Quantum Calculations of Vibrational Energies of $H_3O_2^-$ on an ab Initio Potential

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There has been progress in the experimental investigation of the intermolecular vibrations of the bridging H-atom in the $H_3O_2^-$ and $H_5O_2^+$ complexes.[1−3] These complexes, which are of fundamental importance in liquid water, present very formidable challenges to theory and computation. To date calculations have been simplified in one or more aspects. Very recently, we reported realistic, full-dimensional calculations on $H_5O_2^+$, which pointed out some pitfalls in doing calculations in reduced dimensionality.[4]

In this communication, we consider $H_3O_2^-$ in full dimensionality and focus on the experiments of Johnson and co-workers.[1,2] This group reported four vibrational bands of $H_3O_2^-$, using the messenger technique.[5] The assignment of these bands was based on the results of MP2 ab initio calculations of harmonic normal-mode frequencies.[6] The calculations also determined a slightly asymmetric, double minimum equilibrium structure with the bridging hydrogen (BH) slightly closer to one O atom. More recent ab initio studies of the motion of the BH concluded that it is delocalized over the two minima.[7]

These calculations were done prior to the messenger experiments and so could not address some questions raised by them. First, two broad bands at roughly 3100 and 3400 cm^{-1} were tentatively assigned to the first overtone of each of two bend modes of the BH; however, the band centers are significantly blue-shifted relative to the harmonic estimates (including results reported here). Two narrower, higher-frequency bands, separated by 19 cm^{-1}, were identified tentatively as the antisymmetric and symmetric OH-stretch vibrations, in rough agreement with ab initio harmonic calculations.[6] However, the higher-frequency OH band disappeared with two Ar atoms complexed to $H_3O_2^-$ instead of a single Ar atom. Thus, Price et al. were circumspect in assigning the second band as the symmetric OH fundamental.

Stimulated by these experimental results, we undertook a quantum study of the vibrations of $H_3O_2^-$ in full dimensionality. This is a daunting task because both the potential and the dynamics must confront the high dimensionality of the vibrational space and the "floppy" nature of the vibrational motion. We have been successful in both respects, and report results directly related to the messenger experiments. We also give an explanation for the disappearance of the higher-frequency OH band for the Ar_2 complex, noted above.

The potential energy surface is a compact, least-squares fit of 66,965 CCSD(T)/aug-cc-pVTZ ab initio electronic energies, obtained with MOLPRO 2002.1.[8] The energies were distributed on grids in normal coordinates referenced to the C_2-saddle point separating the two asymmetric equilibrium structures mentioned above. The variables of the fit are all the 10 internuclear distances. This made it convenient for the fit to satisfy the permutational symmetry of identical atoms, as described in a similar application to CH_5^+.[9] The fit is highly precise, with an RMS fitting error of
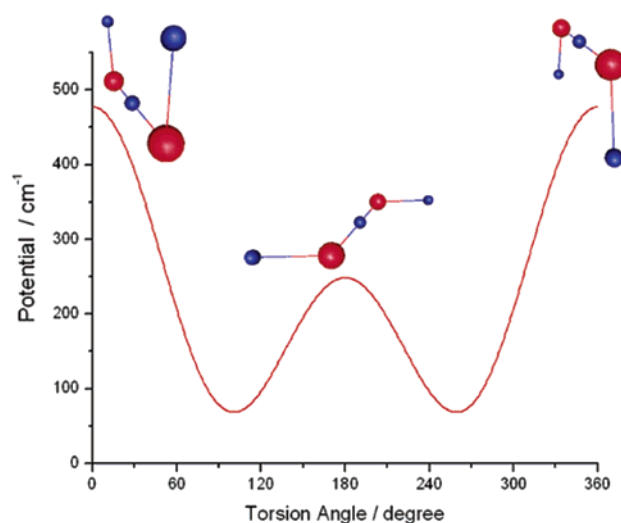
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Figure 1. Torsional potential along the C_2 "reaction path".

13.0 cm^{-1} for potential values up to 15 000 cm^{-1}, and 19.0 cm^{-1} over the entire data set.

An important new aspect of these calculations is a description of the torsional potential of the two OH groups. This potential, from the fit, is shown in Figure 1, for a path where the BH is midway between the two O atoms, and the OO distance and the two OH fragments are relaxed as a function of the torsion angle, τ. The *cis* and *trans* barriers on this path are 477 and 248 cm^{-1}, respectively, and the fully relaxed barriers are 376 and 166 cm^{-1}, respectively. As shown below, the *trans* barrier separating the two minima leads to important tunneling splittings.

The calculation of full dimensional vibrational energies of $H_3O_2^-$ including the torsional motion presents a major challenge to theory. The "Reaction Path Hamiltonian" version of the code MULTI-MODE[10] (MM-RPH) is capable of such calculations, and we follow the procedures given previously in the present calculations.[10b,c] The reference "reaction path" is the one shown in Figure 1, and thus, modes transverse to that path are of C_2 symmetry. Modes 6 and 7 (of *A* and *B* symmetry, respectively) are the BH bends which were implicated in two broad bands in the Price et al. experiments. There is a large variation in the harmonic frequencies of these modes with the torsion, indicating strong mixing of these modes and the torsion mode. The importance of this mixing and mixing to the BH symmetric stretch to the spectrum will be investigated below.

Selected results of the present calculations are given in Table 1. These are the harmonic frequencies, calculated at the C_2 saddle point, and the zero-point and fundamental excitation energies from the full MM-RPH VCI calculation. The states from the latter calculation are labeled "+" and "−" to indicate the parity of each state with respect to reflection about the *trans* barrier, and all

Table 1. Calculated Harmonic and Fundamental Transition Energies (cm^{-1}) Relative to the 0^+ Zero-Point Energy

	0	ν_1 BH stretch	ν_2 OH torsion	ν_3 OH rock	ν_4 OH wag
H.O.	6382	621i	213	572	576
+	6642	819	141	534	552
−	25.1	864	225	595	574
	ν_5 OO stretch	ν_6 BH Bend	ν_7 BH Bend	ν_8 OH anti-sym	ν_9 OH sym-str.
H.O.	631	1618	1525	3814	3815
+	624	1337	1454	3650	3650
−	666	1485	1509	3679	3699

^{a} The harmonic frequencies are for the C_2-sym O···H···O configuration. The "+" and "−" indicate the parity of the torsional component of the wave function. The zero-point energies are also given under the column labeled "0".

Table 2. Calculated Transition Energies (cm^{-1}) for Eight Possible Transitions from the Ground State of even (+) and Odd Parity (−) to the OH Fundamentals of Even and Odd Parity (Modes 8 and 9)

initial state	final state	E	I	experiment^a
0^+	ν_8^+	3650.4	S	
	ν_9^+	3649.4	S	
	ν_8^-	3678.7	M	
	ν_9^-	3699.5	M	3653 (S)
0^-	ν_8^-	3653.6	S$^-$	3672 (M)
	ν_9^-	3674.4	S$^-$	
	ν_8^+	3625.3	M$^-$	
	ν_9^+	3624.3	M$^-$	

^{a} From the band centers reported in ref 1.

energies are given relative to the "+" component of the zero-point level. The 25.1 cm^{-1} splitting in the zero point is large enough to be a significant spectroscopic feature but smaller than or comparable to the thermal energy of the Ar-messenger experiments. Thus, transitions from the "hot band" 0^- will be significant even in relatively cold molecules, and we will focus on these transitions when we consider the monomer OH-stretch fundamentals in Table 2.

First, though, consider the two broad experimental bands in the vicinity of 3100 and 3400 cm^{-1}. These features are blue-shifted from the present harmonic estimates (even more so from estimates equal to twice the fundamentals of the MM-VCI calculations). Thus, these features almost certainly involve combinations of the overtone of the bends with other low-lying states that carry significant oscillator strength. To determine candidate modes, we calculate transition intensities in the double-harmonic approximation at the C_2-saddle point, and find that the BH antisymmetric stretch, ν_1 (the imaginary frequency mode 1 in Table 1), has the largest transition dipole (roughly 200 times larger than the intensity of the two BH-bends). Also, in other calculations we find a large (periodic) variation in the dipole with the torsion angle. Thus, that mode, ν_2, which we have already identified as mixing with the BH-bends is very likely a "bright" contributor to mix with the overtone of the bends. We inspect coefficients of basis functions of vibrational eigenstates, and find 10 states with large $2\nu_6 + n\nu_2$ or $2\nu_7 + n\nu_2$ character. These appear in two groups; the first ranges from 3053 to 3289 cm^{-1}, and the second ranges from 3435 to 3446 cm^{-1}. We also find several eigenstates with contributions from $2\nu_6 + \nu_1$ or $2\nu_7 + \nu_1$ with energies at 3343, 3486, and 3491 cm^{-1}. These energies correspond well to the experimental bands, and so we tentatively assign them to these groups of molecular eigenstates.

Next consider the OH-stretch bands. Table 2 contains the energies of the eight possible transitions from 0^+ and 0^- to the four OH states $\nu_8^{+/-}$ and $\nu_9^{+/-}$. The intensities of these transitions depend on the thermal populations of the 0^+ and 0^- states and the various transition moments. In double harmonic calculations at the C_2-saddle point the $0 \rightarrow n_8$ and $0 \rightarrow n_9$ intensities are roughly equal. Combining this with assumed significant oscillator strength for parity change transitions and significant thermal population of 0^- level, we characterize the eight possible transitions as strong (S) and moderate (M) or S$^-$ or M$^-$ for 0^--transitions. As is seen, there are S and S$^-$ transitions around 3650 cm^{-1} and an S$^-$ transition at 3674 cm^{-1}, in very good agreement with experiment. However, we do not assign the higher energy band to ν_9 as was guardedly done by Price et al, on the basis of previous harmonic calculations. Instead, we assign this band is to a transition to ν_8^-, the torsion-split doublet of ν_8. Also, we predict an M transition to ν_9^- at roughly 3700 cm^{-1} that was not reported by Price et al. (but which may be in the spectrum).

The above explanation for the higher-energy OH-vibrational band immediately suggests an explanation for the disappearance of this feature for complexes with two Ar atoms. For a single Ar complex, the Ar atom is most likely complexed in a collinear arrangement to the H atom in either HO group.[11] However, for two Ar atoms the likely configuration would have each Ar complexed to a separate HO group. Torsional motion would then be severely hindered, i.e., the torsional barrier would be significantly increased, due to the additional mass of the Ar atom, assuming the Ar atom "follows" the HO group, or due to the cost in breaking the Ar−HO bond to allow the HO groups to rotate away from the equilibrium structure. Thus, the splitting in the two OH bands would be greatly reduced, and the transition to the higher-energy OH stretch would disappear, in agreement with the observations of Price et al.

Supporting Information Available: Details of the calculations and fit. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA049801I