THE JOURNAL OF PHYSICAL CHEMISTRY Letters

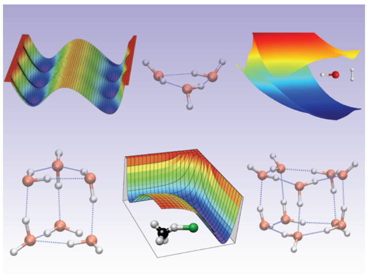
PERSPECTIVE
pubs.acs.org/JPCL

Ab-Initio-Based Potential Energy Surfaces for Complex Molecules and Molecular Complexes

J. M. Bowman,*,[†] B. J. Braams,[†,¶] S. Carter,[†,‡] C. Chen,[†] G. Czakó,[†] B. Fu,[†] X. Huang,[§] E. Kamarchik,[†,⊥] A. R. Sharma,[†] B. C. Shepler,[†] Y. Wang,[†] and Z. Xie[#]

[†]Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, [‡]Department of Chemistry, University of Reading, RG6 2AD England, [§]SETI Institute, 515 North Whisman Road, Mountain View, California 94043, [⊥]Department of Chemistry, University of Southern California, Los Angeles, California 90089, and [#]Mathematics and Computer Science Division, Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT The Born−Oppenheimer potential energy surface(s) underlies theoretical and computational chemistry (whether one considers a single or multiply coupled surfaces). The recent progress in representing these surfaces, rigorously obtained from electronic structure calculations, is the focus of this Perspective. Examples of potentials of complex molecules, namely, CH_3CHO, CH_5^+, and H_5^+, and molecular complexes, namely, water clusters, are given.



The potential energy surface (PES) plays a central role in the theory and computational simulation of virtually all types of molecular interactions of interest to chemists and physical chemists especially. The PES (and here, we consider a single so-called Born−Oppenheimer PES), together with a treatment of the nuclear dynamics, is the major approach taken by theoretical and computational chemists to perform their research. Often times, owing to the complexity of the problem, only stationary points, that is, minima and saddle points, and associated harmonic frequencies are the extent of the PES that is obtained. These data are generally not sufficient for a dynamics study, and instead, they are the input of statistical theories, such as Transition-State Theory. In any case, it is clear that a highly accurate, that is, high-level ab-initio-based, full-dimensional global PES is the ideal,[1−3] as is performing a quantum mechanical treatment of the nuclear dynamics with such a PES.

The potential energy surface (PES) plays a central role in the theory and computational simulation of virtually all types of molecular interactions.

Of course, the reality of a given problem, indeed most problems of interest, is that this ideal approach is just not computationally feasible. Thus, compromises in both the potential and the dynamics are often made, the specifics of which often depend on the problem of interest. For example, for computational modeling of water and/or water clusters, where chemical exchange is not relevant, simple functional forms, based on physical models, (e.g., dipole−dipole interactions etc.) are typically used. The parameters of the function are typically determined empirically, and the nuclear motion is typically treated using classical dynamical or statistical mechanical methods.[4] Of course, even for such nonreactive systems, a highly accurate ab-initio-based PES is desirable. In the case of water clusters, this has been done for rigid monomers[5] and more recently for flexible monomers.[6]

Another class of PESs, which is far more demanding to represent mathematically, are those for chemical reactions. In this case, simple functional forms are highly problematic, and other approaches are often taken. These approaches, in particular, one with which we have had success, are the focus of this Perspective. It important to also note that one can avoid any representation of the PES by employing direct dynamics,[7] also known as ab initio molecular dynamics (AIMD). This generally means running classical trajectory calculations and obtaining the potential and its gradient by direct calls to electronic structure codes at each time step. There is a huge amount of literature about applications of this approach, owing to its obvious appeal and generality. The list of limitations of this approach includes the use of classical mechanics, relatively short total integration times, small numbers of trajectories (less and often much less than 1000), and the use of below the highest level of ab initio theory and basis. These limitations originate from the very large amount of computer time and resources required to implement AIMD, compared to making a function call to a routine that returns a value of the PES at each time step. (Much more efficient semiempirical variations of AIMD are the empirical valence

Received Date: May 13, 2010
Accepted Date: May 28, 2010

bond method[8,9] and semi-emprical electronic theories with specific reaction parameters.[10]) These limitations notwithstanding, the direct dynamics/AIMD method is a very powerful means to investigate the mechanisms of reaction dynamics, as can be appreciated from some recent examples.[11−13]

Returning now to the focus here, substantial progress has been made recently in the mathematical representation of high-dimensional PESs for both reactive and nonreactive systems with up to 10 atoms. This progress has required significant departures from approaches that were developed in the 1970−1980s for triatomic molecules.[1−3] This was required because those approaches scale exponentially with the number of degrees of freedom and thus have not been adopted for larger numbers of atoms. A number of new strategies have been developed for larger molecules.[14−18] Notable among these is the approach by Collins and coworkers,[14,15] which is based on interpolation of local force fields and which has been applied to a number of polyatomic reactions.

> Substantial progress has been made recently in the mathematical representation of high-dimensional PESs for both reactive and nonreactive systems with up to 10 atoms.

We have implemented a different approach, which is based on global fitting of ab initio electronic energies using a fitting basis that is manifestly invariant with respect to all permutations of like atoms.[19,20] This invariance property of the PES should be obvious, and although noted some years ago,[3] it was not systematically exploited as a general fitting method until fairly recently by us. (The approach has been suggested by several groups for the special case of XY_4 molecules[21,22] and nicely applied recently to the challenging cation CH_4^+.[23]) A triatomic molecule that illustrates this invariance property is O_3, for which the symmetric group is of order $3! = 6$. First, it should be clear that the three internuclear distances form a closed set under these permutations. Letting [1, 2, 3] denote the initial arrangement of the three atoms, consider the permutation (2, 3, 1). It is easy to see that this permutation maps the initial internuclear distances r_{12}, r_{13}, r_{23} to r_{23}, r_{12}, r_{13}. Thus, a monomial basis function $r_{12}^a r_{13}^b r_{23}^c$ maps onto $r_{23}^a r_{12}^b r_{13}^c$, and it is easy to see that the sum of these monomials produces a basis function that is invariant under this particular permutation. Application of the remaining four permutations generates four other monomials, and finally the sum of all six monomials yields a basis function that is invariant with respect to all permutations. Clearly then, a set of such symmetrized basis functions can be used to represent the PES. In actual applications of this approach, the variables used for fitting are transformed internuclear distances, that is, $y_\alpha = \exp(-r_\alpha/\lambda)$, where α runs from 1 to $N(N-1)/2$, the number of internuclear distances for an N-atom molecule, and λ is a constant typically in the range of 2−3 bohr.

Clearly this procedure, which we term monomial symmetrization, becomes tedious for larger molecules and clusters such as CH_5^+ and $(H_2O)_3$, which have large symmetric groups. Software to perform the mapping of internuclear distances by the permutations, the generation of symmetrized monomials, and relating at least some of them from lower order ones for virtually any molecule has been written.[24] (For more information, see http://www.mcs.anl.gov/research/projects/msa/.)

The procedure of monomial symmetrization provides a basis for the vector space of invariant polynomials. The basis is typically truncated at some maximum polynomial degree, and expansion coefficients relative to that truncated basis may then be obtained by standard least-squares procedures. The generic basis function that is obtained this way is the sum of $\#G$ terms, where $\#G$ denotes the number of elements of the relevant symmetry group. These basis functions, and therefore the fitted function, are expensive to evaluate.

Fortunately, there is a branch of algebra, computational invariant theory, that provides powerful algorithms to obtain compact representations of the vector space of invariant polynomials.[25] This representation of invariant polynomials relies on the concept of families of so-called primary and secondary invariant polynomials. These are invariant polynomials of the y_α variables. The number of primary invariant polynomials is equal to the number of variables, $N(N-1)/2$, and the number of secondary invariant polynomials depends on the group and its representation and also on the choice of primary invariant polynomials. In terms of these polynomials, the potential can be represented by a compact expression, given elsewhere.[19,20]

For each molecular symmetry group of interest, the generation of primary and secondary invariant polynomials has been done with the computer algebra package MAGMA.[26] A large library of these polynomials for up to 10 atoms exists and is available for download at the Website http://iopenshell.usc.edu/downloads/ezpes/. More details and some examples are given in the recent review by Braams and Bowman.[20]

Examples of Complex Molecules. More than 20 potential energy surfaces have been generated using these fitting methods. These include reactive potentials of considerable complexity, of which CH_3CHO is one example that we briefly consider here. Other PESs describe complex molecules and clusters. Examples that we consider here are CH_5^+, H_5^+, and, very briefly, water clusters.

First consider CH_3CHO. Ohno and co-workers[27] have located 98 stationary points (minima and saddle points) on the PES. This number does not take into account the permutational symmetry of this system. The importance of describing this permutational invariance is illustrated by the radical−radical reaction $CH_3 + HCO \rightarrow H_2 + CH_2CO$. In principle, any of the H and C atoms of the reactants can appear in any combination of the H and C atoms of the products. Of course, energetics and other features of the PES together with the dynamics determine the actual outcomes; however, it is clear

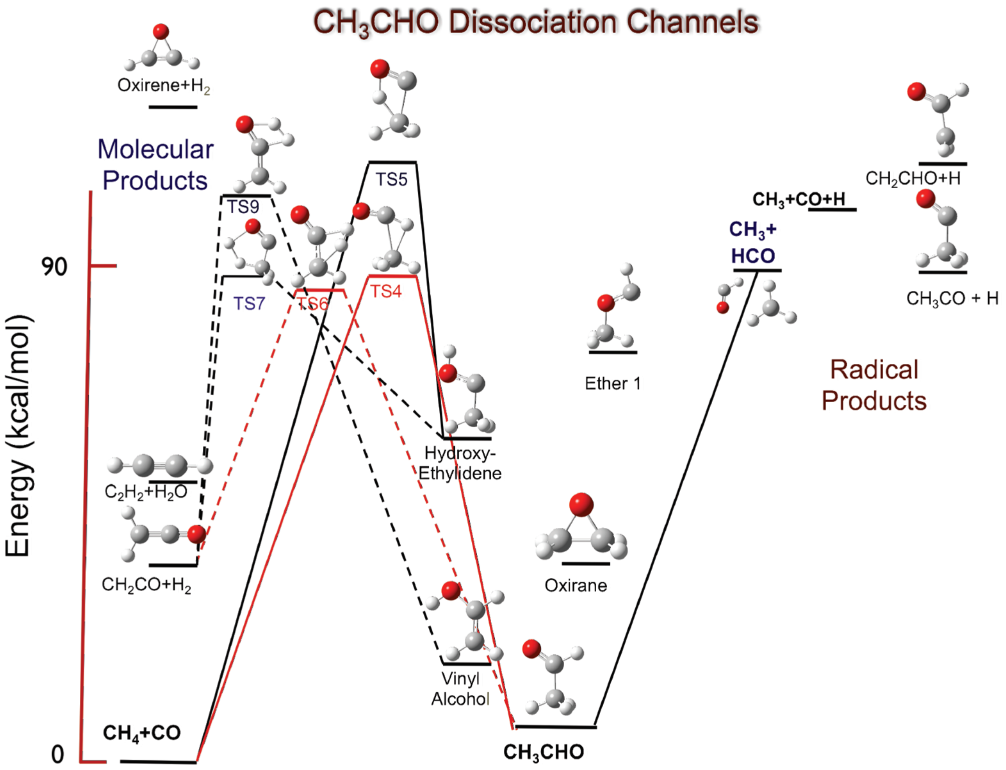


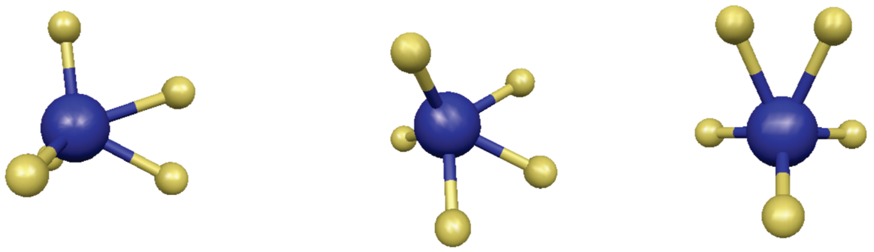
Figure 1. Indicated stationary points of the CH_3CHO potential energy surface and indicated fragments.

that a completely unbiased approach requires that the PES describe all possible pathways. Using the approach described above, we have developed a global PES for this system,[28] which does describe the complexity implied by the number of stationary points as well as the permutational symmetry. (The order of the symmetric group here is 4!2! = 48.) This published PES and a newer unpublished one are fits to roughly 200 000 electronic energies. This is actually a modest number of energies considering that CH_3CHO has 15 vibrational degrees of freedom and 21 internuclear distances, which by either measure is a high dimensionality (and "rugged"). The PES does describe many reaction channels, and these are indicated in Figure 1, with an emphasis on the unimolecular dissociation of acetaldehyde to CH_4 + CO and CH_3 + HCO. Interest in the these channels has focused on the "roaming" pathway to the molecular products, instead of the conventional pathway over the molecular transition state, labeled TS4 in the figure.[28−30]

The next illustrations are to the notoriously floppy carbocation CH_5^+ and the slightly less floppy cation H_5^+. Both cations have a symmetric group of order 5! = 120, and the PES should be invariant with respect to all of those permutations. The first full-dimensional, permutationally invariant PES for CH_5^+ was reported in 2003 and was the first application of the permutationally invariant bases described above.[31] This PES was used in diffusion Monte Carlo (DMC) calculations of the zero-point state to rigorously characterize the degree of delocalization over the 120 minima.[32] A newer PES based on fitting 36 000 CCSD(T)/aug-cc-pVTZ energies that also describes dissociation to CH_3^+ + H_2 was reported in 2006.[33] It should be noted that a PES for CH_5^+ using the interpolation approach of Collins and co-workers and made permutationally invariant by replicating the force fields was developed and used in DMC calculations of the zero-point state.[34] This approach was also used to develop the first global PES for H_5^+.[35] We have reported a newer, permutationally invariant PES for H_5^+.[36]

The equilibrium structures and some relevant low-lying saddle points for CH_5^+ and H_5^+ are shown in Figure 2; these are important in understanding the fluxional nature of these molecules. As seen, CH_5^+ has two low-lying saddle points that separate the global minima. These are easily overcome in the zero-point state (which has an energy of 10917 cm^{-1}), which exhibits complete scrambling of the H atoms across the 120 permutationally equivalent global minima. For H_5^+, the low-lying saddle point indicates that a better picture of this cation is as a proton bound to the H_2 dimer, and indeed, this is born out by rigorous calculations briefly described below.

A variety of dynamics calculations have been done with the latest CH_5^+ PES. In particular, in 2006, we and Anne McCoy reported predictions of the IR spectra of CH_5^+[37] and its deuterated isotopologues.[38,39] The motivation for those predictions was to investigate spectroscopic signatures of "quantum localization" that is induced by D-substitution. That is, by breaking the mass symmetry, it was shown quantitatively that the H atom prefers to concentrate at the H_2 site of the global minimum, shown in Figure 2. A careful analysis of DMC calculations of the zero-point density of these and other isotopologues provided weights for the location of D and H atoms. These weights were used in anharmonic variational



CH_5^+ Global Min (0)   SP1 (29 cm^{-1})   SP2 (341 cm^{-1})

H_5^+ Global Min 0   SP1 (52 cm^{-1})

Figure 2. Equilibrium and low-lying saddle point structures of CH_5^+ and H_5^+.

calculations of the IR spectra for the various configurations and then scaled by the DMC weights to obtain final spectra. The opportunity to test these predictions against experiment has just been made possible by new IR action spectra of isotopologues of CH_5^+.[40] We show a comparison of a subset of the predicted and experimental spectra in Figure 3. The experimental spectra shown here were taken with digitizing software from Figure 2 of ref 40 and do not reproduce the small, high-frequency "noise" superimposed on the signal. As seen, there is very good agreement between theory and experiment, which validates the quantitative predictions of the degree of localization in these isotopologues, as well as the accuracy of the PES.

Turning now to H_5^+, we and Duncan and co-workers recently reported a comparison of calculated and experimental dissociation spectra of H_5^+ and D_5^+ in which the motion of the central proton "shuttling" between the two H_2 groups was shown to have clear spectroscopic signatures.[41] The calculated spectra extended to lower frequencies than experiment and predicted a very intense feature which has been ascribed to the fundamental of the delocalized proton stretch. The spectrum and the ground-state density of the proton stretch are shown in Figure 4. This intense spectral feature awaits experimental verification; however, we are confident that this delocalized shared proton mode is accurately predicted by the calculations.

Here, we briefly consider one of the most widely studied and important molecular complexes, water. The term "complex" here simply means an assembly of many H_2O monomers, which is of course what physical chemists mean by "water." The distinction between "water" and "water clusters" is mainly a matter of the number of monomers and, to some extent, the properties being studied. In any case, we simply wish to briefly indicate the way in which permutationally invariant fitting has made an impact in this area. A detailed account of this work has very recently appeared,[6] and we refer the interested reader there for details. The key element in the approach that we have taken is the established rate of convergence of electronic energies of a number of water clusters in terms of an *N*-body (monomer) representation. Careful work by several groups[5,42,43] has established that the two- and three-body interactions account for roughly 80% and nearly 20% of the total energy, respectively, and thus, these interactions are the crucial building blocks of a general potential for large numbers of monomers. In view of this, we have developed full-dimensional ab-initio-based (and permutationally invariant) PESs for the water dimer/two-body[44−46] and three-body interactions.[47] The family of two-body potentials, denoted HBBn, do accurately describe all of the low-lying stationary points, including of course the global minimum of the water dimer, as indicated in Figure 5. These stationary points describe the two-body H-bonded network, and it is gratifying that the HBB PESs describe them very accurately. That figure also contains the structures of the low-lying stationary points of the water trimer and the lowest-energy (prism) configuration of the important water hexamer, which has only recently been established as the lowest-energy conformation. The two- and three-body PES does correctly predict this result and numerous other important ones. (More details of tests and predictions of the PES are given in refs 6 and 47.) Evidently, both the short-range, that is, hydrogen-bonded and repulsive interactions, and the long-range electrostatic interactions (including induction) are captured by the high-quality ab initio two- and three-body PESs of water. These PESs, especially the three-body one, are computationally demanding relative to model potentials. However, the

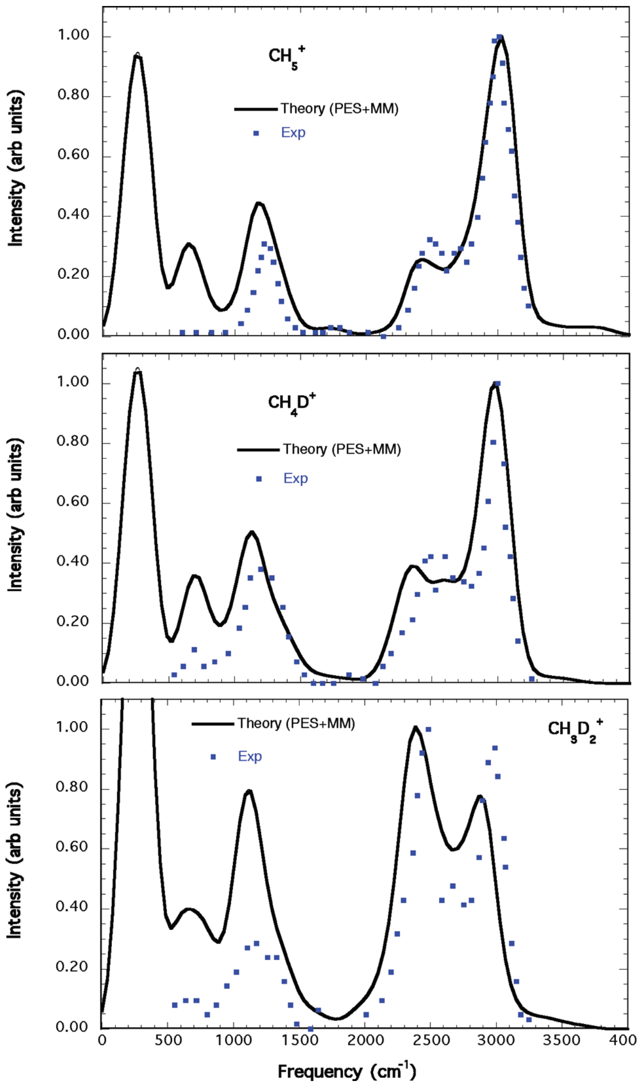


Figure 3. Low-resolution spectra of CH_5^+ and indicated isotopologues from predictions made in 2006 (refs 38 and 39) and recent experiments (ref 40).

rapid increase in available computer power and resources combined with massively parallel computing should make this not a serious obstacle to their use. In any case, they are much faster to evaluate than direct calls to an electronic structure package. Therefore, in short, a highly accurate, ab initio, and flexible PES for water complexes is basically in hand.

A highly accurate, ab initio, and flexible PES for water complexes is basically in hand.

We conclude this brief subsection by noting that a rapidly converging *N*-body representation should also apply to many hydrated solutes. For example, we have begun investigating this for hydrated Cl^- using the two-body HBB PES and a previously published two-body flexible Cl^- H_2O PES.[48] Preliminary results are extremely encouraging for structures, energies, harmonic frequencies, and so forth in tests for $Cl^-(H_2O)_2$ and $Cl^-(H_2O)_3$.

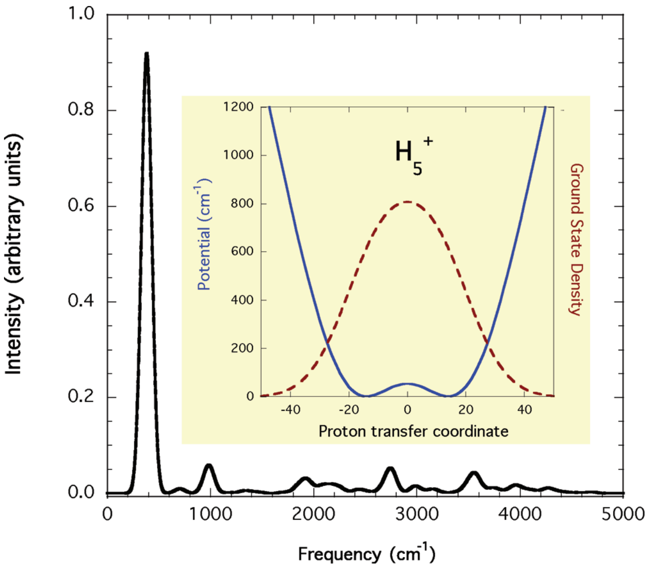


Figure 4. Low-resolution calculated spectra of H_5^+ and the one-dimensional potential and ground-state density of the proton-transfer mode.

Prognosis for Future Directions. The focus of this Perspective has been on the potential energy surface and the central role it plays in theoretical and computational chemistry. In many ways, it is the least "glorious" and yet most onerous component of a simulation of the nuclear dynamics. We have indicated the recent progress that has been made in the mathematical representation of high-dimensional, "rugged" PESs for complex molecules, including those with many reaction fragments and also those with low-energy isomerization pathways. Exploiting the permutational invariance of the PES is the key to the path-to-progress focused on here.

Exploiting the permutational invariance of the PES is the key to the path-to-progress.

Predictions about future directions are more fun than reliable of course. However, with that caveat in mind, here are some thoughts. First, we expect to see ab-initio-based, fully flexible two- and three-body potentials as the foundation of *N*-body interactions for many molecular complexes. For nonreactive complexes, for example, hydrated ions, the progress already discussed above makes this prediction a "safe" one. More problematic is representing potentials of many hundreds of atoms of biomolecules, where parts of the molecule are stiff and other parts are quite floppy and where the potential is highly rugged, that is, with many minima.

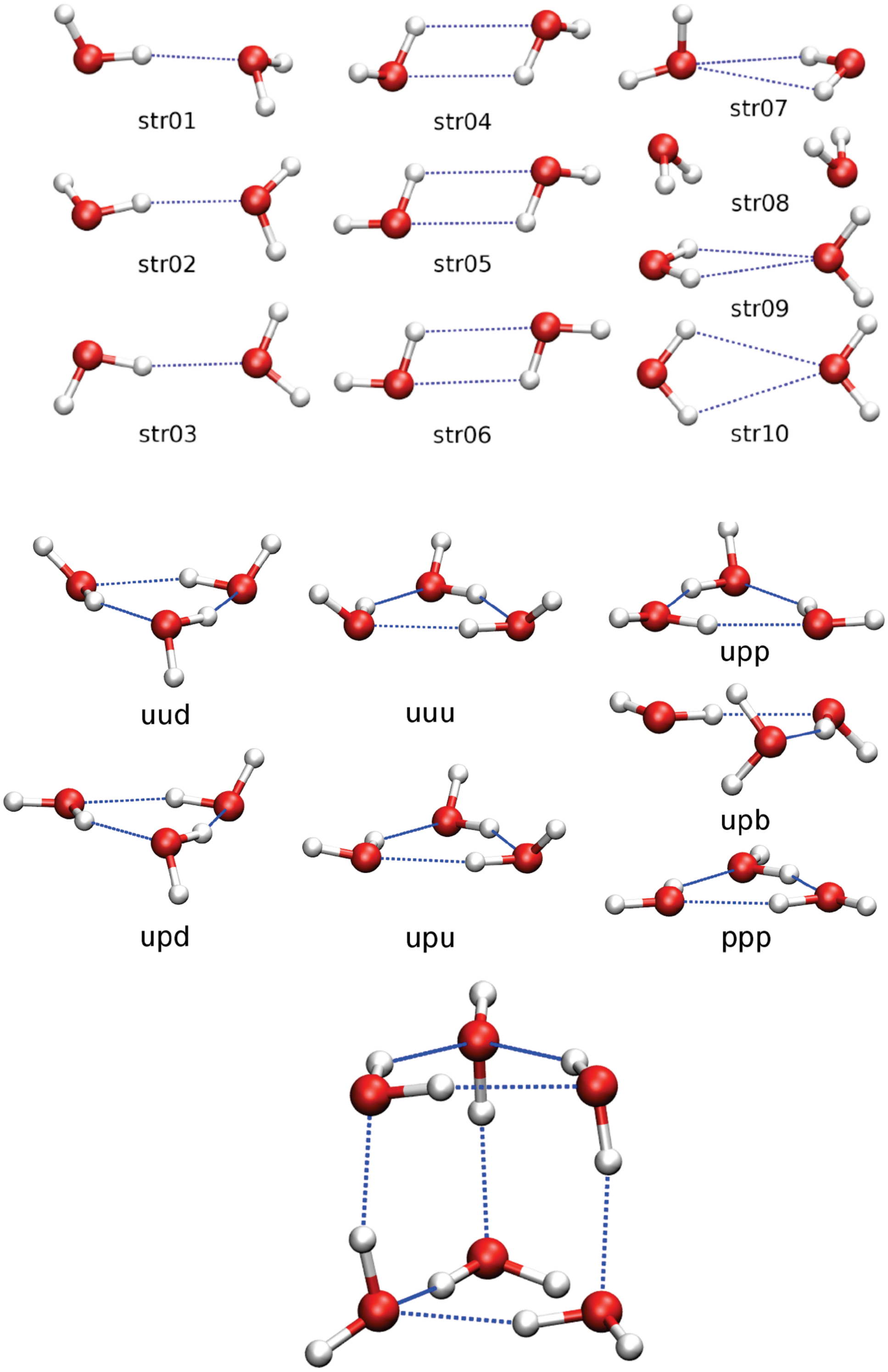


Figure 5. Low-lying stationary points of the water dimer and trimer and the structure of the water hexamer predicted from ab initio two- and three-body potential energy surfaces.

Perhaps a way forward is to emulate, at least in spirit, the highly successful QM/MM approach taken for electronic energies. The analogue for the potential energy surface would be to combine say a permutationally invariant ab-initio-based PES with a molecular mechanics or similar empirical or semiempirical force field for a secondary set of atoms that are not strongly interacting with the primary region. An important step in that direction has been taken by Truhlar and co-workers, using multiconfiguration molecular mechanics.[49] Another possible research area for the future is to somehow hybridize direct dynamics with ab-initio-based PESs.

Finally, with PESs obtained from first principles, that is, not empirical or semiempirical, the treatment of the nuclear dynamics (or statistical mechanics) will in many cases have to consider quantum effects in order to make meaningful comparisons with experiment. This is certainly appreciated already for water, and a number of groups are actively working in this area. This is a huge area for future method development as well as computational algorithms as quantum (many semiclassical) approaches require, in many cases, quite different computational approaches from those used in strictly classical treatments of the dynamics.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. Email: jmbowma@emory.edu.

Present Addresses:

¶ Nuclear Data Section, Division of Physical and Chemical Sciences, International Atomic Energy Agency, P.O. Box 100, Vienna International Centre, AT-1400 Vienna, Austria.

Biographies

Joel Bowman is the Samuel Candler Dobbs Professor of Chemistry at Emory University. His research interests include chemical reaction dynamics, development of potential energy surfaces, vibrational analysis of molecules and clusters, and method development.

Bastiaan Braams is currently at the International Atomic Energy Agency, where he is head of the molecular data unit. His research interests are in mathematical and computational approaches to chemical reaction dynamics, potential energy surfaces, electronic structure, and plasma physics.

Stuart Carter is a Senior Researcher and developer of the code MULTIMODE. His research interests include the accurate treatment of molecular rovibrational spectroscopy and potential energy surfaces.

Chao Chen is a graduate student at Emory University under the supervision of Joel M. Bowman, working on chemical reaction dynamics and the development of potential energy surfaces.

Gábor Czakó is a Postdoctoral Researcher at Emory University in the Department of Chemistry. His research interests involve first-principles (ro)vibrational and reaction dynamics and ab initio thermochemistry. He received a silver medal in the 31st International Chemistry Olympiad, Bangkok, Thailand, and several national awards in Hungary.

Bina Fu is a Postdoctoral Research Fellow in the chemistry department at Emory University. She received her Ph.D. in the State Key Laboratory of Molecular Reaction Dynamics at the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences in July 2009. Her research interests involve ab initio potential energy surface calculations and classical and quantum dynamical studies of polyatomic chemical reactions.

Xinchuan Huang is a Principal Investigator at SETI Institute working on Cooperative Agreement with NASA. He got a B.S. in Applied Chemistry (II) at Fudan University (China) in 1997 and a Ph.D. in Physical Chemistry at Emory University in 2004. His research interests are in the spectroscopy and dynamics of important molecular species in astronomical and atmospherical studies. For more informtaion, see http://www.seti.org/~huang.

Eugene Kamarchik is a Postdoctoral Researcher at Emory University and the University of Southern California. He received his Ph.D. in 2008 from the University of Chicago. His current research focuses on nuclear and vibrational dynamics, particularly those related to electronically excited states.

Amit R. Sharma is a Postdoctoral Research Associate at Emory University in the Department of Chemistry. His research interests are in the chemical dynamics of charged and neutral hydrocarbons in plasma chemistry and combustion chemistry, computational spectroscopy, and photochemistry of molecules in interstellar media.

Benjamin Shepler is currently a Postdoctoral Research Associate at Emory University. He received his Ph.D. from Washington State University in 2006, and his research interests are in the areas of accurate electronic structure theory and chemical reaction dynamics. He will be starting as an Assistant Professor at Georgia Gwinnett College in the fall of 2010.

Yimin Wang recently successfully defended her Ph.D. in Chemistry at Emory University under the supervision of Joel M. Bowman. She received her B.S. degree in Chemical Physics from the University of Science and Technology of China (USTC) in 2005. Her research involves construction of permutationally invariant potential energy surfaces for various molecular systems including water and quantum mechanical approaches to nuclear motion.

Zhen Xie is a Postdoctoral Researcher, Mathematics and Computer Science Division, Argonne National Laboratory. His main research interests involve potential energy surface fitting, molecular dynamics simulation, and mathematical optimization. For more information on his research, see http://www.mcs.anl.gov/~zhenxie.

ACKNOWLEDGMENT Financial support from the Office of Naval Research, the Department of Energy, and the National Science Foundation is gratefully acknowledged.

REFERENCES

(1) Schatz, G. C. The Analytical Representation of Electronic Potential-Energy Surfaces. *Rev. Mod. Phys.* **1989,** *61*, 669–688.

(2) Hollebeek, T.; Ho, T. S.; Rabitz, H. Constructing Multidimensional Molecular Potential Energy Surfaces from Ab Initio Data. *Annu. Rev. Phys. Chem.* **1999,** *50*, 537–570.

(3) Murrell, J. N.; Carter, S.; Farantos, S. C.; Huxley, P.; Varandas, A. J. *Molecular Potential Energy Functions*; John Wiley: Chichester, U.K.; New York, 1984.

(4) See, for example: Fanourgakis, G. S.; Xantheas, S. S. Development of Transferable Interaction Potentials for Water. V. Extension of the Flexible, Polarizable, Thole-Type Model Potential (TTM3-F, v. 3.0) to Describe the Vibrational Spectra of Water Clusters and Liquid Water. *J. Chem. Phys.* **2008,** *128*, 074506/1–074506/11 and references therein .

(5) Szalewicz, K.; Leforestier, C.; van der Avoird, A. Frontiers Article: Towards the Complete Understanding of Water by a First-Principles Computational Approach. *Chem. Phys. Lett.* **2009,** *482*, 1–14.

(6) Wang, Y.; Bowman, J. M. Frontiers Article: Towards an Ab Initio Flexible Potential for Water, And Post-Harmonic Quantum Vibrational Analysis of Water Clusters. *Chem. Phys. Lett.* **2010,** *491*, 1–10.

(7) Lourderaj, U.; Song, K.; Windus, T. L.; Zhuang, Y.; Hase, W. L. Direct Dynamics Simulations Using Hessian-Based Predictor-Corrector Integration Algorithms. *J. Chem. Phys.* **2007,** *126*, 044105/1–044105/11.

(8) Warshel, A.; Weiss, R. M. An Empirical Valence Bond Approach for Comparing Reactions in Solutions and in Enzymes. *J. Am. Chem. Soc.* **1980,** *102*, 6218–6226.

(9) Sonnenberg, J. L.; Wong, K. F.; Voth, G. A.; Schlegel, H. B. Distributed Gaussian Valence Bond Surface Derived from Ab Initio Calculations. *J. Chem. Theory Comput.* **2009,** *5*, 949–961.

(10) Gonzàlez-Lafont, A.; Truong, T. N.; Truhlar, D. G. Direct Dynamics Calculations with Neglect of Diatomic Differential Overlap Molecular Orbital Theory with Specific Reaction Parameters. *J. Phys. Chem.* **1991,** *95*, 4618–4627.

(11) López, J. G.; Vayner, G.; Lourderaj, U.; Addepalli, S. V.; Kato, S.; de Jong, W. A.; Windus, T. L.; Hase, W. L. A Direct Dynamics Trajectory Study of $F^- + CH_3OOH$ Reactive Collisions Reveals a Major Non-IRC Reaction Path. *J. Am. Chem. Soc.* **2007,** *129*, 9976–9985.

(12) Yeung, L. Y.; Okumura, M.; Paci, J. T.; Schatz, G. C.; Zhang, J.; Minton, T. K. Hyperthermal O-Atom Exchange Reaction $O_2 + CO_2$ through a CO_4 Intermediate. *J. Am. Chem. Soc.* **2009,** *131*, 13940–42.

(13) Page, A. J.; Irle, S.; Morokuma, K. Polyyne Chain Growth and Ring Collapse Drives Ni-Catalyzed SWNT Growth: A QM/MD Investigation. *J. Phys. Chem. C* **2010,** *114*, 8206–8211.

(14) Collins, M. A. Molecular Potential-Energy Surfaces for Chemical Reaction Dynamics. *Theor. Chem. Acc.* **2002,** *108*, 313–324.

(15) Moyano, G. E.; Collins, M. A. Interpolated Potential Energy Surface for Abstraction and Exchange Reactions of $NH_3 + H$ and Deuterated Analogues. *Theor. Chem. Acc.* **2005,** *113*, 225–232.

(16) Dawes, R.; Passalacqua, A.; Wagner, A.; Sewell, T. D.; Minko, M.; Thompson, D. L. Interpolating Moving Least-Squares Methods for Fitting Potential Energy Surfaces: Using Classical Trajectories to Explore Configuration Space. *J. Chem. Phys.* **2009,** *130*, 144107/1–144107/9.

(17) Zhang, L.; Luo, P.; Huang, Z.; Chen, H.; Varandas, A. J. C. Vibrational Relaxation Of Highly Vibrationally Excited O_3 In Collisions With OH. *J. Phys. Chem. A* **2008,** *112*, 7238–7243.

(18) Manzhos, S.; Carrington, T. Using redundant Coordinates to Represent Potential Energy Surfaces with Lower-Dimensional Functions. *J. Chem. Phys.* **2007,** *127*, 014103/1–014103/10.

(19) Huang, X.; Braams, B. J.; Bowman, J. M. Ab Initio Potential Energy and Dipole Moment Surfaces For $H_5O_2^+$. *J. Chem. Phys.* **2005,** *122*, 044308/1–044308/12.

(20) Braams, B. J.; Bowman, J. M. Permutationally Invariant Potential Energy Surfaces in High Dimensionality. *Int. Rev. Phys. Chem.* **2009,** *28*, 577–606.

(21) Schmelzer, A.; Murrell, J. The General Analytic Expression for S_4-Symmetry-Invariant Potential Functions of Tetra-Atomic Homonuclear Molecules. *Int. J. Quantum Chem.* **1985,** *28*, 287–295.

(22) Cassam-Chenaï, P.; Patras, F. Symmetry-Adapted Polynomial Basis for Global Potential Energy Surfaces-Applications to XY_4 Molecules. *J. Math. Chem.* **2008,** *44*, 938–966.

(23) Opalkaa, D.; Domcke, W. High-Order Expansion of $T_2 \times t_2$ Jahn–Teller Potential-Energy Surfaces in Tetrahedral Molecules. *J. Chem. Phys.* **2010,** *132*, 154108/1–154108/14.

(24) Xie, Z.; Bowman, J. M. Permutationally Invariant Polynomial Basis for Molecular Energy Surface Fitting via Monomial Symmetrization. *J. Chem. Theory Comput.* **2010,** *6*, 26–34.

(25) Derksen, H.; Kemper, G. *Computational Invariant Theory*; Springer-Verlag: Berlin, Germany, 2002.

(26) Bosma, W.; Cannon, J.; Playoust, C. The Magma Algebra System I: The User Language. *J. Symbolic Comput.* **1997,** *24*, 235–265.

(27) Yang, X.; Maeda, S.; Ohno, K. Insight into Global Reaction Mechanism of [C2, H4, O] System from ab Initio Calculations by the Scaled Hypersphere Search Method. *J. Phys. Chem.* **2007,** *111*, 5099–5110.

(28) Shepler, B. C.; Braams, B. J.; Bowman, J. M. Roaming Dynamics in CH_3CHO Photodissociation Revealed on a Global Potential Energy Surface. *J. Phys. Chem. A* **2008,** *112*, 9344–9351.

(29) Heazlewood, B. R.; Jordan, M. J. T.; Kable, S. H.; Selby, T. M.; Osborn, D. L.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. Roaming is the Dominant Mechanism for Molecular Products in Acetaldehyde Photodissociation. *Proc. Natl. Acad. Sci. U.S.A.* **2008,** *105*, 12719–12724.

(30) Houston, P. L.; Kable, S. H. Photodissociation of Acetaldehyde As a Second Example of the Roaming Mechanism. *Proc. Natl. Acad. Sci. U.S.A.* **2006,** *103*, 16079–16082.

(31) Brown, A.; Braams, B. J.; Christoffel, K. M.; Jin, Z.; Bowman, J. M. Classical and Quasiclassical Spectral Analysis of CH_5^+ Using an Ab Initio Potential Energy Surface. *J. Chem. Phys.* **2003,** *119*, 8790–8793.

(32) Brown, A.; McCoy, A. B.; Braams, B. J.; Zhong, J.; Bowman, J. M. *Ab Initio* Diffusion Monte Carlo Calculations of the Quantum Behavior of CH_5^+ in Full Dimensionality. *J. Chem. Phys.* **2004,** *121*, 4105–4116.

(33) Zin, J.; Braams, B. J.; Bowman, J. M. An Ab-Initio-Based Global Potential Energy Surface describing $CH_5^+ \rightarrow CH_3^+ + H_2$. *J. Phys. Chem. A* **2006,** *110*, 1569–1574.

(34) Thompson, K. C.; Crittenden, L.; Jordan, M. J. T. CH_5^+: Chemistry's Chameleon Unmasked. *J. Am. Chem. Soc.* **2005,** *127*, 4954–4958.

(35) Moyano, G. E.; Collins, M. A. Interpolated Potential Energy Surface and Classical Dynamics for H_3^+ HD and $H_3^+ + D_2$. *J. Chem. Phys.* **2003,** *119*, 5510–5517.

(36) Xie, Z.; Braams, B. J.; Bowman, J. M. *Ab Initio* Global Potential Energy Surface for $H_5^+ \rightarrow H_3^+ + H_2$. *J. Chem. Phys.* **2005,** *122*, 224307–224315.

(37) Huang, X.; McCoy, A. B.; Bowman, J. M.; Johnson, L. M.; Savage, C.; Dong, F.; Nesbitt, D. J. Quantum Deconstruction of the Infra-Red Spectrum of CH_5^+. *Science* **2006,** *311*, 60–63.

(38) Huang, X.; Johnson, L. M.; Bowman, J. M.; McCoy, A. B. Deuteration Effects on the Structure and Infrared Spectrum of CH_5^+. *J. Am. Chem. Soc.* **2006,** *128*, 3478–3479.

(39) Johnson, L. M.; McCoy, A. B. Evolution of Structure in CH_5^+ and Its Deuterated Analogues. *J. Phys. Chem. A* **2006,** *110*, 8213–8220.

(40) Ivanov, S. D.; Asvany, O.; Witt, A.; Hugo, E.; Mathias, G.; Redlich, B.; Marx, D.; Schlemmer, S. Quantum-Induced Symmetry Breaking Explains Infrared Spectra of CH_5^+ Isotopologues. *Nat. Chem.* **2010,** *2*, 298–302.

(41) Cheng, T. C.; Bandyopadyay, B.; Wang, Y.; Carter, S.; Braams, B. J.; Bowman, J. M.; Duncan, M. A. Shared-Proton Mode Lights up the Infrared Spectrum of Fluxional Cations H_5^+ and D_5^+. *J. Phys. Chem. Lett.* **2010,** *1*, 758–762.

(42) Xantheas, S. S.; Burnham, C. J.; Harrison, R. J. Development of Transferable Interaction Models for Water. II. Accurate Energetics of the First Few Water Clusters from First Principles. *J. Chem. Phys.* **2002,** *116*, 1493–1499.

(43) Kumar, R.; Wang, F.-F.; Jenness, G. R.; Jordan, K. D. A Second Generation Distributed Point Polarizable Water Model. *J. Chem. Phys.* **2010,** *132*, 014309/1–014309/12.

(44) Huang, X.; Braams, B. J.; Bowman, J. M. Ab Initio Potential Energy and Dipole Moment Surfaces of $(H_2O)_2$.. *J. Phys. Chem. A* **2006,** *110*, 445–451.

(45) Huang, X.; Braams, B. J.; Bowman, J. M.; Kelly, R. E. A.; Tennyson, J.; Groenenboom, G. C.; van der Avoird, A. New *Ab Initio* Potential Energy Surface and the Vibration−Rotation−Tunneling Levels of $(H_2O)_2$ and $(D_2O)_2$. *J. Chem. Phys.* **2008,** *128*, 034312/1–034312/9.

(46) Shank, A.; Wang, Y.; Kaledin, A.; Braams, B. J.; Bowman, J. M. Accurate Ab Initio and "Hybrid" Potential Energy Surfaces, Intramolecular Vibrational Energies, And Classical Ir Spectrum of the Water Dimer. *J. Chem. Phys.* **2009,** *130*, 144314/1–144314/11.

(47) Wang, Y.; Shepler, B. C.; Braams, B. J.; Bowman, J. M. Full-Dimensional, *Ab Initio* Potential Energy and Dipole Moment Surfaces for Water. *J. Chem. Phys.* **2009,** *131*, 054511/1–054511/18.

(48) Rheinecker, J. L.; Bowman, J. M. The Calculated Infrared Spectrum of Cl^-H_2O Using a New Full Dimensional *Ab Initio* Potential Surface and Dipole Moment Surface. *J. Chem. Phys.* **2006,** *125*, 133206/1–133206/10.

(49) Tishchenko, O.; Truhlar, D. G. Gradient-Based Multiconfiguration Shepard Interpolation for Generating Potential Energy Surfaces for Polyatomic Reactions. *J. Chem. Phys.* **2010,** *132*, 084109/1–084109/6.