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## Vacuum ultraviolet photochemistry of sulfuric acid vapor: a combined experimental and theoretical study

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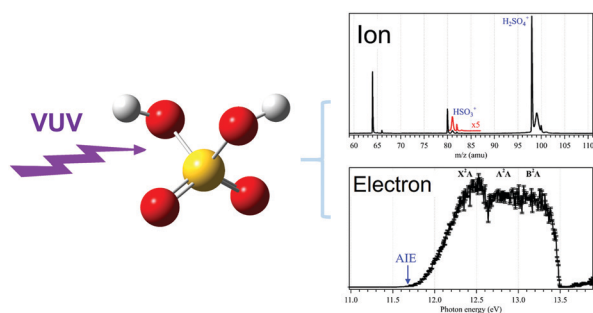
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### Vacuum ultraviolet photochemistry of sulfuric acid vapor: a combined experimental and theoretical study

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Bo Long, Weijun Zhang and Laurent Nahon

VUV photoionization of gas-phase  $\text{H}_2\text{SO}_4$  has been studied by using  $i^2$ PEPICO. Three electronic states of  $\text{H}_2\text{SO}_4^+$  have been prepared and their ionization energies are determined, as well as the adiabatic appearance energy of fragments.

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# Vacuum ultraviolet photochemistry of sulfuric acid vapor: a combined experimental and theoretical study†

Cuihong Zhang,<sup>‡,abc</sup> Xiaoxiao Lin,<sup>id</sup> <sup>‡,a</sup> Xiaofeng Tang,<sup>id</sup> <sup>\*a</sup> Christa Fittschen,<sup>c</sup> Sebastian Hartweg,<sup>d</sup> Gustavo A. Garcia,<sup>id</sup> <sup>\*d</sup> Bo Long,<sup>id</sup> <sup>e</sup> Weijun Zhang<sup>a</sup> and Laurent Nahon<sup>id</sup> <sup>d</sup>

We present a vacuum ultraviolet (VUV) photoionization study of the gas-phase sulfuric acid ( $\text{H}_2\text{SO}_4$ ) molecule in the 11–14 eV energy range by using the method of synchrotron radiation-based double imaging photoelectron photoion coincidence ( $i^2\text{PEPICO}$ ) spectroscopy complemented with accurate theoretical calculations. The slow photoelectron spectrum (SPES) of  $\text{H}_2\text{SO}_4$  has been acquired and the three electronic states of  $\text{H}_2\text{SO}_4^+$ ,  $X^2A$ ,  $A^2A$  and  $B^2A$  have been populated and assigned. The adiabatic ionization energy of the  $\text{H}_2\text{SO}_4$  molecule towards the  $X^2A$  cationic ground state is measured at  $11.684 \pm 0.006$  eV, in accordance with high-level calculated findings. With increasing photon energies, the  $\text{H}_2\text{SO}_4^+$  cation dissociates into  $\text{HSO}_3^+$  and OH fragments and their adiabatic appearance energy is measured at  $13.498 \pm 0.007$  eV. Then, the enthalpies of formation for the species involved in the photoionization and dissociative photoionization have been determined through a thermochemical cycle.

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## 1. Introduction

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) as a key precursor plays an essential role in the formation of new particles, secondary aerosols and clouds in the earth's atmosphere, and has received much attention from both theoretical and experimental groups in recent years.<sup>1–3</sup> In the atmosphere,  $\text{H}_2\text{SO}_4$  is mainly formed from the reaction of water vapor with sulfuric trioxide ( $\text{SO}_3$ ), which is generated from the hydroxyl radical (OH) reaction with sulfuric dioxide ( $\text{SO}_2$ ) emitted, for instance, from fossil fuel and biomass burning.<sup>2,4,5</sup> Due to its extremely low vapor pressure, the nascent  $\text{H}_2\text{SO}_4$  molecule can easily get supersaturated and then enhance the homogenous nucleation rates of water and other compounds significantly. Presently, it is well-known that

gas-phase  $\text{H}_2\text{SO}_4$  molecules tend to form hydrates at the beginning of nucleation, that is, to produce small clusters consisting of a few water molecules associated with one or several  $\text{H}_2\text{SO}_4$  molecules.<sup>6–8</sup> Thus, the structure and spectroscopy of  $\text{H}_2\text{SO}_4$  and the sulfuric acid–water clusters are of considerable importance for understanding their chemistry in the atmosphere.

There have been several theoretical studies on  $\text{H}_2\text{SO}_4$  and sulfuric acid–water clusters, in which their optimized structures and spectra have been calculated using various levels of theory.<sup>9–12</sup> For example, the theoretical results show that  $\text{H}_2\text{SO}_4$  has two conformers depending on the relative position of the two OH groups: the most stable one is the *trans* form having a  $C_2$  symmetry, while the *cis* form has a  $C_1$  symmetry and an energy of +4.6 kJ mol<sup>−1</sup> with respect to the *trans* conformer.<sup>9</sup> The energy barrier of isomerization was calculated to be 12.6 kJ mol<sup>−1</sup> relative to the *trans* conformer.<sup>9</sup> Theoretical studies on the uptake of water molecules, leading to the hydration of  $\text{H}_2\text{SO}_4$ , have yielded the structure of these complexes, and it has been predicted that progressive hydration increases the probability of proton transfer from the acid to water, with the resulting ion-pair structures corresponding to the global energy minima.<sup>9,11</sup>

Experimentally, spectroscopic techniques such as microwave rotational spectroscopy, infrared (IR) spectroscopy and Raman spectroscopy have been employed to probe  $\text{H}_2\text{SO}_4$  and hydrated complexes.<sup>13–17</sup> The structures, vibrational spectra

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1 and frequencies of  $\text{H}_2\text{SO}_4$  and the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  cluster were  
obtained. Mass spectrometry, as a convenient analytical  
method, has also been applied in the past. For instance, the  
mass spectrum of  $\text{H}_2\text{SO}_4$  vapor was acquired by Snow and  
Thomas using electron impact ionization mass spectrometry  
(EIMS) and its ionization energy was roughly measured at 12.4  
eV, together with the appearance energies of its major fragment  
ions,  $\text{H}_2\text{O}^+$ ,  $\text{SO}_3^+$  and  $\text{HSO}_3^+$ .<sup>18</sup> The positive and negative ion  
distributions of the sulfuric acid–water clusters as well as their  
equilibrium constants were measured by Froyd and Lovejoy  
using EIMS.<sup>19,20</sup> Recently, the formation of mixed sulfuric acid–  
water clusters with different concentrations of water and  $\text{H}_2\text{SO}_4$   
has been investigated by electron attachment and negative ion  
mass spectrometry.<sup>21</sup> However, the abovementioned mass spec-  
trometry methods lack the energy resolution to distinguish  
contributions from all possible isomers. Moreover, much of  
the thermochemical data of  $\text{H}_2\text{SO}_4$  and the sulfuric acid–water  
clusters are not precisely known.<sup>22</sup>

The purpose of this study is to investigate the vacuum  
ultraviolet (VUV) photodynamics of  $\text{H}_2\text{SO}_4$ . Photoionization  
and dissociative photoionization of  $\text{H}_2\text{SO}_4$  in the energy range  
of 11–14 eV are analyzed by using the method of double  
imaging photoelectron photoion coincidence ( $i^2$ PEPICO)  
spectroscopy complemented with high-level theoretical calcula-  
tions. Three cationic electronic states of  $\text{H}_2\text{SO}_4^+$  have been  
prepared and assigned in the slow photoelectron spectrum  
(SPES). In particular, the adiabatic ionization energies (AIEs)  
of the *trans* and *cis* conformers of  $\text{H}_2\text{SO}_4$ , towards the  $X^2\text{A}$   
cationic ground state, have been measured precisely for the  
first time, as well as the adiabatic appearance energy ( $\text{AE}_{0\text{K}}$ ) of  
the  $\text{HSO}_3^+$  fragment ion from the dissociation of  $\text{H}_2\text{SO}_4^+$ . The  
enthalpies of formation for the species involved in the photo-  
ionization and dissociative photoionization are also deter-  
mined through a thermochemical cycle.

## 2. Materials and methods

The experiments were carried out on the beamline DESIRS  
equipped with an  $i^2$ PEPICO spectrometer, DELICIOUS III, at  
the French national synchrotron radiation facility SOLEIL. The  
detailed configurations of the synchrotron beamline and the  
spectrometer<sup>23–25</sup> have already been introduced in our previous  
publications and only a short description is presented here.  
Briefly, photons emitted from a variable polarization undulator  
were dispersed by a 6.65 m normal incidence monochromator  
equipped with a 200 L  $\text{mm}^{-1}$  grating, which was set to provide  
an energy resolution of  $\sim 3$  meV. A gas filter located upstream  
of the beamline and filled with Ar gas was employed to  
suppress high harmonics emitted from the undulator. The  
absolute photon energy of the beamline was calibrated online  
with a precision of  $\pm 2.5$  meV using the ionization energy  
of water.

The  $i^2$ PEPICO spectrometer is composed of a modified  
Wiley–McLaren ion time-of-flight (TOF) 3D-momentum ima-  
ging device and an electron velocity map imaging (VMI)

analyzer, equipped with two position-sensitive detectors (PSDs)  
for the analysis of ions and electrons, respectively.<sup>24</sup> A mixture  
of helium carrier gas (1.5 bars), water vapor (from the vaporiza-  
tion of liquid water at room temperature) and  $\text{H}_2\text{SO}_4$  vapor,  
generated from the vaporization of liquid  $\text{H}_2\text{SO}_4$  (95% purity) in  
an in-vacuum oven heated at 180 °C, was expanded through a  
70  $\mu\text{m}$  diameter nozzle to form a continuous molecular beam  
which was skimmed twice before reaching the center of the  
spectrometer.<sup>25,26</sup> The multiplex coincidence scheme between  
the ion and electron yields mass-selected photoelectron spectra  
(PES) as a function of photon energy, which are then reduced to  
SPES, as previously detailed.<sup>27,28</sup> Meanwhile, the coincidence  
scheme can provide spectral fingerprints to identify and sepa-  
rate isomers, and accurately measure thermochemical data  
such as fragment appearance energies and bond  
energies.<sup>29–31</sup>

We have performed theoretical calculations to assign the  
experimental spectra. The AIE and the vertical ionization  
energy (VIE) of the  $X^2\text{A}$  ground electronic state of  $\text{H}_2\text{SO}_4^+$  were  
calculated at the CCSD(T)-F12A/aug-cc-pVTZ level of theory as  
implemented in MOLPRO software.<sup>32</sup> The VIEs of the first ( $A^2\text{A}$ )  
and the second ( $B^2\text{A}$ ) excited electronic states of  $\text{H}_2\text{SO}_4^+$  were  
computed using time-dependent density functional theory (TD-  
DFT), TD-M062X/6-311++G(d,p).<sup>33</sup> The Franck–Condon factors  
in the photoionization towards the  $X^2\text{A}$  cationic ground state,  
as well as for the required geometry optimizations and the  
vibrational frequency computations with a harmonic approxi-  
mation, were calculated at the M062X/6-311++G(d,p) level of  
theory with the Gaussian package using the time-independent  
adiabatic Hessian Franck–Condon model.<sup>33</sup>

## 3. Results and discussion

### 3.1 TOF mass spectra

Synchrotron radiation photoionization TOF mass spectra of the  
gas mixture have been recorded in the 11–14 eV photon energy  
range and are presented as a matrix in Fig. 1, as well as their  
integrated mass spectra. Several mass peaks can be observed  
and have been assigned within a mass range of  $m/z = 60$ –110.  
For example, the most intense mass peak at  $m/z = 98$  is assigned  
to  $\text{H}_2\text{SO}_4$ , the  $m/z = 80$  mass peak is assigned to  $\text{SO}_3$  and the  
 $m/z = 64$  peak is attributed to  $\text{SO}_2$ , based on their narrow widths in  
the mass spectra.<sup>25</sup> Indeed, the width of the TOF peak is  
proportional to the square root of the ion translational energy  
along the detection axis, so that narrow peaks correspond to  
parent ions formed by direct ionization of the neutrals in the  
molecular beam, while broad peaks originate from fragment  
ions formed by dissociative ionization.<sup>25,30</sup> Besides these three  
intense mass peaks, their isotopic peaks can be observed in the  
mass spectra too, *i.e.*, the  $^{33}\text{SO}_2$  isotopic species at  $m/z = 65$ ,  
 $^{34}\text{SO}_2$  at  $m/z = 66$ ,  $^{34}\text{SO}_3$  at  $m/z = 82$  and  $\text{H}_2^{34}\text{SO}_4$  at  $m/z = 100$   
with relative intensities corresponding to their individual nat-  
ural abundances, as listed in Table S1 (ESI<sup>†</sup>).<sup>34</sup>

$\text{SO}_3$  is formed from the equilibrium reaction of  $\text{H}_2\text{SO}_4(\text{g}) \leftrightarrow$   
 $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g})$  inside the oven, and  $\text{SO}_2$  is produced from the



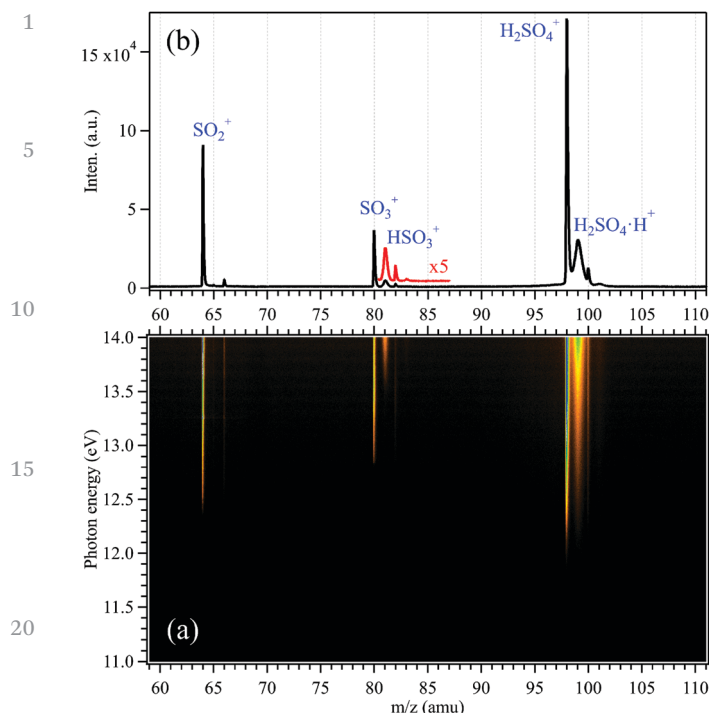


Fig. 1 (a) Synchrotron photoionization mass spectra matrix in the 11–14 eV energy range and (b) their integrated mass spectrum, together with 5 times magnified data in red.

reduction reaction of  $\text{H}_2\text{SO}_4$  with the metallic parts of the oven. The appearance energies of  $\text{SO}_3$  and  $\text{SO}_2$  can be obtained from the mass spectra matrix of Fig. 1(a) and both of them agree with their individual ionization energies,<sup>35</sup> confirming their assignments as neutral nascent species formed in the oven. Note that  $\text{SO}_3^+$  and  $\text{SO}_2^+$  were also observed in a previous study based on

EIMS, but both were assigned as fragment ions from the dissociation of  $\text{H}_2\text{SO}_4^+$  by Snow and Thomas.<sup>18</sup>

Normally, in Fig. 1, the mass peak at  $m/z = 81$  should be assigned as the  $^{33}\text{SO}_3$  isotopic species in the mass spectra. But, its relative intensity ( $\sim 28\%$  of  $^{32}\text{SO}_3$ ) measured in the mass spectrum is much higher than the natural abundance of  $^{33}\text{SO}_3$  ( $\sim 0.91\%$ ),<sup>34</sup> and its peak width is much wider than that of the  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  mass peak. In addition, as shown in the mass spectra matrix, the appearance energy of the  $m/z = 81$  species is not the same as and much higher than that of  $\text{SO}_3$  ( $m/z = 80$ ). Therefore, the  $m/z = 81$  peak in the mass spectra is not contributed from the isotope  $^{33}\text{SO}_3$  and corresponds to the  $\text{HSO}_3^+$  fragment ion from the dissociative ionization of  $\text{H}_2\text{SO}_4$ , as inferred from its broad shape due to the kinetic energy release in the fragmentation. Note that the contribution from the isotope  $^{33}\text{SO}_3$  ( $\sim 0.91\%$ )<sup>34</sup> to the  $m/z = 81$  channel is considered negligible and has not been subtracted here. Similarly, due to its large width, the more intense peak at  $m/z = 99$  is attributed to the  $\text{H}_2\text{SO}_4 \cdot \text{H}^+$  fragment ion produced from the dissociative photoionization of the  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  complexes formed in the molecular beam, with again a negligible contribution from the  $\text{H}_2^{33}\text{SO}_4^+$  isotopic species. Note that a complete study of water complexes and clusters of sulfuric acid will be reported in a forthcoming work.

### 3.2 Mass-selected slow photoelectron spectra

The mass-selected photoelectron matrices corresponding to the  $\text{H}_2\text{SO}_4^+$  parent ion ( $m/z = 98$ ) and the  $\text{HSO}_3^+$  fragment ion ( $m/z = 81$ ) showing the signal as a function of electron kinetic energy (Ele KE) and photon energy are depicted in Fig. 2(a and c), respectively. Here, diagonal lines are the product of energy conservation and thus correspond to constant cationic states.

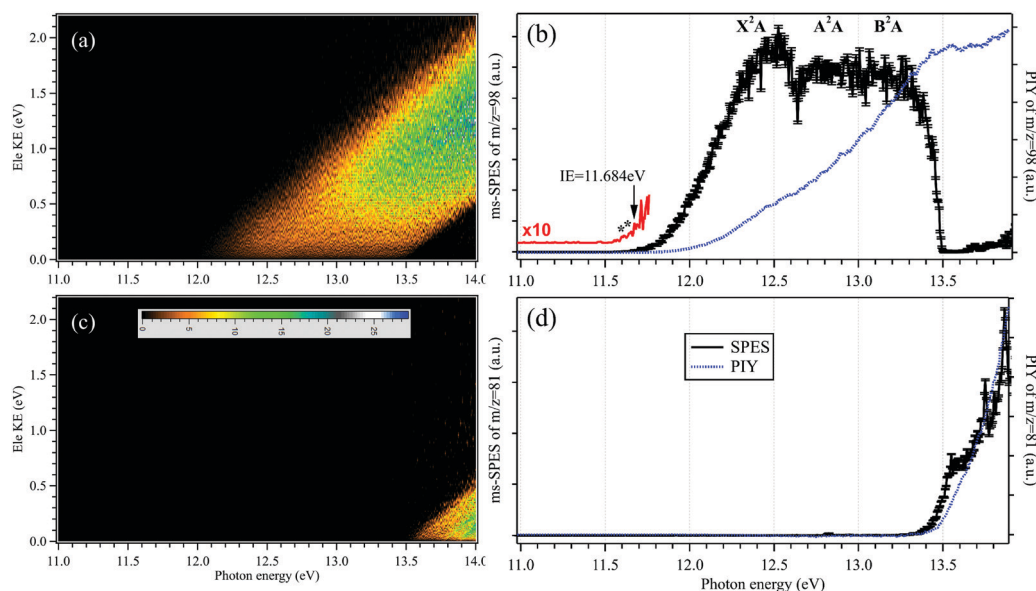


Fig. 2 Mass-selected photoelectron matrices, slow photoelectron spectra (SPES, black solid lines) and photoionization yields (PIYs, blue dotted lines) corresponding to (a and b) the  $\text{H}_2\text{SO}_4^+$  parent ion and (c and d) the  $\text{HSO}_3^+$  fragment ion. The 10 times magnified SPES in red shows the onset of  $\text{H}_2\text{SO}_4^+$ .

The mass-selected SPES corresponding to the  $\text{H}_2\text{SO}_4^+$  parent ion and the  $\text{HSO}_3^+$  fragment ion are obtained from the photoelectron matrices and presented in Fig. 2(b and d), respectively, as well as their photoionization yields (PIYs).<sup>27,28</sup> In Fig. 2(b), the SPES of  $\text{H}_2\text{SO}_4$  is rather unstructured although an onset can be observed at  $h\nu = 11.684 \pm 0.006$  eV in the SPES. The uncertainty of the photon energy calibration, the influence of the scanning step size (5 meV) and the signal-to-noise ratio of the SPES have been taken into account and included in the given error bars.<sup>36</sup>

As mentioned in the introduction, the gas-phase  $\text{H}_2\text{SO}_4$  molecule has two conformers, *trans* and *cis*, and their optimized structures as the neutrals as well as their cations in the  $X^2A$  cationic ground state have been calculated and are presented in Fig. 3, agreeing well with previous results.<sup>9,37</sup> The *trans* conformer has a  $C_2$  symmetry structure and is the global minimum with an energy of  $\sim 4.6$  kJ mol<sup>-1</sup> below the *cis* conformer with a  $C_1$  symmetry.<sup>9</sup> The temperature of the molecules in the molecular beam is estimated at 150 K (see Section 3.3 below), which would mean that the *trans* conformer is dominant, with only  $\sim 2\%$  for the *cis* conformer. However, the flash cooling in the adiabatic expansion might lead to a different conformer population than the one expected assuming thermal equilibrium.

Upon photoionization, an electron is removed from the outer valence orbital of the neutral  $\text{H}_2\text{SO}_4$  molecule leading to the formation of the  $\text{H}_2\text{SO}_4^+$  cation. The structure of the *trans* conformer relaxes in the cation and its symmetry changes from  $C_2$  to  $C_1$  during the photoionization, as shown in Fig. 3, while the *cis* conformer geometry undergoes smaller changes. The AIE of the  $X^2A$  ground electronic state of the *trans*- $\text{H}_2\text{SO}_4^+$  has been calculated at 11.688 eV using the CCSD(T)-F12A/aug-cc-pVTZ method with zero-point corrections (ZPEs).<sup>32</sup> Note that no scaling factor has been used for the determination of harmonic frequencies and ZPEs. The calculated values are consistent with the onset of the experimental curve and their differences are within 10 meV. Although some structures are seen in the region where the AIEs are predicted in our experimental spectra, the unfavorable Franck-Condon factors and consequent lack of

structure do not allow a definite assignment of the experimental AIE. Nevertheless, in view of the good agreement between the calculated AIE and the feature at 11.684 eV, we tentatively offer this value as the AIE of the *trans* conformer. The very weak features at 11.643 and 11.609 eV (marked with two asterisks in the 10 times magnified data of Fig. 2b) might be ascribed to the *cis* conformer, with the former being assigned to the AIE of the  $X^2A$  ground state, for which the value is calculated at 11.635 eV, and the latter originating from a hot band in the photoionization, *i.e.*, from the  $\nu_2$  vibrational mode of the *cis* conformer whose frequency is calculated at 289.32 cm<sup>-1</sup> using the M062X/6-311++G(d,p) method. However, we note that purely thermal arguments would not allow for the presence of the *cis* conformer, nor a hot band, at the presently estimated temperature of 150 K. In a previous study based on EIMS, restricted by the electron energy resolution, the ionization energy of  $\text{H}_2\text{SO}_4$  was measured at  $12.4 \pm 0.05$  eV (see Table 1), which would actually correspond to the VIE measured in this work.<sup>18</sup>

The Franck-Condon factors for the photoionization of  $\text{H}_2\text{SO}_4$  towards the cationic  $X^2A$  ground electronic state of  $\text{H}_2\text{SO}_4^+$  have been calculated at the M062X/6-311++G(d,p) level of theory, using the time-independent adiabatic Hessian Franck-Condon model.<sup>33</sup> Note that the influences of inconsequential internal rotations are not included in this model and thus, the differences of the two conformers are not considered in the Franck-Condon factors. The simulated PES is subsequently generated by convolving the stick spectrum with a Gaussian function (FWHM = 100 cm<sup>-1</sup>, full width at half maximum) and is shown in Fig. S1 (ESI<sup>†</sup>), with an energy offset of 50 meV to fit the experimental result. Although the simulated PES fits the experimental SPES very well at the beginning of the  $X^2A$  state, an apparent difference can be observed between them at the high energy part, indicating that other factors need to be considered, such as the appearance of cationic excited electronic states. Indeed, the VIEs of the  $A^2A$  excited electronic state and the  $B^2A$  electronic state of  $\text{H}_2\text{SO}_4^+$  have been calculated at 12.84 and 13.10 eV, respectively, at the TD-M062X/6-

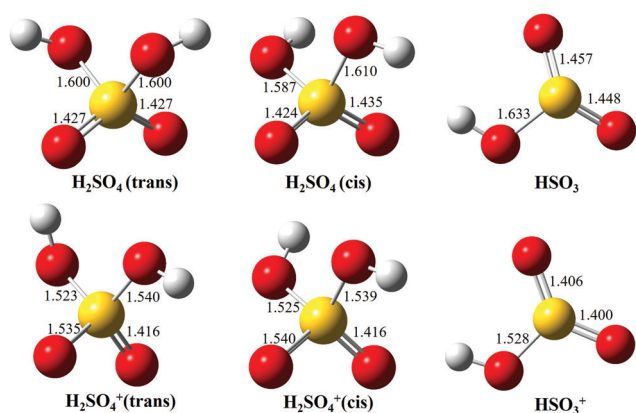


Fig. 3 Optimized structures of  $\text{H}_2\text{SO}_4$  (*trans* and *cis* conformers) and  $\text{HSO}_3$ , as well as their individual cations, in the ground electronic states.

Table 1 Ionization energies of  $\text{H}_2\text{SO}_4$  and the appearance energy of the  $\text{HSO}_3^+$  fragment ion (unit: eV).

State	IE( $\text{H}_2\text{SO}_4$ )	AE( $\text{HSO}_3^+$ )	Method	Ref.
Expt.	$12.4 \pm 0.05$		EIMS	18
		$13.9 \pm 0.1$	EIMS	18
		$13.498 \pm 0.007$	SPES	<sup>e</sup>
$X^2A$ ( <i>trans</i> )	$11.684 \pm 0.006^a$		SPES	<sup>e</sup>
$X^2A$ ( <i>cis</i> )	$11.643 \pm 0.006^a$		SPES	<sup>e</sup>
$X^2A$	$12.53 \pm 0.05^b$		SPES	<sup>e</sup>
$A^2A$	$12.80 \pm 0.05^b$		SPES	<sup>e</sup>
$B^2A$	$13.20 \pm 0.05^b$		SPES	<sup>e</sup>
Calc.	$X^2A$ ( <i>trans</i> )	$11.688^a$	CCSD(T) <sup>c</sup>	<sup>e</sup>
	$X^2A$ ( <i>cis</i> )	$11.635^a$	CCSD(T) <sup>c</sup>	<sup>e</sup>
	$X^2A$	$12.54^b$	CCSD(T) <sup>c</sup>	<sup>e</sup>
	$A^2A$	$12.84^b$	TD-M062X <sup>d</sup>	<sup>e</sup>
	$B^2A$	$13.10^b$	TD-M062X <sup>d</sup>	<sup>e</sup>

<sup>a</sup> AIE. <sup>b</sup> VIE. <sup>c</sup> CCSD(T)-F12A/aug-cc-pVTZ. <sup>d</sup> TD-M062X/6-311++G(d,p). <sup>e</sup> This work.

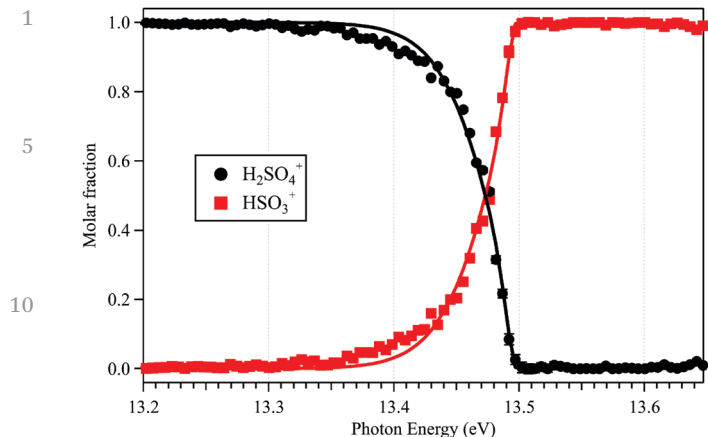


Fig. 4 Breakdown diagram of the  $\text{H}_2\text{SO}_4^+$  parent ion ( $m/z = 98$ ) and  $\text{HSO}_3^+$  fragment ion ( $m/z = 81$ ). Solid circles represent the experimental data, while lines correspond to the statistical model (see text for details).

311++G(d,p) level of theory, and have been assigned in the experimental SPES too. In the SPES of Fig. 2(b), the VIEs of the  $\text{A}^2\text{A}$  and  $\text{B}^2\text{A}$  cationic states are estimated at  $12.80 \pm 0.05$  and  $13.20 \pm 0.05$  eV, respectively, as listed in Table 1, agreeing well with the calculated results.

### 3.3 The thermochemical cycle

The sharp high energy cut-off of the electron signal in the parent SPES of Fig. 2(b) is due to the dissociative photoionization of  $\text{H}_2\text{SO}_4$ , in accordance with the sharp appearance of the electron signal in the SPES of the  $\text{HSO}_3^+$  fragment ion in Fig. 2(d). The  $\text{HSO}_3^+$  fragment ion was also observed in the electron impact ionization mass spectra of Snow and Thomas, and its appearance energy was measured at  $13.9 \pm 0.1$  eV.<sup>18</sup> Fig. 4 presents the breakdown diagram of the sulfuric acid cation, showing the molar fractions of the unimolecular reaction  $\text{H}_2\text{SO}_4^+ \rightarrow \text{HSO}_3^+ + \text{OH}$  as a function of the photon energy, as extracted from the parent and fragment SPES in Fig. 2. The curves in the breakdown diagram can be modelled assuming that the initial internal thermal energy stored in the parent neutral molecule can be directed towards fragmentation.<sup>38</sup> Assuming that dissociation is fast within the acceleration time-scales of the experimental setup (a few microseconds), the only parameters affecting the model are the temperature and the 0 K appearance energy of the  $\text{HSO}_3^+$  fragment. These are optimized within a least squares fit to the data which yields values of  $150 \pm 20$  K for the temperature, and  $\text{AE}_{0\text{K}}(\text{HSO}_3^+) = 13.498 \pm 0.007$  eV, very far from the data reported by Snow and Thomas. Note that we cannot resolve contributions from *cis* and *trans* conformers in the breakdown diagram, so that we assume that the same  $\text{AE}_{0\text{K}}$  applies to both, *i.e.*, that the eventual barriers towards dissociation are equal.

Based on the AIE of the  $\text{X}^2\text{A}$  ground state of  $\text{H}_2\text{SO}_4^+$  and the  $\text{AE}_{0\text{K}}$  of the  $\text{HSO}_3^+$  fragment ion, the bond energy of  $\text{H}_2\text{SO}_4^+$  associated with the  $\text{HSO}_3^+$  and OH fragments is calculated at  $1.814 \pm 0.008$  eV for the *trans* conformer. Through a thermochemical cycle, as shown in Fig. 5, the enthalpies of formation

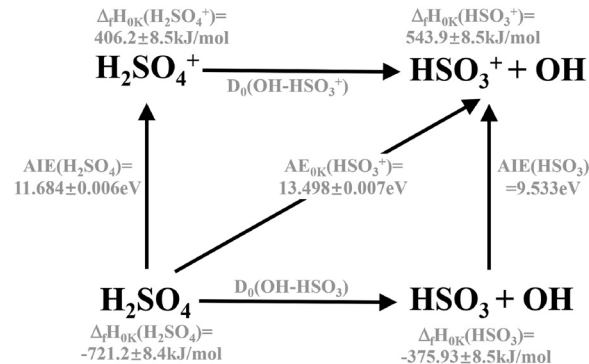


Fig. 5 The thermochemical cycle in photoionization and dissociative photoionization of  $\text{H}_2\text{SO}_4$ .

for the cations of  $\text{H}_2\text{SO}_4^+$  and  $\text{HSO}_3^+$  are obtained at  $\Delta_f H_{0\text{K}}(\text{H}_2\text{SO}_4^+) = 406.2 \pm 8.5$  kJ mol<sup>-1</sup> and  $\Delta_f H_{0\text{K}}(\text{HSO}_3^+) = 543.9 \pm 8.5$  kJ mol<sup>-1</sup>, with the aid of the available thermochemical data in the literature, *i.e.*,  $\Delta_f H_{0\text{K}}(\text{H}_2\text{SO}_4) = -721.2 \pm 8.4$  kJ mol<sup>-1</sup><sup>39</sup> and  $\Delta_f H_{0\text{K}}(\text{OH}) = 37.252 \pm 0.026$  kJ mol<sup>-1</sup>,<sup>40</sup> and assuming barrierless fragmentations. In addition, the AIE of the  $\text{HSO}_3$  radical is calculated at 9.533 eV with the CCSD(T)-F12A/aug-cc-pVTZ high-level of theory,<sup>32</sup> so that we report the enthalpy of formation for  $\text{HSO}_3$  at  $\Delta_f H_{0\text{K}}(\text{HSO}_3) = -375.9 \pm 8.5$  kJ mol<sup>-1</sup>.

## 4. Conclusions

In summary, VUV photoionization and dissociative photoionization of  $\text{H}_2\text{SO}_4$  in the 11–14 eV energy range have been investigated by using the *i*<sup>2</sup>PEPICO technique complemented with accurate theoretical calculations on the structures and ionization energies. The  $\text{H}_2\text{SO}_4$  molecule in the oven is seen to decompose to form  $\text{SO}_2$  and  $\text{SO}_3$  and these can be discarded by the coincidence scheme and are distinguished from the dissociative ionization product, the  $\text{HSO}_3^+$  fragment ion. The “pure” high-resolution SPES of  $\text{H}_2\text{SO}_4$  without contaminations from other species in the continuous molecular beam has been acquired for the first time. The three cationic electronic states,  $\text{H}_2\text{SO}_4^+$ ,  $\text{X}^2\text{A}$ ,  $\text{A}^2\text{A}$  and  $\text{B}^2\text{A}$ , are observed and assigned in the SPES, with the aid of the high-level theoretical calculated results. The  $\text{H}_2\text{SO}_4$  molecule has two conformers, *trans* and *cis*, and their individual AIEs of the  $\text{X}^2\text{A}$  cationic ground state have been tentatively measured at  $11.684 \pm 0.006$  and  $11.643 \pm 0.006$  eV, respectively. The VIEs of the three electronic states are also determined. With increasing photon energies, the  $\text{H}_2\text{SO}_4^+$  cation dissociates into the  $\text{HSO}_3^+$  and OH fragments and their adiabatic appearance energy is measured at  $13.498 \pm 0.007$  eV. Furthermore, the enthalpies of formation for the cations  $\text{H}_2\text{SO}_4^+$  and  $\text{HSO}_3^+$  are acquired through the thermochemical cycle in the photoionization and dissociative photoionization.

## Author contributions

Cuihong Zhang: investigation; Xiaoxiao Lin: formal analysis; Xiaofeng Tang: conceptualization, methodology, investigation,

1 project administration, writing – original draft, and writing –  
 review and editing. Christa Fittschen: investigation; Sebastian  
 Hartweg: investigation; Gustavo A. Garcia: methodology, data  
 curation, investigation, writing – original draft, and writing –  
 5 review and editing; Bo Long: formal analysis; Weijun Zhang:  
 formal analysis; Laurent Nahon: methodology, investigation,  
 and writing – review and editing.

## 10 Conflicts of interest

There are no conflicts to declare.

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