

Quantum calculations of vibrational energies of H_3O_2^- on an *ab initio* potential

Xinchuan Huang, Bastiaan J. Braams, Stuart Carter, Joel M. Bowman*

*Cherry L. Emerson Center of Scientific Computation, Dept. of Chemistry,
Emory University, Atlanta, GA 30322*

Supplementary material

S.1 Details of the *ab initio* calculations:

These were done by calculating 37,716 *ab initio* electronic energies on grids in normal coordinates. The coordinates were obtained using the barrier separating the two minima described above as the reference geometry. The resulting nine normal modes are of C_2 -symmetry: five are of *A* symmetry and 4 are of *B* symmetry, including the mode with an imaginary frequency. *Ab initio* energies were calculated over a large number of grids at the CCSD(T)/aug-cc-pVTZ level of the theory, using MOLPRO 2002.1. These grids varied in dimensionality from one to four, following the n-mode representation of the potential, used in our vibrational code MULTIMODE. For the eight normal coordinates with real frequencies, 14, 12, 6, and 4 unequally spaced quadrature points were selected for the 1d, 2d, 3d and 4d grids, respectively. For the corresponding grids involving the imaginary-frequency mode 28, 20, 6, and 6 grid points were used, respectively. A total of 34,326 energies were calculated, which resulted in a set of 63,702 symmetry-equivalent points. This large computational effort took just over 25 days on 30 nodes of our Dual-Xeon 2.4GHz Beowulf Linux Cluster (a total of 1500 cpu-days). This data set was augmented by 3,290 additional points distributed around the *cis*- and *trans*- reference configurations, in order to give a more complete coverage of the *cis-trans* isomerization path, which we discuss in detail below. Excluding 27 1-d points of extremely high energies, our final potential fit contains 66,965 points.

The C_1 minimum and C_2 -symmetric reference geometries are fit extremely well, and the barrier for the BH transfer on the fit is 68.5 cm^{-1} , which compares very well with the directly calculated CCSD(T) value of 74 cm^{-1} . The normal-mode frequencies at the global minimum from the fit agree very well with those directly obtained from the present *ab initio* calculations (12) and also with previous, lower-level *ab initio* calculations (6).

S.2 The Fit

The general form of the fit is a multinomial

$$V(\rho_1, \dots, \rho_{12}) = \sum_{m=0}^N \sum_{i=1}^{12} C_{n_1, \dots, n_{12}} \rho_1^{n_1} \rho_2^{n_2} \dots \rho_{12}^{n_{12}}; \sum_{i=1}^{12} n_i = m,$$

where N is the maximum overall order of the multinomial and

$$\rho_i = \frac{a_i}{r_i} \quad \text{or} \quad \rho_i = a_i \ln(r_i)$$

where r_i is an ordered set of internuclear distances. This expression is not invariant with respect to interchange of identical nuclei, as it should be. Of course a faithful fit over a data set is that contains all configurations corresponding to all permutations will approximately obey permutational invariance. That is certain coefficients will be determined numerically to be nearly equal.

For low values of N, e.g. N = 2, it is easy to re-assemble the above expression so that it does obey permutational symmetry. We have not yet succeeded in deriving an expression or algorithm to develop a permutationally invariant expression for general N. We have developed such an expression on a "case-by-case" basis. For the present case of H_3O_2^- , N is seven and the multinomial consists of 1976 terms.

S.3 The normal mode frequencies at the global minimum (in cm^{-1}) from the fit and directly from the present *ab initio* calculations are in decreasing order:

3838, 3793, 1718, 1568, 1363, 583, 479, 319, 206 (from fit)

3835, 3784, 1702, 1554, 1353, 596, 476, 305, 191 (*ab initio*).

S.4 The barrier for hydrogen exchange on the present potential surface is found at a saddle point of C_s -symmetry with an energy of 2430 cm^{-1} . This compares remarkably well with CCSD(T) calculations that were done subsequent to the fit, which give a barrier of 2477 cm^{-1} .

S.5 MM calculations

These two important aspects of the torsional motion of H_3O_2^- have not been pointed out previously, and they present a major challenge to a method to obtain exact vibrational energies. Fortunately, the "Reaction Path Hamiltonian" version of MULTIMODE (MM-RPH) is capable of such calculations. We applied this code with the full-dimensional potential just described. The torsional path used in these calculations is the one shown in Fig. 1. The choice of this path permits the efficient use of C_2 -symmetry, which reduces the computational effort, with no loss in accuracy. (This choice of path is also consistent with the earlier observation that the zero-point motion of H_3O_2^- in one dimension is delocalized over the two global minima(7). Our calculations fully support the conclusion of this model study.)

For each value of τ from 0 to 360 degree (0.5 degree each, 721 points in all), the energy is minimized with respect to the remaining atomic coordinates. At each point along the path, the system is rotated to the principal axis system, taking care to ensure that the resulting coordinates form a smoothly-varying path. The second derivative force constant matrix is determined, and the three translations, three rotations plus the torsional coordinate τ are projected out of this matrix (10) which is diagonalized to give $3N-7$ normal modes perpendicular to the path. We have confirmed that the normal coordinate

vectors at τ and $\tau+0.5$ vary smoothly and the ordering of the modes at the starting point (*cis*-) and the end point (*trans*-) are consistent with respect to their symmetries in C_2 , and that there were no spurious interchanges at any point along the path.

S.6 Convergence of the energies reported here was tested by performing smaller calculations, both in the number of coupled modes and the size of the CI-bases. Based on these tests, the energies reported here are believed to be converged to a few cm^{-1} or less for the OH-stretches, and to within 10-20 cm^{-1} for the overtone of the BH bends.

S.7 Along the torsion path, harmonic frequencies of mode 6 and 7 for the *cis*-configuration, 1266 and 1794 cm^{-1} , respectively, would change to 1799 and 1269 cm^{-1} , respectively, at the *trans*-configuration (a near perfect reversal).

S.8 *Ab initio* calculations of harmonic normal mode frequencies and double-harmonic IR fundamental intensities in parentheses (km/mol) were done with MOLPRO using MP2/aug-cc-pVTZ calculations at the global minimum (GM) and the C_2 -saddle point (SP). Harmonic frequencies^a followed by intensities^b in parentheses for H_3O_2^- at the global minimum and the C_2 -saddle point are :

Mode	GM	SP
1	209 (89)	215(91)
2	309 (530)	488i (4269)
3	498 (192)	574 (14)
4	587 (12)	580 (865)
5	1294 (3347)	622 (3)
6	1405 (410)	1504 (16)
7	1665 (52)	1603 (14)
8	3841 (5.51)	3855 (1.00)
9	3873 (1.31)	3856 (0.88)

^a cm^{-1} , ^b km/mol

In this table, both at GM and SP, mode 1 is torsion.

At SP, mode 2 is the imaginary mode (BH stretch), mode 5 is O...O sym stretch; mode 6 & 7 are BH bends, mode 8 is symmetric OH stretch, mode 9 is anti-symmetric OH stretch.

At GM, mode 2-5 is not easily correlated with SP modes. Mode 6 and mode 7 correspond to a coupling of the water bend with the hydrogen-bonded OH stretch. Mode 8 is O-H stretch of OH-, while mode 9 is O-H stretch in $-\text{OH}_2$.