# **Electronic Supporting Information**

Full-dimensional, ab initio potential energy surface for formic acid dimer, zero-point energy, selected anharmonic fundamental energies and the tunneling splitting calculated in relaxed 1–4-mode subspaces

Chen Qu and Joel M. Bowman

#### **Details of diffusion Monte Carlo calculations**

In the DMC simulations, the simple unbiased algorithm was applied, and the details of this implementation are given in Ref. 1. In brief, we use an ensemble of walkers to represent the nuclear configurations of the molecule. At each step, a random walk is assigned to each atom in each walker, and then these walkers are propagated via birth-death process. After each step, the reference energy,  $E_{ref}(\tau)$ , is calculated as  $E_{ref}(\tau) = V(\tau)\alpha[N(\tau)N(0)]/N(0)$ , where  $\tau = it$  is the imaginary time;  $V(\tau)$  is the average potential over all the walkers that are alive, at imaginary time  $\tau$ ;  $N(\tau)$  is the number of live walkers at time  $\tau$ ;  $\alpha$  is a parameter that can control the fluctuations of the number of walkers and the reference energy. Finally, the average of the reference energy over the imaginary time gives an estimate of the zero-point energy (ZPE), and the distribution of the walkers, when properly normalized, represents the ground state wave function.

To compute the ZPE of the formic acid dimer, ten simulations were performed, and in each simulation, 30000 walkers were initiated at the saddle point and were propagated for 40000 steps with step size,  $\Delta \tau$ , of 5.0 au. The first 10000 steps were used for equilibration, and the remaining 30000 steps to compute the ZPE.

# Description of normal modes and the vectors

The vector, wavenumber, and description of each normal mode are given below. For normal modes of the minimum, the symmetry of each mode is also given.

#### Minimum normal modes



#### Saddle point normal modes



#### Details of anharmonic vibrational calculations

To theoretically calculate the fundamental frequencies of FAD, we applied vibrational self-consistentfield and virtual-state configuration interaction (VSCF+VCI) method,<sup>2</sup> using our own code "Multimode".<sup>3,4</sup> The calculation used the minimum geometry as reference, since the barrier separating the two minima is quit high and the tunneling splitting cannot be resolved in most of the spectra. Fulldimensional calculations for the fundamental frequencies are not feasible, either. Therefore, we performed the calculation in reduced dimensionality, and the same strategy was also applied in the calculation for the IR spectrum of H<sub>7</sub><sup>+</sup> and D<sub>7</sub><sup>+</sup>.<sup>5</sup> In brief, we solved the reduced-dimensional *m*-mode (with m < 3N - 6) Schrödinger equation  $\hat{H}(Q)\psi(Q) = E\psi(Q)$  with zero total angular momentum, where  $Q = [Q_1 \cdots Q_m]$  denotes the *m* modes coupled in the calculation. The kinetic energy operator for J = 0is given by<sup>6</sup>

$$\hat{T} = \frac{1}{2} \sum_{\alpha,\beta} \hat{\pi}_{\alpha} \mu_{\alpha\beta} \hat{\pi}_{\beta} - \frac{1}{8} \sum_{\alpha} \mu_{\alpha\alpha} - \frac{1}{2} \sum_{k=1}^{m} \frac{\partial^2}{\partial Q_k^2}.$$

In this kinetic energy operator,  $\mu_{\alpha\alpha}$  is the inverse of the effective moment of inertia tensor, and

$$\hat{\pi}_{lpha} = -i \sum_{k,l=1}^m \zeta^{lpha}_{k,l} Q_k rac{\partial}{\partial Q_l}$$

are vibrational angular momentum terms and  $\zeta_{k,l}^{\alpha}$  are Coriolis coupling constants. The potential V(Q) in the Hamiltonian is the full potential of FAD with the remaining modes fixed at zero.

Since here we are particularly interested in the C–H and O–H stretches, which are in-plane modes, all the out-of-plane modes were not considered in the anharmonic calculation, and they were fixed at zero. Fifteen modes of the minimum were coupled in our calculation. These 15 modes are mode 4, 7, 8, and 13–24 (see the table above), and they belong to  $A_g$  and  $B_u$  symmetry of  $C_{2h}$  point group.

In Multimode, the potential is written as a hierarchical *n*-mode representation (*n*MR):

$$V(Q_1, Q_2, \cdots, Q_m) = \sum_i V_i^{(1)}(Q_i) + \sum_{i < j} V_{ij}^{(2)}(Q_i, Q_j) + \sum_{i < j < k} V_{ijk}^{(3)}(Q_i, Q_j, Q_k) + \sum_{i < j < k < l} V_{ijkl}^{(4)}(Q_i, Q_j, Q_k, Q_l) + \cdots$$

In our calculation, this representation is truncated at the 4MR.

In the VSCF calculation, the total vibrational wavefunction is given as a direct product of one mode functions, and these one-mode functions are optimized using the self-consistent-field procedure. For this specific calculation of FAD, harmonic basis functions were used to optimize the one-mode

functions: 23 harmonic basis functions were used for mode 4; 17 basis functions for mode 7 and 8; 15 basis functions for mode 13–20; and 13 basis functions for mode 21–24. The solutions of the VSCF equations give the VSCF ground state and virtual states.

The VSCF ground state and those virtual states are used as basis functions in the VCI procedure. Here we use an "*m*-mode basis" to restrict the excitation space to a maximum of *m* modes excited simultaneously, and in the calculation, we allowed up to 4-mode basis, i.e., 4 modes at most can be excited simultaneously. To reduce the size of the Hamiltonian matrix, we also applied two constraints at the same time: the maximum excitation for each mode (referred to as MAXBAS later) and the sum of quanta of excitation (referred to as MAXSUM). In 1-mode basis, the MAXBAS is 14 for mode 4; 8 for mode 7 and 8; 6 for mode 13–20; and 4 for mode 21–24. In 2-mode basis, the MAXBAS's are 13, 7, 5, and 3 for mode 4, mode 7–8, mode 13–20, and mode 21–24, respectively. In 3-mode basis, the MAXBAS's are 12, 6, 4, 2, and in the 4-mode basis, they are 11, 5, 3, 2. The MAXSUM is always 14 for 1-, 2-, 3-, and 4-mode basis. With all these restrictions, the size of the Hamilton matrix in two symmetry blocks are 94247 and 88805, respectively. The matrix size was reduced to 23,270 and 23,034 based on a perturbation test to eliminate the rows and columns of the matrices, which has been described in detail in Ref. 7 and 8

## Potential energy surface

The PES is available as a zip file in the supplementary material. The codes are written in Fortran 90 and the library and module files are pre-compiled with Intel Fortran compiler (ifort). Please contact the authors (CQ: cqu3@emory.edu and JMB: jmbowma@emory.edu) if you have any questions about the PES and the codes.

### References

- [1] I. Kosztin, B. Faber and K. Schulten, Am. J. Phys., 1996, 64, 633-644.
- [2] K. M. Christoffel and J. M. Bowman, Chem. Phys. Lett., 1982, 85, 220.
- [3] J. M. Bowman, S. Carter and X. Huang, Int. Rev. Phys. Chem., 2003, 22, 533.
- [4] S. Carter, J. M. Bowman and N. C. Hancy, Theor. Chem. Acc., 1998, 100, 191–198.
- [5] C. Qu, R. Prosmiti and J. M. Bowman, Theor. Chem. Acc., 2013, 132, 1413.
- [6] J. K. G. Watson, Mol. Phys., 1968, 15, 479.

- [7] N. C. Handy and S. Carter, Mol. Phys., 2004, 102, 2201-2205.
- [8] X. Wang, S. Carter and J. M. Bowman, J. Phys. Chem. A, 2015, 11632–11640.