



Theoretical study of ultraviolet induced photodissociation dynamics of sulfuric acid



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ABSTRACT

Photodissociation dynamics of sulfuric acid after excitation to the first and second excited states (S_1 and S_2) were studied by an on-the-fly *ab initio* molecular dynamics simulations based on the Zhu–Nakamura version of the trajectory surface hopping (ZN-TSH). Forces acting on the nuclear motion were computed on-the-fly by CASSCF method with Dunning's augmented cc-pVDZ basis set. It was newly found that the parent molecule dissociated into two reaction-channels (i) $\text{HSO}_4(1^2A'') + \text{H}(^2S)$ by S_1 -excitation, and (ii) $\text{HSO}_4(2^2A'') + \text{H}(^2S)$ by S_2 -excitation. The direct dissociation dynamics yield products different from the $\text{SO}_2 + 2\text{OH}$ fragments often presented in the literature. Both channels result in the same product and differs only in the electronic state of the HSO_4 fragment. The trajectories running on S_2 do not hop with S_0 and a nonadiabatic transition happens at the S_2 – S_1 conical intersection located at a longer OH bond-length than the S_1 – S_0 intersection producing an electronic excited state ($2^2A''$) of HSO_4 product.

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1. Introduction

The sulfur atom can produce a large variability of compounds with physical properties that are key to understand the optical and formation properties of clouds and haze of planetary atmospheres. In today's planet Earth, natural and anthropogenic emissions of sulfur compounds in many oxidation states into the atmosphere are oxidized to sulfuric acid (H_2SO_4) and hydrolyzed to form aerosols. H_2SO_4 , therefore, exists mostly within water clusters which are the first step in the formation of cloud condensation nuclei (CCN) [1]. H_2SO_4 also exists in significant amounts in the forms of vapor and aerosols in the atmosphere of Venus [2] and it has been shown that this compound was present at the Earth's Archean atmosphere [3], the early atmosphere of Mars [4] and recently sulfur compounds are speculated to exist in exoplanetary atmospheres [5]. Despite of the importance of the H_2SO_4 molecule, studies about absolute absorption cross-sections are limited. Reports by Burkholder et al. [6] and Hintze et al. [7] have estimated upper limits of 10^{-21} , 10^{-19} and 10^{-18} cm^2 molecules⁻¹ for 330–195 nm, 195–170 nm and 170–140 nm spectral region. All these estimations were made by simultaneous measurements of H_2SO_4 , SO_3 and H_2O gas mixtures casting doubt on the reliability of the

reported absorption cross-sections. Theoretical calculations have reported a lowest lying electronic excitation [8]. However, there are no reported mechanisms that explain the exit channels of UV induced photodissociation. The mechanism accepted today for the atmospheric photodissociation of H_2SO_4 involves an overtone OH stretching activated by absorptions in the infrared and near-infrared [7,9]. Studies on the mechanism of light induced atmospheric dissociation of H_2SO_4 [9,10] assumes an oxidizing type of atmosphere where electronic transitions produced by UV light is greatly depleted by oxygen and ozone. A Lyman- α absorption band has also been reported [11] and although this is a very narrow band the absorption cross-sections are large and therefore it constitutes an important photodissociation channel for atmospheric systems. A third photodissociation mechanism involving a double excitation [12] has been reported, yet this report needs to be confirmed by further calculations and measurements.

The isotopic imprint of sulfur bearing compounds is an important tool to understand the sulfur cycle of planetary atmospheres. Sulfur isotopologues have been used for many years to study the rise of oxygen in Earth during the Archean period [13,14] and to understand the size, strength and emission features of stratospheric volcanic eruptions [15,16]. Sulfur isotopes and non-mass dependent (NMD) fractionation effects have been applied to the study of meteorites [17] and in the study which links the deep sulfur cycle and in the Martian atmosphere [18]. Recent experimental

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and theoretical studies [19,20] have presented the strong evidence for the involvement of intersystem crossings as a potential origin of NMD fractionation for photoexcitation (SO_2^+) species and their importance for explaining the isotopic imprint of the geological record. Furthermore, a recent study by Danielache et al. [21] has reported on the importance of nonadiabatic crossings for the NMD effect during the photodissociation of SO.

In the present work, on-the-fly classical molecular dynamics are performed using the Zhu–Nakamura approach to the trajectory surface hopping (ZN-TSH) method [22]. This allows treating electronically nonadiabatic transitions; the Zhu–Nakamura theory [22] gives us the exact formula for curve crossing problems, which was incorporated into the TSH method. This allows us to properly take into account the contribution of the so-called classically forbidden transitions and thus significantly improve the quality of our calculations. In comparison with the well-known “fewest switches” TSH method [23], the ZN-TSH method requires less number of trajectory hops because it avoids the “overcoherence problem” [24] [25] and provides accurate results for trajectories with low energies by treating non-vertical hops. In a recent study conducted for the photodissociation of SO [21] it was shown that nonadiabatic transitions produce a non-linear isotopic effect to the ultraviolet absorption spectra at large vibrational numbers. The accurate treatment of nonadiabatic transitions in photoexcitation dynamics is therefore vital to accurately describe isotopic effects and a necessary condition to the application of these studies to atmospheric photochemistry.

This paper is structured as follows. In Section 2, the methodology used is presented. In Section 3, the results of on-the-fly *ab initio* molecular dynamics after the excitations to the first (S_1) and the second excited (S_2) states of H_2SO_4 , and topography of effective PESs are presented and discussed. A brief summary is presented in Section 4.

2. Methodology

2.1. *Ab initio* electronic state calculations

The complete active space self-consistent field [26–28] (CASSCF) approach was used for *ab initio* quantum chemical calculations with diffuse function augmented, correlation consistent, polarized valence, double- ζ [29–31] (AVDZ also known as aug-cc-pVDZ) basis function for sulfuric acid (H_2SO_4). In order to define the active space of CASSCF calculation, the large-scale CAS(16e, 12o)SCF calculation was first performed with the electron-configurations spanned by occupation of 16 electrons in 12 orbitals, $[(18a)(19a)(20a)(21a)(22a)(23a)(24a)(25a)(26a)(27a)(28a)(29a)]^{16}$, where the twenty second molecular orbital (MO) is denoted by (22a) in C_1 symmetry and the superscript number is the occupation number of the MO. The results at the several molecular structures exhibited the major electronic configurations involving no excitations from the inner orbitals than the twenty second orbital (22a) for S_1 , S_2 , and S_3 electronic states. Additionally, the CAS(10e,11o) SCF calculation defined with $[(21a)(22a)(23a)(24a)(25a)(26a)(27a)(28a)(29a)(30a)(31a)]^{10}$ was also carried out. But these four electronic states (S_0 , S_1 , S_2 , and S_3) were not described in terms of any dominant component which features electron-excitations to the outer orbitals than the twenty ninth orbital (29a). The CAS(8e,8o) was therefore employed in CASSCF calculation; the configuration state functions (CSFs) in the CASSCF calculation were generated with

$$[(22a)(23a)(24a)(25a)(26a)(27a)(28a)(29a)]^8.$$

Naturally there might be some possibility of excitations to these orbitals outside of CAS(8e, 8o) in some molecular geometry,

nevertheless our time-evolved trajectories did not indicate any discontinuity for potential energies of all electronic states as shown in Figs. 3 and 7. Thus, the CSFs spanned by CAS(8e, 8o) would be reasonable for the lowest-lying four electronic states. These four roots were also included in our state-averaged CASSCF calculation. The main configuration of the ground state (S_0) of H_2SO_4 is written as (inner occupied orbitals) 42 (22a) 2 (23a) 2 (24a) 2 (25a) 2 (26a) 0 (27a) 0 (28a) 0 (29a) 0 . The natural orbitals were obtained by the CASSCF calculation. The character of each MO is mentioned in the latter section.

To make sure of the accuracy of our CASSCF calculation, the vertical excitation energies obtained by multireference configuration interaction with Davidson energy-correction (MRCI+Q) [32,33] method are also listed in Table 2. The number of CSFs for CAS(8e, 8o)SCF is 1764. On the other hand, the multireference configuration interaction (MRCI) wave functions were comprised of 15,914,052 uncontacted CSFs.

2.2. *Ab initio* molecular dynamics

On-the-fly classical molecular dynamics (MD) combined with *ab initio* quantum chemical computations were carried out in which nonadiabatic transitions are taken into account. The state-averaged CAS(8e, 8o)SCF/AVDZ approach was also used for electronic structure calculations.

The velocity Verlet algorithm [34] was employed to evolve classical trajectories for the nuclear motion. The initial molecular coordinates and momenta were generated using random numbers subject to a Wigner distribution; [35] the distribution reflects the vibrational wave function at the Zero Point Energy (ZPE), which was computed with the use of the analytical Hessian matrix obtained by the CASSCF calculation for the ground state. Once the molecule was vertically excited to the S_1 or S_2 state, the trajectory starts on each of these states with the initial coordinates and momenta. Each trajectory separately keeps conservation law of energy. The excitation-energy would however change with depending on the initial molecular geometry determined by the random numbers imposed on Wigner distribution; this classical approximation follows the Franck–Condon principle. The time step for the time-evolution of the trajectories is 0.025 fs. If the bond length for a running trajectory becomes twice larger than the bond length of the optimized geometry, it was considered as the bond was dissociated and the trajectory calculation was stopped.

The trajectory surface hopping procedure is based on the Zhu–Nakamura theory, which provides a complete set of solutions for a potential energy curve-crossing problem, covering the entire energy range. The multidimensional ZN-TSH scheme has been previously successfully applied to a number of systems [36–39].

The procedure is summarized as follows. The nonadiabatic coupling vector is calculated, when the energy difference between the two adjacent adiabatic potential energy surfaces is a local minimum. The one-dimensional adiabatic potential curves are calculated in the direction of the coupling vector and the transition probability for this one-dimensional curve crossing is calculated using analytical formulas of the Zhu–Nakamura theory. The decision whether the transition to the adjoining potential energy surface (PES) occurs or the trajectory stays on the same PES is made using an *ant-eater* method [40], i.e. using a random number. The parameters of the trajectory after hops are calculated so that the energy of the trajectory is conserved. When the kinetic energy is not enough for the vertical hop, the transition becomes non-vertical [41]. This treatment was adopted to ensure the energy conservation of the system. A non-vertical hop corresponds to a classically forbidden transition due to tunneling. The classically allowed transitions at the energies near the crossing point can also be accurately treated in the present scheme. The computational

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