

## “Morphing” of *ab initio*-based interaction potentials to spectroscopic accuracy: Application to $\text{Cl}^-(\text{H}_2\text{O})^*$

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*Abstract:* We present anharmonic vibrational calculations for the  $\text{Cl}^-(\text{H}_2\text{O})$  cluster and their convergence with the *n*-mode representation of the interaction potential. Extension of this representation up to 4-mode couplings produces results that appear to be converged to within  $10\text{ cm}^{-1}$  or less relative to the exact 6-mode representation for this system. This methodology, in conjunction with the “morphing” technique, which is based on the scaling of the internal coordinates, provides an effective means of fitting intermolecular potentials to measured vibrational spectra. Application of this approach to the chloride–water interaction produces a revision of a previously developed empirical interaction potential which now reproduces the measured fundamental and first overtone frequencies to within an average absolute deviation of  $1.75\text{ cm}^{-1}$  in the 4-mode coupling representation.

The calculation of (ro)vibrational energies and properties of the corresponding wavefunctions for polyatomic molecules, clusters, adsorbates, etc. currently represents one of the major challenges of computational chemistry. Such theoretical calculations produce results that can be directly compared to experimental spectroscopic measurements which constitute one of the most detailed probes of the potential energy surfaces (PESs) of these systems. Obtaining the PES is the necessary prerequisite for carrying out the vibrational calculations. The most rigorous approach of connecting experimental data with theoretical results is based on a high-level first-principles calculation of the PES as a function of the nuclear coordinates followed by an exact quantum treatment of the nuclear motion governed by the potential. Although current state-of-the-art *ab initio* calculations of PESs are highly accurate, in order to achieve spectroscopic accuracy it is usually necessary to adjust the *ab initio* potential in order to account for small errors due to basis set and/or electron correlation incompleteness [1]. To this end, available experimental spectroscopic data for the fundamentals of molecular vibrations and their overtones/combination bands can be used in the adjustment of the potential parameters provided that there exists a versatile and accurate method for computing vibrational anharmonicities given the potential function.

A particularly challenging set of systems that has been recently studied both experimentally [2,3] and theoretically [4–9] is halogen anion–water complexes. Scientific interest in these systems stems from the fact that they can be used as simple models in probing—at the molecular level—the fundamental interactions involved in the hydration of negative ions in water. Experimentally, there has been

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\*Lecture presented at the European Molecular Liquids Group (EMLG) Annual Meeting on the Physical Chemistry of Liquids: Novel Approaches to the Structure, Dynamics of Liquids: Experiments, Theories, and Simulation, Rhodes, Greece, 7–15 September 2002. Other presentations are published in this issue, pp. 1–261.

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great progress in measuring the infrared spectra of a variety of halogen anion–water clusters [2,3]. Infrared (IR) spectroscopy serves as an important tool in probing the vibrations of these systems while first-principles electronic structure calculations offer qualitative assignments of the spectra to structures [10]. This “structural-spectral” correspondence can be quite successful for rigid systems at very low temperatures but breaks down for systems exhibiting large amplitude vibrations and/or at temperatures high enough to induce large sampling of the available phase space [5].

Previous theoretical/computational work on these systems has focused mainly on the optimum cluster geometries and harmonic vibrational frequencies from electronic structure calculations [4a,5]. These calculations, although they provide a useful starting point in understanding the structural and dynamical properties of these systems, nevertheless neglect the important effects of anharmonicities and mode coupling that are essential in order to obtain a quantitative comparison with experiment as well as account for important temperature effects in the modeling of the spectra. Several efforts have been recently made to incorporate the effects of anharmonicity and mode coupling in the  $\text{Cl}^-(\text{H}_2\text{O})$  cluster. Dorsett, Watts, and Xantheas (DWX) have previously used high-level ab initio data to parametrize a global potential for  $\text{Cl}^-(\text{H}_2\text{O})$  and account for temperature effects in the spectra of the  $\text{Cl}^-(\text{H}_2\text{O})_2$  cluster [5]. Recently, Gerber and coworkers reported a direct ab initio calculation of the vibrations of  $\text{Cl}^-(\text{H}_2\text{O})$ , including effects of anharmonicity and mode coupling via a limited 2-mode coupling representation of the potential [7,8]. These calculations were performed using both second-order perturbation (MP2) and density functional (B3LYP) methods for evaluating the energies incorporating orbital basis sets of double (DZP) and triple (TZP) zeta quality. While these calculations are breaking new ground in the techniques to obtain vibrational energies directly from ab initio calculations, they are not expected to yield results that are of spectroscopic accuracy, i.e., to within a few wavenumbers of experiment. This is due to both the limitations of the electronic structure methodology used, as well as the adopted 2-mode representation of the potential. The latter has been shown by Carter and Bowman not to yield results of spectroscopic accuracy, for a given potential, for several tetraatomic systems [11] as well as for  $\text{CH}_4$  [12]. Irlé and Bowman have also very recently performed direct ab initio calculations of the vibrational energies of  $\text{Cl}^-(\text{H}_2\text{O})$ , using 2-, 3-, and 4-mode representations of the potential and found significant differences between them for the six fundamentals [9].

Here we report on an alternative strategy for obtaining accurate interaction potentials for polyatomic systems that relies on a combination of ab initio and experimentally measured spectroscopic data. The means of connecting the former with the latter is the capability to perform accurate vibrational calculations that can be used to offset the small errors in the ab initio potential via a “morphing” procedure as described below. The vibrational calculations are carried out with “Multimode”, a code that is capable of doing essentially exact (ro)vibrational calculations of polyatomic molecules, for a given potential [13]. We used the DWX potential as the starting point in the “morphing” process which has been developed [14,15] in order to slightly modify a potential with the goal of producing vibrational energies that are of near spectroscopic accuracy, i.e., within a few wavenumbers or less of experiment.

“Multimode” is a computer code that yields the eigenvalues and eigenfunctions of the complete Watson Hamiltonian for rotating molecules. In order to apply this code to fairly large molecules, several novel approaches have been adopted. The major one is the representation of the potential by the following hierarchical expansion in terms of the  $N$  normal coordinates that completely specify the vibrations of a molecule:

$$V(Q_1, Q_2, \dots, Q_N) = \sum_{i=1}^N V_i^{(1)}(Q_i) + \sum_{i,j=1}^N V_i^{(2)}(Q_i, Q_j) + \sum_{i,j,k=1}^N V_i^{(3)}(Q_i, Q_j, Q_k) + \sum_{i,j,k,l=1}^N V_i^{(4)}(Q_i, Q_j, Q_k, Q_l) + \dots \quad (1)$$

In this expression, the *1-mode representation* of the potential is defined as the first sum of  $V_i^{(1)}(Q_i)$  terms, i.e., the potential along cuts of each normal coordinate with all other normal coordinates set to

zero, the *2-mode representation* consists of the 1-mode representation plus all the  $V_{ij}^{(2)}(Q_i, Q_j)$  terms, the *3-mode representation* consists of the first three summations, and the *4-mode representation* consists of the four summations explicitly indicated above (note that the 3-mode representation is exact for triatomic molecules).

The current implementation of "Multimode" extends couplings up to 4 modes, as indicated above. This representation of the potential makes the dimensionality of integrals involving  $V$  at most four for any number of normal coordinates, and thus makes it feasible to consider fairly large molecules and/or clusters. Several approaches aiming at improving its efficiency have been recently added. These include replacing standard Gauss–Hermite numerical quadratures with "potential optimized" quadrature points. The optimized quadrature points significantly reduce the size of the 2-, 3-, and 4-mode grids relative to Gauss–Hermite quadrature grids, and accordingly the computer time associated with the calculation of the potential matrix elements. These smaller grids also significantly reduce the computational effort in a direct calculation of *ab initio* energies at the grid points. Interfacing "Multimode" with electronic structure codes is currently being done by us [9] as well as others [16].

Given that the computational effort grows considerably in going from the 2-mode representation to the more accurate 3- and 4-mode representations of the potential, it would be highly advantageous if the 2-mode representation yielded results that are essentially exact, for a given potential. Our tests indicate that this is in general not the case [9], and that it is necessary to examine the convergence of (ro)vibrational energies with respect to the level of  $n$ -mode representation. For a given  $n$ -mode representation of the potential, several options have been implemented in order to obtain the eigenvalues and eigenfunctions of the Watson Hamiltonian. The starting point is a vibrational self-consistent field (VSCF) calculation [13]. Intermode correlation effects can be treated essentially exactly using two "configuration interaction" (CI) approaches. One CI approach, denoted VSCF+CI, is based on mixing a group of VSCF states leading to a generalized eigenvalue problem, as the VSCF states are not orthogonal. A second CI approach, denoted VCI, uses the orthonormal basis of eigenfunctions of a single VSCF Hamiltonian, usually the one for the ground state.

As noted earlier, the accuracy of the (ro)vibrational calculations are critically dependent on the interaction potential  $V$ . For systems with a few degrees of freedom, it is currently feasible to obtain large parts of their PESs from *ab initio* calculations and obtain the (ro)vibrational levels either on-the-fly or by using an analytical function that the data are fitted to. The former approach is preferred for smaller systems but suffers from the fact that the number of points that need to be evaluated currently prohibits the use of electronic structure methods that are of "spectroscopic accuracy", i.e., produce results within several wavenumbers from experiment. The use of an analytical function to fit the *ab initio* data is more attractive for larger systems as it offers the advantage of requiring less *ab initio* points, a fact which, however, prohibits a uniform sampling of the PES, especially as the size of the system increases. Oftentimes, only parts of the reaction and/or minimum energy paths on multidimensional PESs are sampled via *ab initio* calculations. Such was the case for the DWX potential which was fitted to a handful (<20) of *ab initio* MP4 energies computed with the aug-cc-pVTZ basis set for the minimum energy path as the Cl–O bond distance was varied from 2.5 to 7 Å. The RWK2 empirical flexible water potential of Watts and coworkers [17] was incorporated in order to render full flexibility of the intramolecular water vibrations. The fitting was performed in order to reproduce the changes in the intra- and intermolecular internal coordinates of water along the minimum energy path as a function of the Cl–O distance while no attempt was made to fit the shape of the PES away from this minimum energy path. As a consequence, the harmonic frequencies for the DWX PES exhibit differences from the *ab initio* ones. The largest difference, 193  $\text{cm}^{-1}$ , was for the intramolecular "hydrogen-bonded" OH stretch which has the largest IR intensity and therefore represents the cluster's "spectroscopic signature" that is probed in the IR experiments. Moreover, 2-, 3-, and 4-mode vibrational calculations with the original DWX model yielded results that were in disagreement with experiment, especially for the intramolecular "hydrogen-bonded" and "free" OH stretches [5].

The original DWX potential, although not intended to produce results of spectroscopic accuracy, does provide a suitable template for applying the “morphing” procedure. This refers to scaling the coordinates as a means of making smooth, small changes to a potential. In its simplest form, a coordinate, say an internuclear distance, is scaled as follows:

$$r' = \alpha(r - r_e) + r'_e \quad (2)$$

where  $r_e$  is the equilibrium distance on the original surface and  $r'_e$  is the adjusted equilibrium value. Since the original potential was fitted to the ab initio equilibrium geometry and dissociation energy, the five internuclear distances,  $r_{\text{OH}}$ ,  $r_{\text{OH}'}$ ,  $r_{\text{HH}'}$ ,  $r_{\text{ClO}}$ , and  $r_{\text{ClH}'}$  were scaled without changing their equilibrium values (H and H' denote the “free” and “hydrogen-bonded” H atoms, respectively). The scaling parameters  $\alpha$  were determined by a straightforward trial and error method in order to improve agreement with experiment for the vibrational energies which were obtained using the 4-mode representation of the potential (cf. eq. 1). In some applications, as in the present one, it may be desirable to remove this scaling in the dissociation limit. This can be achieved quite easily by using a switching function that “undoes” the scaling. The results are shown in Table 1, along with the corresponding 4-mode results for the original potential. These results clearly demonstrate the usefulness of the “morphing” technique in obtaining accurate fundamental and overtone frequencies. In the present case, the average absolute deviation from experiment decreases from 154  $\text{cm}^{-1}$  (original potential) to 1.75  $\text{cm}^{-1}$  (“morphed” potential).

**Table 1** Four-mode vibrational energies ( $\text{cm}^{-1}$ ) for the original and “morphed” DWX potential for  $\text{Cl}^-(\text{H}_2\text{O})$ .

State	Original DWX	“Morphed” DWX	Exp <sup>a</sup>
$\nu_1$	183	212	210
$\nu_2$	405	434	
$\nu_3$	803	844	
$\nu_4$	1788	1639 <sup>b</sup>	
$\nu_5$	3323	3130	3130
$\nu_6$	3764	3691	3690
$2\nu_4$	3451	3279	3283

<sup>a</sup>Reference [2].

<sup>b</sup>Strongly mixed with  $2\nu_3$ .

The optimized scaling factors for the internuclear distances  $r_{\text{OH}}$ ,  $r_{\text{OH}'}$ ,  $r_{\text{HH}'}$ ,  $r_{\text{ClO}}$ , and  $r_{\text{ClH}'}$  are 0.959, 0.978, 0.932, 1.07, and 1.074, respectively. In the potential subroutine, these scale parameters are all switched to unity for  $r_{\text{ClO}} > 6.5 \text{ \AA}$  (the equilibrium value of  $r_{\text{ClO}}$  in the complex is 3.19  $\text{\AA}$ ). The switching is done smoothly with a simple switching function that has zero first and second derivatives at the switch boundary. Thus, in the dissociation limit the potential reverts to the original RWK2 model of Watts and coworkers. This potential is highly accurate for the fundamentals and low-lying overtones and combination bands of  $\text{H}_2\text{O}$ . It is interesting to note that the optimized scaling factors for the water internuclear distances in  $\text{Cl}^-(\text{H}_2\text{O})$  are significantly less than 1, indicating some major perturbations of the monomer potential upon complexation with  $\text{Cl}^-$ .

To determine whether this “morphed” potential represents an accurate representation of the six degrees of freedom in the  $\text{Cl}^-(\text{H}_2\text{O})$  system, two conditions must be satisfied. First, the  $n$ -mode representation of the potential must be accurate to within several wavenumbers, and second, the “morphed” potential should be much closer to the exact potential than the original one.

The first condition can be checked by performing vibrational calculations using the 2- and 3-mode representations of the “morphed” potential and comparing the results to those using the 4-mode representation. The results, shown in Table 2, indicate that the agreement between the 3- and 4-mode

calculations is generally much better than the one between the 2- and 4-mode ones. Note that the largest differences between the 2- and 4-mode results are for the intramolecular modes and the monomer bend. The largest difference in these vibrational energies between the 2- and 4-mode representations of the potential is  $164\text{ cm}^{-1}$  (for  $2\nu_4$ ) and the average absolute difference is  $60.7\text{ cm}^{-1}$ . These numbers can be compared to 20 (for  $2\nu_4$ ) and  $12.4\text{ cm}^{-1}$  (average absolute difference) respectively, for the 3- and 4-mode representations of the potential. The large decrease in the differences of the vibrational energies between the 3- and 4-mode representations relative to the 2- and 4-mode differences, strongly suggests that the 4-mode results are converged, relative to the exact 6-mode representation, i.e., to within  $10\text{ cm}^{-1}$  or less.

**Table 2** Comparison of low-lying 2-mode (2MR), 3-mode (3MR), and 4-mode (4MR) vibrational energies ( $\text{cm}^{-1}$ ) for the "morphed" DWX potential.

State	2MR	3MR	4MR
$\nu_1$	273	227	212
$\nu_2$	451	438	434
$\nu_3$	868	865	844
$\nu_4$	1788	1649 <sup>a</sup>	1639 <sup>a</sup>
$\nu_5$	3127	3140	3130
$\nu_6$	3696	3698	3691
$2\nu_4$	3441	3297	3277

<sup>a</sup>Strongly mixed with  $2\nu_3$ .

To address the second condition, ideally a detailed comparison of the "morphed" potential with spectroscopically accurate, high-level electronic structure calculations would be done. As already noted, such calculations are not currently feasible for this system. However, it is possible to compare the harmonic frequencies of the "morphed" potential with those from reasonably accurate *ab initio* calculations. These were carried out at the second- and fourth-order Møller–Plesset perturbation (MP2 and MP4) levels of theory with the family of correlation-consistent basis sets [18] of double- through quadruple-zeta quality ( $av_xz$ ,  $x = d, t, q$ ) and are listed in Table 3. The changes for the intermolecular modes 1–3 are small ( $17\text{ cm}^{-1}$  or less). In contrast, the corresponding changes for the intramolecular (water) modes 4–6 are much larger, with the larger change occurring for modes 4 and 5 corresponding to the water bend ( $139\text{ cm}^{-1}$ ) and hydrogen-bonded OH stretch ( $170\text{ cm}^{-1}$ ). With the aug-cc-pVTZ basis set the effect of higher correlation (MP4 vs. MP2) amounts to  $7\text{ cm}^{-1}$  or less for the intermolecular modes 1–3. The effect is similar ( $\sim 10\text{ cm}^{-1}$ ) for the intramolecular bend and the "hydrogen-bonded" OH stretch (modes 4 and 5) but somewhat larger ( $45\text{ cm}^{-1}$ ) for mode 6 which is the "free" OH stretch. Nevertheless, the "morphed" potential produces harmonic frequencies that are in much better agreement with the ones at the MP4/avtz level when compared to the original model. This suggests that the "morphing" process, although used in fitting the observed fundamentals, also produces harmonic frequencies of better quality when compared to the *ab initio* calculations.

In summary, we examine the convergence of vibrational calculations with the  $n$ -mode representation of the underlying interaction potential. We have found that representations beyond the 2-mode ones are necessary in order to obtain converged results for the vibrational states. This technique represents a powerful tool in obtaining *ab initio*-based potentials of spectroscopic accuracy when used in conjunction with a "morphing" process. For the case of  $\text{Cl}^-(\text{H}_2\text{O})$ , we have shown that accurate 4-mode vibrational calculations can be used as an effective vehicle to adjust a potential originally derived from just a few *ab initio* points to spectroscopic accuracy for the experimentally observed fundamentals and overtones.

**Table 3** Comparison of harmonic frequencies for the original and “morphed” DWX potential surfaces with a variety of ab initio calculations.

MP2			MP4			DWX	
avdz	avtz	avqz	avdz	avtz	Original	“Morphed”	
187	203	203	185	202	193	202	
355	366	359	350	368	404	401	
730	753	750	719	747	817	817	
1666	1669	1674	1673	1679	1819	1712	
3371	3338	3355	3383	3341	3482	3331	
3882	3893	3912	3846	3848	3925	3836	

## ACKNOWLEDGMENTS

JMB thanks the National Science Foundation (CHE-0131482). Part of this work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy. Battelle operates the Pacific Northwest National Laboratory for the Department of Energy.

## REFERENCES

1. H. Partridge and D. W. Schwenke. *J. Chem. Phys.* **106**, 4618 (1997).
2. P. Ayotte, G. H. Weddle, J. Kim, M. A. Johnson. *J. Am. Chem. Soc.* **120**, 12361 (1998).
3. J. H. Choi, K. T. Kuwata, Y. B. Cao, M. Okumura. *J. Phys. Chem. A* **102**, 503 (1997).
4. (a) S. S. Xantheas. *J. Phys. Chem. A* **100**, 9703 (1996); (b) S. S. Xantheas and T. Dunning. In *Advances in Molecular Vibrations and Collision Dynamics*, Vol. III, J. M. Bowman and Z. Bacic (Eds.), pp. 281–309 and references therein, JAI Press (1998).
5. H. E. Dorsett, R. O. Watts, S. S. Xantheas. *J. Phys. Chem. A* **103**, 3351 (1999).
6. K. Satoh and S. Iwata. *Chem. Phys. Lett.* **312**, 522 (1999).
7. G. Chaban, J. O. Jung, R. B. Gerber. *J. Chem. Phys.* **111**, 1823 (1999).
8. (a) N. J. Wright and R. B. Gerber. *J. Chem. Phys.* **112**, 2598 (2000); (b) N. J. Wright, R. B. Gerber, D. J. Tozer. *Chem. Phys. Lett.* **324**, 206 (2000).
9. S. Irle and J. M. Bowman. *J. Chem. Phys.* **113**, 8401 (2000).
10. J. M. Weber, J. A. Kelley, S. B. Nielsen, P. Ayotte, M. A. Johnson. *Science* **287**, 2461 (2000).
11. X. C. Huang, S. Carter, J. M. Bowman. *J. Phys. Chem. B* **106**, 8182 (2002); J. M. Bowman, X. C. Huang, S. Carter. *Spectrochim. Acta A* **58**, 839 (2002); F. Dzegilenko, J. M. Bowman, S. Carter. *J. Chem. Phys.* **109**, 7506 (1998); S. Carter, J. M. Bowman, L. B. Harding. *Spectrochim. Acta A* **53**, 1179 (1997).
12. S. Carter and J. M. Bowman. *J. Phys. Chem. A* **104**, 2355 (2000).
13. (a) S. Carter, S. J. Culik, J. M. Bowman. *J. Chem. Phys.* **107**, 10458 (1997); (b) S. Carter and J. M. Bowman. *J. Chem. Phys.* **108**, 4397 (1998); (c) S. Carter, J. M. Bowman, N. Handy. *Theo. Chem. Accnts.* **100**, 191 (1998); (e) on-line documentation: <www.emory.edu/CHEMISTRY/faculty/bowman/multimode>
14. (a) J. M. Bowman and B. Gazdy. *J. Chem. Phys.* **94**, 816 (1991); (b) J. M. Bowman and B. Gazdy. *J. Chem. Phys.* **95**, 6309 (1991); (c) K. A. Peterson, S. Skokov, J. M. Bowman. *J. Chem. Phys.* **111**, 7445 (1999).
15. M. Meuwly and J. M. Hutson. *J. Chem. Phys.* **110**, 8338 (1999).
16. K. Yagi, T. Taketsugu, K. Hirao, M. S. Gordon. *J. Chem. Phys.* **113**, 1005 (2000).
17. J. R. Reimers, R. O. Watts, M. L. Klein. *Chem. Phys.* **64**, 95 (1982); J. R. Reimers and R. O. Watts. *Mol. Phys.* **52**, 357 (1984); D. F. Coker, R. E. Miller, R. O. Watts. *J. Chem. Phys.* **82**, 3554 (1985).

18. T. H. Dunning, Jr. *J. Chem. Phys.* **90**, 1007 (1989); R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison. *J. Chem. Phys.* **96**, 6796 (1992); D. E. Woon and T. H. Dunning, Jr. *J. Chem. Phys.* **98**, 1358 (1993).