1103	21	3	OCH bend
14	1094	1067	1064	1048	94	30	CO str
15	721	851	827		167		
16	252	652	614		256		
17	209	496	432		8		
18	188	309	284		21		
19	99	413	270		15		
20	81	350	102		6		
21	75	215	192		23		

[a] Reference 35.

harmonic level by VSCF, should be very useful for the prediction and interpretation of experimental spectra.

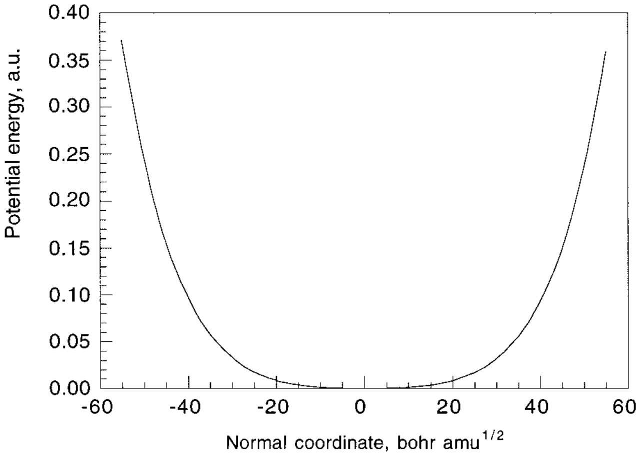

Figure 5. Effective VSCF potential for the central H atom movement in $H_5O_2^+$.

Conclusions

In this paper, we use an extension of the method introduced earlier,[17] which allows calculation of anharmonic vibrational spectra for molecular systems of up to 12−15 atoms. The method is a combination of the vibrational SCF method with direct use of ab initio potential surfaces. No analytical potential functions are used; therefore, the method is very general and applicable to any chemical system for which a sufficient number of ab initio potential surface points are computationally obtainable. The method is implemented as a part of the electronic structure package GAMESS. The combined ab initio/VSCF method can serve as a superior alternative to the existing techniques based on scaling the harmonic vibrational frequencies obtained by electronic structure methods.

The accuracy of the method is dominated by the level of the electronic structure used to obtain potentials. The ab initio level tested in this paper, MP2 with triple-ζ + polarization basis set, is found to give the resulting vibrational OH stretching frequencies with the accuracy typically of the order of 50 cm^{-1}. This level is suggested as a reasonable compromise between the requirements for a good accuracy and a high enough efficiency. It is however of significant interest to test other (e.g., DFT[40] and semiempirical) electronic structure methods in the combination with vibrational SCF for obtaining spectroscopic properties.

The proposed ab initio VSCF method was applied in this paper to a number of highly anharmonic hydrogen-bonded systems: water clusters, complexes of Cl^- with water, positively charged complexes H_3O^+ and $H_5O_2^+$, and complexes of methanol with water. Vibrational frequencies and IR intensities calculated using the proposed method, though not spectroscopically accurate, are in much better agreement with experiment than harmonic frequencies and should be useful for the purposes of experimental assignments, as well as for the cases where experimental data are difficult to obtain. It should be noted that our conclusions on the accuracy of the proposed method pertain mostly to the stiff intramolecular vibrations, for which more experimental data is available. Our results may be less accurate for weak intermolecular vibrations of hydrogen-bonded clusters, especially for those that involve large nuclear displacements. In such cases, use of normal coordinates and of separability approximation becomes problematic and more rigorous treatments are needed. Such extensions of VSCF are being currently developed.

Comparison of our results for water clusters with the earlier work that employed empirical potentials[12] shows that potentials obtained at the MP2 level of ab initio are at least as good as, and in some cases probably better than, the leading available empirical potentials. Although using ab initio potentials is much more expensive, their great advantage is applicability to a larger variety of chemical systems for which empirical potentials are not available. Another big advantage of using ab initio over the empirical potentials is the ability to calculate reliable enough dipole moments to estimate IR intensities in addition to vibrational frequencies. This gives more complete information on vibrational spectra which is very useful for interpretation of experimental results or prediction of new spectra.

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