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Dynamics of Vibrational Overtone Excitations of H_2SO_4, $H_2SO_4-H_2O$: Hydrogen−Hopping and Photodissociation Processes

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Sulfuric acid (H_2SO_4) is of major importance in atmospheric chemistry. This molecule acts as a nucleating species for aerosols and for cloud formation at a wide range of altitudes. Gas-phase H_2SO_4 is the most abundant sulfur compound in the atmosphere at altitudes above 35 km.[1,2] The photolysis of H_2SO_4, especially at high altitudes, is recognized to play an important role in atmospheric chemistry, but the mechanisms and pathways involved have not been characterized with any certainty yet. Recently, Hintze et al.[5] established that photodissociation of H_2SO_4 in the ultraviolet region cannot be relevant at atmospheric conditions. As an alternative mechanism, it was proposed that overtone excitation of the OH stretching vibration of H_2SO_4, and its hydrate, can lead to dissociation of the molecule into sulfur trioxide (SO_3) and water.[6,7] This mechanism, which involves transitions in the visible solar spectrum, was analyzed and used to estimate the yield of the process in atmospheric conditions.[5] This mechanism is, however, not yet supported by direct experiments or by theoretical calculations. The dynamics of the process, its yield, the time scale of the reaction, and the issue whether the process can also take place in $H_2SO_4-H_2O$ remain to be investigated.

The objective of this communication is to characterize the overtone-induced processes in H_2SO_4 and $H_2SO_4-H_2O$ by classical trajectory simulations, using potential surfaces from semiempirical electronic structure theory (PM3).[8,9] Several surprising features of the overtone-excited states are predicted, such as the occurrence of fast "hopping" events of the hydrogen atom between the oxygen atoms. The calculations show that the fifth OH overtone excitation in H_2SO_4 leads to 5% dissociation over a time scale of 400 picoseconds. On the other hand, the results show that the dissociation into SO_3 and $2H_2O$ is completely suppressed for overtone excited $H_2SO_4-H_2O$, where the only significant process is breaking of the cluster into H_2SO_4 and H_2O. The present study follows an approach used recently by Miller et al.,[10] studying overtone-induced processes in HNO_3, HNO_3-H_2O, and HONO. The study also supports the validity of the PM3 potential surface for these related systems.[10] Here we only give a brief outline of the methodology.

In this approach, the dynamics of the process are studied by classical trajectory calculations. Essential for this purpose is the sampling of the initial conditions for the trajectories, which should correspond to the initial excited state. We used the vibrational self-consistent field (VSCF) method, and specifically the CC−VSCF (correlation-corrected VSCF) variant of the algorithm[11,12] to compute the initial energy level and wave function of the overtone-excited molecules. CC−VSCF was already applied to vibrational spectroscopy calculations of H_2SO_4, $H_2SO_4-H_2O$, and related species,[13,14] with results that compare well with experiment, also for overtone and combination-mode transitions. An advantage of VSCF methods is that they include anharmonic effects, both the intrinsic anharmonicity of individual modes and the anharmonic coupling between different modes. Further, VSCF and CC−VSCF can be applied directly to potential surfaces from electronic structure theory.[12] All the calculations here were carried out with the electronic structure code package GAMESS,[15] in which the VSCF algorithms are also implemented. The potential energy surfaces used both in the VSCF and in the classical trajectory calculations were from the PM3 semiempirical electronic structure algorithm.[8,9] This method compares less well with spectroscopy experiments[13] than the ab inito MP2/TZP.[16,17] Nevertheless, the spectroscopic results of PM3 are reasonable, and our tests, as well as experience for similar systems,[10] indicate that these potential surfaces are at least semiquantitively valid. In particular, PM3 equilibrium geometries for the two systems are in good accord with ab initio MP2/TZP calculations.

The calculations are as follows. Using the approximate VSCF level of the algorithm that is separable, a vibrational wave function for the overtone-excited state is computed $\Psi(Q) = \prod_i \psi_i(Q_i)$ where Q_i is the normal-mode coordinate of mode i, Q denotes collectively the vibrational modes, and $\psi_i(Q_i)$ is the VSCF approximate wave function of mode i. Initial configurations for the classical trajectory simulations are sampled according to $|\Psi(Q)|^2$. The initial momentum values for each mode were determined classically, using the separable mode approximation (VSCF).[11]

The overtone transitions used correspond to the OH stretching excitations and are $\nu = 6$ for H_2SO_4 and $\nu = 3$ for $H_2SO_4-H_2O$. It should be noted that these vibrational states are the highest vibrational levels of the OH stretching vibration that could be obtained by the CC−VSCF calculations. For higher overtone levels, the VSCF calculations fail to converge, indicating that the corresponding states are very short-lived and probably not experimentally relevant. The overtone levels studied here have lifetimes that correspond to well-defined (narrow) overtone frequencies. The OH asymmetric stretching overtone excitation band in H_2SO_4 for $\nu = 6$ is 21 511 cm^{-1} (~61.5 kcal mol^{-1}), and the free OH stretch of H_2SO_4 and the H-bonded OH stretch of H_2SO_4 in the monohydrate cluster for $\nu = 3$ are 10 855 cm^{-1} (~31 kcal mol^{-1}) and 9835 cm^{-1} (~28.1 kcal mol^{-1}), respectively.

The PM3 potentials and forces were computed "on the fly" in propagation of the trajectories: 98 trajectories were computed for H_2SO_4 in $\nu = 6$; 50 trajectories were obtained for the $\nu = 3$ excitation of the free OH of $H_2SO_4-H_2O$; and 50 trajectories were used to study the $\nu = 3$ excitation of the H-bonded OH in $H_2SO_4-H_2O$. Each trajectory was propagated for a maximum of 400 ps.

Hydrogen-Hopping in H_2SO_4: In 22% of the trajectories for H_2SO_4 ($\nu = 6$), hopping of the hydrogen atom from the overtone-excited OH to another oxygen atom in the molecule was observed. The mean time scale for this process is 13 ps, and it was found to take place only once for any of the trajectories where it occurs. An approximate transition state was identified for this hydrogen hopping from the trajectories, and it was found that the partial charge on the H atom in the transition state for the hopping is $\sim +0.4$.

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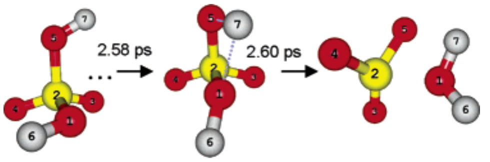

Figure 1. Snapshots of the dissociation of H_2SO_4 into SO_3 and H_2O.

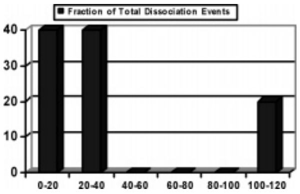

Figure 2. The distribution in time (picoseconds) of dissociation events of H_2SO_4 into SO_3 and H_2O during the simulations.

Therefore, the process predicted here corresponds to intramolecular proton-transfer induced by overtone excitation. It should be noted that intramolecular hopping of the H atom induced by OH overtone excitation of HNO_3 was predicted by Miller et al.[10] However, our recent calculations have shown that in the transition state for H hopping in HNO_3, the H is not protonic, but rather hydridic, carrying a negative partial charge.

Isomerization of H_2SO_4: Isomerization from cis to trans structure of H_2SO_4 was observed in all trajectories. The energy difference between these two isomers is ~1 kcal mol^{-1}. The structures of four rotamers of H_2SO_4 (including the cis and trans isomers) were recently obtained in ab initio calculations.[19] We note that all of the four rotamers were observed in the course of the dynamics in our simulations. The time scale of the cis to trans isomerization is less than 1 ps and it appears back and forward during the simulations.

Overtone-Induced Dissociation of H_2SO_4: One of the main objectives of this paper is to test the mechanism proposed by Vaida et al.[6] for H_2SO_4 and $H_2SO_4-H_2O$. We note that recently estimates for the yield of this dissociation mechanism in contact with atmospheric processes were given by Mills et al.[20] Dissociation of H_2SO_4 into SO_3 and H_2O was found in 5% of the trajectories. The implications of this for the yield at atmospheric conditions depend, of course, on the frequency of deactivating collisions and on the vibrational fluorescence time scale. Snapshots from a typical trajectory leading to dissociation are shown in Figure 1. A histogram showing the time distribution of dissociation events is presented in Figure 2. The most probable dissociation time is 9 ps. As Figure 1 shows, the dissociation is the consequence of a H-hopping event, when the migrating H atom from one OH lands on the oxygen of the other OH. The time scale of 9 ps dissociation, for 5% of the trajectories in runs of 400 ps, shows an efficient dynamical mechanism in which intramolecular vibrational energy redistribution is incomplete. Energetically, the $\nu = 6$ excitation of the OH stretching mode, of the order of 61.5 kcal mol^{-1}, is much above the barrier for the process, about 32−40 kcal mol^{-1}. [21,22] The barrier for the reverse process, formation of H_2SO_4 from SO_3 and H_2O, was recently studied both by ab initio calculations[21,22] and experimentally. [23]

Comparison with MP2 results for transition state and barrier, not given here, are good.

Overtone-Induced Dynamics of $H_2SO_4-H_2O$: It was suggested[6] that overtone-induced dissociation into SO_3 and water takes place also for $H_2SO_4-H_2O$. The energy computed for this process is ~25 kcal mol^{-1}. [22,23] Excitations to $\nu = 3$ of the free OH of H_2SO_4 and to $\nu = 3$ of the H-bonded OH of H_2SO_4 in $H_2SO_4-H_2O$ have energies of ~31 kcal mol^{-1} and ~28 kcal mol^{-1}, respectively. Thus, energetically, the proposed overtone-induced dissociation into SO_3 and $2H_2O$ is feasible. However, all 100 trajectories failed to show such a process. Instead, in all cases, excitation led to fast, picosecond time scale decomposition of the cluster into the monomers H_2SO_4 and H_2O, due to the strong coupling between the OH vibration and the intermolecular modes involving relative motions of the H_2SO_4 and H_2O. We note that there is evidence for such strong coupling between these modes from CC−VSCF calculations of the vibrational states of $H_2SO_4-H_2O$, and experimental spectroscopic results indirectly support this. While the decomposition of the cluster clearly partly deactivates the OH stretch of H_2SO_4, the mode remains partly excited in the monomer after the process. When a semiclassical "box quantization" approximation was used, it was found that for the initially excited free OH stretch of H_2SO_4 in $H_2SO_4-H_2O$, 60% of the H_2SO_4 produced in the decomposition is in the $\nu = 2$ state. For the initially excited H-bonded OH, 98% of the H_2SO_4 resulting from the decomposition is in the $\nu = 2$ state. A comment is due on higher overtone excitation of $H_2SO_4-H_2O$. Previous CC−VSCF calculations[13] suggested that $\nu > 3$ overtone excited states probably do not exist as long-lived species. The VSCF calculations diverge as a consequence of strong IVR, indicating that such states are short-lived resonances.

In summary, first simulations are reported here on the overtone-induced dynamics of H_2SO_4 and $H_2SO_4-H_2O$, by classical trajectory calculations, using potentials from semiempirical electronic structure theory. For H_2SO_4, fast intramolecular proton transfer is predicted. Dissociation into SO_3 and H_2O is also found, with a characteristic time scale of ~9 ps. Over a time window of 400 ps, the dissociation yield is 5%. On the other hand, the calculations show no dissociation into SO_3 and water for $H_2SO_4-H_2O$. In this case, the excitation leads to decomposition of the cluster.

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References

(1) Burkholder, J. B.; Mills, M.; McKeen, S. *Geophys. Res. Lett.* **2000**, *27*, 2493.
(2) Brasseur, G.; Solomon, S. *Aeronomy of the Middle Atmosphere*; Reidel: Dordecht, Holland, 1984.
(3) Burkholder, J. B.; McKeen, S. *Geophys. Res. Lett.* **1997**, *24*, 3201.
(4) Mills, M. J.; Toon, O. B.; Solomon, S. *Geophys. Res. Lett.* **1999**, *26*, 1133.
(5) Hintze, P. E.; Kjaergaard, H. G.; Vaida, V.; Burkholder, J. B. *J. Phys. Chem. A* **2003**, *107*, 1112.
(6) Vaida, V.; Kjaergaard, H. G.; Hintze, P. E.; Donaldson, D. J. *Science* **2003**, *299*, 1566.
(7) Donaldson, D. J.; Tuck, A. F.; Vaida, V. *Chem. Rev.* **2003**, *103*, 4717.
(8) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.
(9) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.
(10) Miller, Y.; Chaban, G. M.; Finlayson-Pitts, B. J.; Gerber, R. B. *J. Phys. Chem. A* **2006**, *110*, 5342.
(11) Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1996**, *105*, 10332.
(12) Chaban, G. M.; Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1999**, *111*, 1823.
(13) Miller, Y.; Chaban, G. M.; Gerber, R. B. *J. Phys. Chem. A* **2005**, *109*, 6565.
(14) Miller, Y.; Chaban, G. M.; Gerber, R. B. *Chem. Phys.* **2005**, *313*, 213.
(15) http://www.msg.ameslab.gov/GAMESS/GAMESS.html.
(16) Pople, J. A.; Binkely, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.
(17) Dunning, T. H. *J. Chem. Phys.* **1971**, *56*, 716.
(18) Stewart, J. J. P.; Davis, L. P.; Burggraf, L. W. *J. Comput. Chem.* **1987**, *8*, 1117.
(19) Havey, D. K.; Feierabend, K. J.; Vaida, V. *J. Mol. Struct.: THEOCHEM* **2004**, *680*, 243.
(20) Mills, M. J.; Toon, O. B.; Vaida, V.; Hintze, P. E.; Kjaergaard, H. G.; Schofield, D. P.; Robinson, T. W. *J. Geophys. Res., [Atmos.]* **2005**, *110* (D8), Art. No. D08201.
(21) Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.
(22) Larson, L. J.; Kuno, M.; Tao, F. M. *J. Chem. Phys.* **2000**, *112*, 8830.
(23) Kolb, C. E.; Jayne, J. T.; Worsnop, D. R.; Molina, M. J.; Meads, R. F.; Viggiano, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 10314.

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