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Cuihong Zhang, Xiaoxiao Lin, Xiaofeng Tang, Christa Fittschen, Sebastian Hartweg, et al.. Vacuum ultraviolet photochemistry of sulfuric acid vapor: a combined experimental and theoretical study. *Physical Chemistry Chemical Physics*, 2022, 24 (4), pp.2015-2021. 10.1039/D1CP05237C . hal-03872639v2

**HAL Id: hal-03872639**

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Submitted on 25 Nov 2022

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

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**ABSTRACT:** 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 ( $i^2$ PEPICO) spectroscopy complemented with accurate theoretical calculations. Threshold photoelectron spectrum (TPES) 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  $\text{H}_2\text{SO}_4$  molecule has two conformers, *trans* and *cis*, and their adiabatic ionization energies in the  $X^2A$  cationic ground state are measured at  $11.684 \pm 0.005$  and  $11.632 \pm 0.006$  eV, respectively, in accordance with high-level calculated findings. 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  $13.493^{+0.010}_{-0.004}$  eV. Then the enthalpies of formation for the species involved in the photoionization and dissociative photoionization have been determined through a thermochemical cycle.



## 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>2,3</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 the 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>4-6</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 the sulfuric acid-water clusters, in which their optimized structures and spectra have been calculated with various levels of theory.<sup>7-10</sup> For example, theoretical results show that the  $\text{H}_2\text{SO}_4$  molecule has two conformers depending on the relative position of the two OH groups: the most stable one is the *trans* form having  $\text{C}_2$  symmetry, while the *cis* form has  $\text{C}_1$  symmetry and an energy of  $+1.1 \text{ kcal mol}^{-1}$  with respect to the *trans* conformer.<sup>7</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 predict 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>7,9</sup>

Experimentally, many spectroscopic methods such as microwave rotational

spectroscopy, infrared (IR) and Raman spectroscopy have been employed to probe  $\text{H}_2\text{SO}_4$  and hydrated complexes.<sup>11-15</sup> The structures, vibrational spectra and frequencies of  $\text{H}_2\text{SO}_4$  and the  $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$  cluster were obtained. Mass spectrometry, as a convenient analytical method, has also been applied. 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 and its ionization energy was roughly measured, together with the appearance energies of its major fragment ions,  $\text{H}_2\text{O}^+$ ,  $\text{SO}_3^+$  and  $\text{HSO}_3^+$ .<sup>16</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 electron impact ionization mass spectrometry.<sup>17, 18</sup> Recently, the formation of mixed sulfuric acid-water clusters with different concentrations of water and  $\text{H}_2\text{SO}_4$  was investigated by electron attachment and negative ion mass spectrometry.<sup>19</sup> However, the above-mentioned mass spectrometry 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 is not precisely known.<sup>20</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 calculations. Three cationic electronic states of  $\text{H}_2\text{SO}_4^+$  have been prepared and assigned in the threshold photoelectron spectrum (TPES). In particular, the adiabatic ionization energies (AIEs) of the *trans* and *cis* conformers of  $\text{H}_2\text{SO}_4$ , towards the  $X^2A$  cationic ground state, have been measured precisely for the first time, as well as the adiabatic appearance energy ( $\text{AE}_{0K}$ ) of the  $\text{HSO}_3^+$  fragment ion. The enthalpies of formation for the species involved in the photoionization and dissociative photoionization are also determined through a thermochemical cycle.

## 2. Methods

The experiments were carried out on the beamline DESIRS equipped by a  $i^2$ PEPICO spectrometer, DELICIOUS III, at the French national synchrotron radiation facility SOLEIL. The detailed configurations of the synchrotron beamline and the spectrometer<sup>21-23</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  $200 \text{ l.mm}^{-1}$  grating, which was set to provide an energy resolution of  $\sim 3 \text{ meV}$ . 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 an accuracy of  $\pm 1 \text{ meV}$  using the resonant absorption lines of Ar atoms in the gas filter.

The  $i^2$ PEPICO spectrometer is composed of a modified Wiley-McLaren ion time-of-flight (TOF) 3D-momentum imaging 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>22</sup> A mixture of helium carrier gas (1.5 bars) and  $\text{H}_2\text{SO}_4$  vapor, generated from vaporization of liquid  $\text{H}_2\text{SO}_4$  (95% purity) in an in-vacuum oven heated at  $180 \text{ }^\circ\text{C}$ , was expanded through a  $70 \text{ }\mu\text{m}$  diameter nozzle to form a continuous molecular beam which was skimmed twice before reaching the center of the spectrometer.<sup>23, 24</sup> The multiplex coincidence scheme between ion and electron yields mass-selected photoelectron spectra (PES) as a function of photon energy, which are then reduced to TPES, sometimes also referred to as slow PES (SPES), as previously detailed.<sup>25</sup> Meanwhile, the coincidence scheme can provide spectral fingerprints to identify and separate isomers, and accurately measure thermochemical data such as the appearance energy of fragment and bond energies.<sup>25-27</sup>

We have performed theoretical calculations to assign the experimental spectra. The AIE and the vertical ionization energy (VIE) of the  $X^2A$  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 the MOLPRO software.<sup>28</sup> The VIEs of the A<sup>2</sup>A first and the B<sup>2</sup>A second excited electronic states of H<sub>2</sub>SO<sub>4</sub><sup>+</sup> were computed using time dependent density functional theory (TD-DFT), TD-M06X/6-311++G(d,p).<sup>29</sup> The Franck–Condon factors in the photoionization towards the X<sup>2</sup>A cationic ground state, as well as for the required geometry optimizations and the vibrational frequency computations with a harmonic approximation, were calculated at the M06X/aug-cc-pVTZ level of theory with the Gaussian package using the time-independent adiabatic Hessian Franck–Condon model.<sup>29</sup>

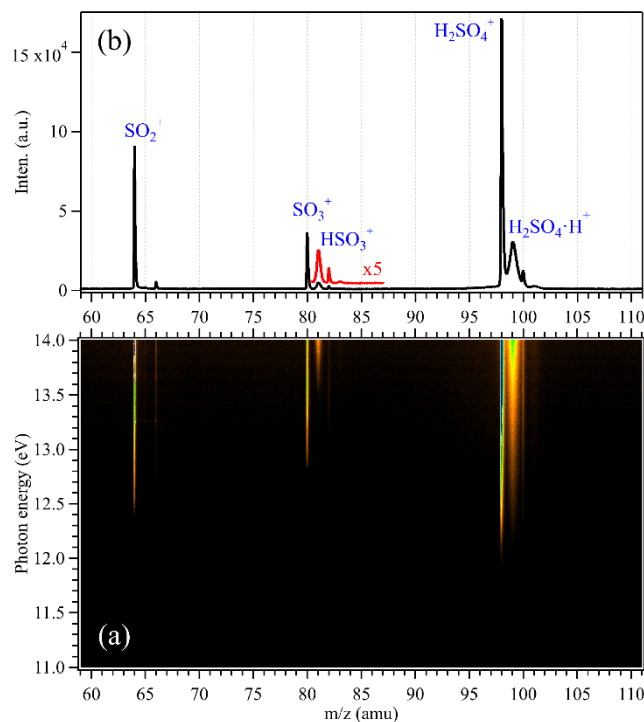
### 3. Results and Discussion

#### 3.1 TOF mass spectra

Synchrotron radiation photoionization TOF mass spectra of the gas mixture have been measured in the 11-14 eV photon energy range and are presented as a matrix in Fig. 1, as well as their integrated mass spectrum. Several mass peaks can be observed and have been assigned within the mass range of  $m/z = 60-110$ . For example, the most intense mass peak at  $m/z = 98$  is assigned to H<sub>2</sub>SO<sub>4</sub>, the  $m/z = 80$  mass peak is assigned to SO<sub>3</sub> and the  $m/z = 64$  peak is attributed to SO<sub>2</sub>, based on their narrow widths in the mass spectra.<sup>23</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>23, 26</sup> Besides these three intense mass peaks, their isotopic peaks can be observed in the mass spectra too, *i.e.*, the <sup>33</sup>SO<sub>2</sub> isotopic species at  $m/z = 65$ , <sup>34</sup>SO<sub>2</sub> at  $m/z = 66$ , <sup>34</sup>SO<sub>3</sub> at  $m/z = 82$  and H<sub>2</sub><sup>34</sup>SO<sub>4</sub> at  $m/z = 100$  with relative intensities corresponding to their individual natural abundances, as listed in Table S1.<sup>30</sup>

SO<sub>3</sub> is formed from the equilibrium reaction of H<sub>2</sub>SO<sub>4</sub>(g) ↔ SO<sub>3</sub>(g) + H<sub>2</sub>O(g) inside the oven, and SO<sub>2</sub> is produced from the reduction reaction of H<sub>2</sub>SO<sub>4</sub> 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 well with their individual ionization energies,<sup>31</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 upon electron impact ionization mass spectrometry, but were both assigned as fragment ions from dissociation of  $\text{H}_2\text{SO}_4^+$  by Snow and Thomas.<sup>16</sup>



**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.

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>30</sup> and the width of its mass peak 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  $\text{SO}_3$  ( $m/z = 80$ ). The  $m/z = 81$  peak in the mass spectra corresponds therefore to the  $\text{HSO}_3^+$  fragment ion from dissociative ionization of  $\text{H}_2\text{SO}_4$ , as inferred from its broad shape due to the

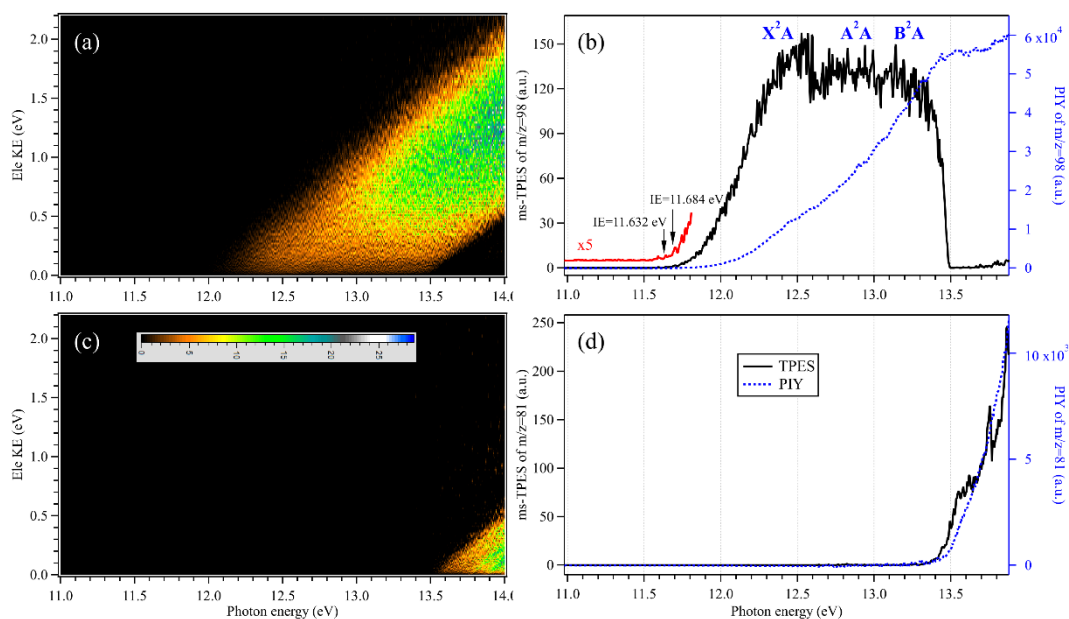


kinetic energy release in the fragmentation. Note that the contribution from the isotope  $^{33}\text{SO}_3$  ( $\sim 0.91\%$ <sup>30</sup>) to the  $m/z = 81$  channel is considered negligible and has not been subtracted here. Similarly, due to its large width, the more intense peak at  $m/z = 99$  is attributed to the  $\text{H}_2\text{SO}_4\text{H}^+$  fragment ion produced from 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 acids will be reported in a forthcoming work.

### 3.2 Mass-selected threshold photoelectron spectra

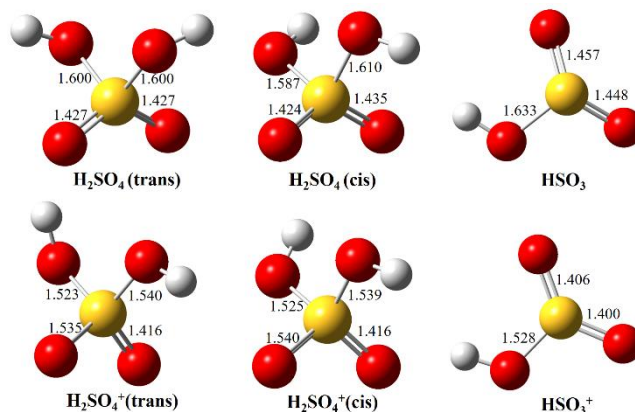
The mass-selected photoelectron matrices corresponding to the  $\text{H}_2\text{SO}_4^+$  parent ion ( $m/z = 98$ ) and the  $\text{HSO}_3^+$  fragment ion ( $m/z = 81$ ) showing the signal as a function of electron kinetic energy (Ele KE) and photon energy are depicted in Fig. 2(a) and (c), respectively.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

The mass-selected TPES 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 (PIY). In Fig. 2(b), the TPES of  $\text{H}_2\text{SO}_4$  is rather unstructured although an apparent onset can be observed at  $h\nu = 11.684 \pm 0.005$  eV in the TPES. The uncertainty of the photon energy calibration, the influence of the scanning step size (5 meV) and the signal-to-noise ratio of the TPES have been taken into account and included in the given error bars.<sup>32</sup>



**Fig. 2** Mass-selected photoelectron matrices, threshold photoelectron spectra (TPES, black solid lines) and photoionization yields (PIY, blue dotted lines) corresponding to (a, b) the  $\text{H}_2\text{SO}_4^+$  parent ion and (c, d) the  $\text{HSO}_3^+$  fragment ion. The 5 times magnified TPES shown in red to show the onset of  $\text{H}_2\text{SO}_4^+$ .

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  $X^2A$  ground electronic state are presented in Fig. 3, agreeing well with previous results.<sup>7, 33</sup> The *trans* conformer has a  $C_2$  symmetry structure and is the global minimum with an energy of  $\sim 1.1$  kcal mol<sup>-1</sup> below the *cis* conformer with a  $C_1$  symmetry.<sup>7</sup> The energy difference is small and both of them can be populated under the present experimental conditions.



**Fig. 3** Optimized structures of H<sub>2</sub>SO<sub>4</sub> (*cis* and *trans* conformers) and HSO<sub>3</sub>, as well as their individual cations, in the ground electronic states.

Upon photoionization, an electron is removed from the outer valence orbital of the neutral H<sub>2</sub>SO<sub>4</sub> molecule leading to the formation of the H<sub>2</sub>SO<sub>4</sub><sup>+</sup> cation. The structure of the *trans* conformer relaxes in the cation and its symmetry changes from C<sub>2</sub> to C<sub>1</sub> during the photoionization, as shown in Fig. 3, while the *cis* conformer geometry undergoes smaller changes. The AIE of the X<sup>2</sup>A ground electronic state of the *trans*-H<sub>2</sub>SO<sub>4</sub><sup>+</sup> has been calculated at 11.688 eV at the CCSD(T)-F12A/aug-cc-pVTZ level of theory,<sup>28</sup> in accordance with the experimental onset of 11.684 ± 0.005 eV, as shown in the TPES of Fig. 2(b). The AIE of the X<sup>2</sup>A ground state of the *cis*-H<sub>2</sub>SO<sub>4</sub><sup>+</sup> is also calculated with the same level of theory and locates at 11.635 eV. In the TPES of Fig. 2(b) the weak onset at hv = 11.632 ± 0.006 eV might be ascribed to the AIE of the X<sup>2</sup>A ground state of the *cis*-H<sub>2</sub>SO<sub>4</sub><sup>+</sup>. Another weak transition can be observed at hv = 11.596 ± 0.006 eV in the TPES, and is assigned as originating from a hot band in the photoionization. In a previous study based upon electron impact ionization mass spectrometry, restricted by the electron energy resolution, the ionization energy of H<sub>2</sub>SO<sub>4</sub> was measured at 12.4 ± 0.05 eV (see Table 1), which would actually correspond to the VIE measured in this work.<sup>16</sup>

**Table 1** Ionization energies of H<sub>2</sub>SO<sub>4</sub> and the appearance energy of the HSO<sub>3</sub><sup>+</sup> fragment ion. (Unit: eV)

State	IE(H <sub>2</sub> SO <sub>4</sub> )	AE(HSO <sub>3</sub> <sup>+</sup> )	Method	Reference
Expt.	12.4±0.05		EIMS	16
		13.9±0.1	EIMS	16
		13.493 <sup>+0.010</sup> <sub>-0.004</sub>	TPES	This work
X <sup>2</sup> A ( <i>cis</i> )	11.632±0.006 <sup>a</sup>		TPES	This work
X <sup>2</sup> A ( <i>trans</i> )	11.684±0.005 <sup>a</sup>		TPES	This work
X <sup>2</sup> A	12.53±0.05 <sup>b</sup>		TPES	This work

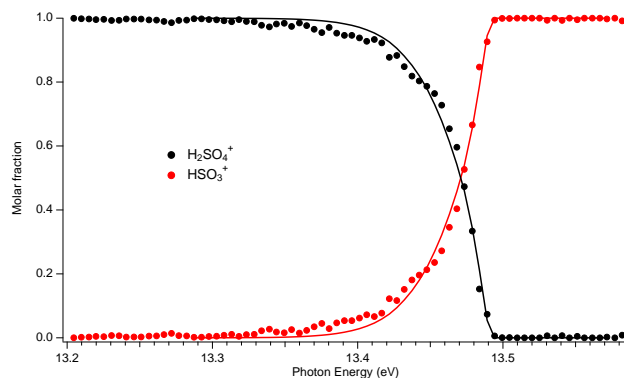
	A <sup>2</sup> A	12.80±0.05 <sup>b</sup>	TPES	This work
	B <sup>2</sup> A	13.20±0.05 <sup>b</sup>	TPES	This work
Calc.	X <sup>2</sup> A ( <i>cis</i> )	11.635 <sup>a</sup>	CCSD(T) <sup>c</sup>	This work
	X <sup>2</sup> A ( <i>trans</i> )	11.688 <sup>a</sup>	CCSD(T) <sup>c</sup>	This work
	X <sup>2</sup> A	12.54 <sup>b</sup>	CCSD(T) <sup>c</sup>	This work
	A <sup>2</sup> A	12.84 <sup>b</sup>	TD-M06X <sup>d</sup>	This work
	B <sup>2</sup> A	13.10 <sup>b</sup>	TD-M06X <sup>d</sup>	This work

a. AIE. b. VIE. c. CCSD(T)-F12A/aug-cc-pVTZ. d. TD-M06X/6-311++G(d,p).

The Franck-Condon factors for the photoionization of H<sub>2</sub>SO<sub>4</sub> towards the cationic X<sup>2</sup>A ground electron state of H<sub>2</sub>SO<sub>4</sub><sup>+</sup> have been tentatively calculated at the M06X/6-311++G(d,p) level of theory, using the time-independent adiabatic Hessian Franck–Condon model.<sup>29</sup> Note that the influences of the 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 = 200 cm<sup>-1</sup>, full width at half maximum) and is shown in Fig. S1, with an energy offset of ~ 80 meV to fit the experimental result. Although the simulated PES fits the experimental TPES very well at the beginning of the X<sup>2</sup>A 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<sup>2</sup>A excited electronic state and the B<sup>2</sup>A electronic state of H<sub>2</sub>SO<sub>4</sub><sup>+</sup> have been calculated at 12.84 and 13.10 eV, respectively, at the TD-M06X/6-311++G(d,p) level of theory, and have been assigned in the experimental TPES too. In the TPES of Fig. 2(b), the VIEs of the A<sup>2</sup>A and B<sup>2</sup>A cationic states are estimated at 12.80 ± 0.05 and 13.20 ± 0.05 eV, respectively, as listed in Table 1, agreeing well with the calculated results.

### 3.3 The thermochemical cycle

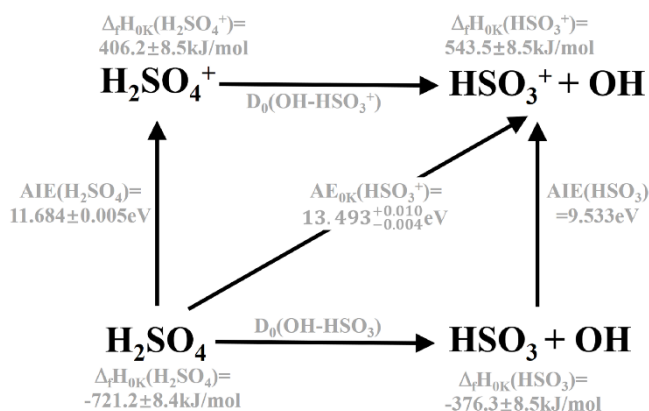
The sharp high energy cut-off of the electron signal in the parent TPES of Fig. 2(b) is due to the dissociative photoionization of  $\text{H}_2\text{SO}_4$ , in accordance with the sharp appearance of the electron signal in the TPES of the  $\text{HSO}_3^+$  fragment ion in Fig. 2(d). The  $\text{HSO}_3^+$  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>16</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 TPES of Fig. 2. The curves in the breakdown diagram are modeled assuming that the initial internal thermal energy stored in the parent neutral molecule directedly towards fragmentation.<sup>34</sup> Assuming that dissociation is fast within the acceleration timescales of the experiment (a few  $\mu\text{sec}$ ), the only parameters affecting the model are the temperature and the OK appearance energy of the  $\text{HSO}_3^+$  fragment. These are optimized within a least squares fit to the data which yields values of  $140_{-20}^{+40}$  K for the temperature, and  $\text{AE}_{\text{OK}}(\text{HSO}_3^+) = 13.493_{-0.004}^{+0.010}$  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  $\text{AE}_{\text{OK}}$  applies to both, *i.e.*, that the eventual barriers towards dissociation are equal.



**Fig. 4** Breakdown diagram of  $\text{H}_2\text{SO}_4^+$  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).

Based on the AIE of the  $X^2A$  ground state of  $\text{H}_2\text{SO}_4^+$  and the  $\text{AE}_{\text{OK}}$  of the  $\text{HSO}_3^+$

fragment ion, the bond energy of  $\text{H}_2\text{SO}_4^+$  associating with the  $\text{HSO}_3^+$  and OH fragments is calculated at  $1.809 \pm 0.008$  eV for the *trans* conformer. Through a thermochemical cycle, as shown in Fig. 5, the enthalpies of formation for the cations of  $\text{H}_2\text{SO}_4^+$  and  $\text{HSO}_3^+$  are obtained at  $\Delta_f\text{H}_{0\text{K}}(\text{H}_2\text{SO}_4^+) = 406.2 \pm 8.5$  kJ mol<sup>-1</sup> and  $\Delta_f\text{H}_{0\text{K}}(\text{HSO}_3^+) = 543.5 \pm 8.5$  kJ mol<sup>-1</sup>, with the aid of the available thermochemical data in the literature, *i.e.*,  $\Delta_f\text{H}_{0\text{K}}(\text{H}_2\text{SO}_4) = -721.2 \pm 8.4$  kJ mol<sup>-1</sup><sup>35</sup> and  $\Delta_f\text{H}_{0\text{K}}(\text{OH}) = 37.252 \pm 0.026$  kJ mol<sup>-1</sup>,<sup>36</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>28</sup> as listed in Table 1, so that we report the enthalpy of formation for  $\text{HSO}_3$  at  $\Delta_f\text{H}_{0\text{K}}(\text{HSO}_3) = -376.3 \pm 8.5$  kJ mol<sup>-1</sup>.



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

## 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 and complemented by accurate theoretical calculations on the structures and ionization energies. The  $\text{H}_2\text{SO}_4$  molecule in the oven decompose to  $\text{SO}_2$  and  $\text{SO}_3$  and these can be discarded by the coincidence scheme and are distinguished from the dissociative ionization product,  $\text{HSO}_3^+$  fragment ion. The “pure” high resolution TPES of  $\text{H}_2\text{SO}_4$  without contamination from other species in the continuous molecular beam has been acquired for the first time. The three cationic electronic

states of  $\text{H}_2\text{SO}_4^+$ ,  $\text{X}^2\text{A}$ ,  $\text{A}^2\text{A}$  and  $\text{B}^2\text{A}$ , are observed and assigned in the TPES, 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 measured precisely and locate at  $11.684 \pm 0.005$  and  $11.632 \pm 0.006$  eV, respectively. The VIEs of the 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 the adiabatic appearance energy is measured at  $13.493_{-0.004}^{+0.010}$  eV. Furthermore, the enthalpies of formation for the cations of  $\text{H}_2\text{SO}_4^+$  and  $\text{HSO}_3^+$  are acquired through the thermochemical cycle in the photoionization and dissociative photoionization.

## Author contributions

Conception and design: X.T.; Acquisition of data: C.Z., C.F., S.H. G.G. L.N.; Theoretical calculations: X.L., B.L., W.Z.; Analysis and interpretation of data: X.T., G.G.; Writing-original draft preparation: X.T.; Writing-review and editing: . All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

X.T. would like to acknowledge the financial support from the National Natural Science Foundation of China (Nos. 91961123, 21773249, 42120104007), the International Partnership Program of Chinese Academy of Sciences (No. 116134KYSB20170048) and the Key Program of Research and Development of Hefei Science Center, CAS (No. 2020HSCKPRD001). The authors are grateful to the SOLEIL general staff for smoothly running the facility and providing synchrotron beamtime under the proposal 20200490. In particular Jean-François Gil is warmly thanked for his help in setting up the experiment.

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