High resolution threshold photoelectron spectrum and autoionization processes of S₂ up to 15.0 eV

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ABSTRACT
VUV photoionization dynamics of the S₂ molecule were re-investigated from threshold up to 15.0 eV, using synchrotron radiation coupled with double imaging photoelectron/photoion coincidence featuring high resolution capabilities. We measured the first threshold photoelectron spectrum of S₂ achieving higher resolution than previous literature to derive accurate spectroscopic constants for a few electronic states of the cation including the X²Π ground state and the a²Σ̂g⁻ and b²Σ̂g⁻ states. We also recorded the total ion yield for S₂ up to a photon energy of 15.0 eV which, combined with the threshold photoelectron spectrum, led to the assignment of various autoionizing Rydberg series.

1. Introduction

Sulfur and its chemistry are not only an integral component of biochemical processes [1] but are omnipresent in the interstellar medium as well [2]. Neutral S₂ has been found in cometary comae [3,4], on Jupiter near the G impact site after the collision of Shoemaker-Levy 9 [5], in volcanic plumes on Io [6,7], and has been invoked as a contributor to stratospheric heating of hot Jupiters [8]. However, somewhat intriguingly, in primitive molecular clouds and star-forming regions, sulfur is increasingly depleted [9,10]. An abundance of sulfur-bearing molecules has been detected recently in the interstellar medium [11–15], but all-together it does not sufficiently account for the apparently missing sulfur. A theory gaining traction presumes that sulfur cation collects on interstellar dust grains where it is processed by UV and X-rays to form universal sulfur sinks such as S₂ [16]. In this context it is important to revisit the photoionization of the sulfur dimer, S₂, as it is a potentially important reactive intermediate in interstellar regions whose chemistry is driven by UV and X-ray radiation.

Since the recording of the first photoelectron spectra of the S₂ diradical [17,18], the spectroscopy of the S₂⁺ cation has been explored by means of flowing afterglow [19–21], electron impact ionization [22], optical spectroscopy [23], photoluminescence in Ne matrices [24], and absorption spectroscopy of sulfur-doped silica glass [25]. The photoionization efficiency (PIE) curve of S₂ was measured up to 20.7 eV by Liao and Ng [26] and theoretical efforts pertaining to the ground state and excited states of the S₂⁺ radical have been recently summarized [27]. Experimental efforts to study breakdown products from the interaction of disulfide bridge-containing molecules with high energy photons found that S₂⁺ was persistently formed at energies in the low-keV regime, attesting its chemical stability [28].

The work of Rosinger et al. [22], revealed several features in the recorded ionization efficiency curves which were attributed to autoionization processes, and Liao and Ng [26] further inspected these autoionizing features which had clearly visible bands in the PIE curve of S₂. While they noted that it was likely that these vibrational bands could be grouped into more than one vibrational progression, only a handful were assigned.

By using the double-imaging photoelectron/photoion coincidence (iPEPICO) technique [29] coupled with synchrotron radiation we present the threshold photoelectron spectra (TPES) and total ion yield (TIY) from threshold up to 15.0 eV. The TIY allows us to assign features corresponding to autoionization of neutral Rydberg states converging to different vibronic states of S₂⁺, which are in turn assigned using the TPES. We also present a two-dimensional kinetic energy vs photon energy matrix of the cation signal which further evidences these ionization dynamics.
2. Methodologies

Experiments were performed on the DESIRS VUV undulator beamline [30] located at the third generation French national synchrotron facility SOLEIL. The experimental apparatus that was used is the permanent molecular beam end-station SAPHIRS [31] which is equipped with the $i^\text{th}$PEICO spectrometer DELICIOUS [32]. Ions and electrons were detected in coincidence with an imaging Wiley-McLaren time-of-flight analyzer and a velocity map imaging (VMI) setup, respectively. The DESIRS beamline monochromator was set to deliver a photon energy resolution of 3 meV at 8 eV and a gas filter [33] upstream was filled with either krypton or argon depending on the energy range, to filter out higher harmonics of the beamline undulator, OPHELIE2 [34].

$S_2$ was produced by recombinations of S atoms which were formed by double H-abstraction from H$_2$S in a flow-tube placed inside the SAPHIRS chamber [35]. The $S_2$ diradicals were produced as secondary products of the process initially set up to produce SH radicals. All the experimental parameters pertaining to this experiment have been described in detail previously [36].

Three energy scans were performed; one from threshold up to 12.0 eV and two scans from 11.9 eV to 15.0 eV, one in which the particle acceleration was achieved with a DC electric field of 53 V·cm$^{-1}$ and one where it was increased to 177 V·cm$^{-1}$ to collect all coincident events related to $S_2^+$ ions up to 15 eV. Autoionizing resonances corresponding to transitions in neutral atomic sulfur were used for absolute photon energy calibration. This does not account for the Stark shift in the recorded TPES which is induced by the applied DC electric field to achieve particle acceleration. The Stark shift can be quantified by calculating $6\sqrt{F}$ (in cm$^{-1}$ with $F$ denoting the electric field in V·cm$^{-1}$) [29] which gives a shift of 5.4 meV in the case of the 53 V·cm$^{-1}$ scans that were used to record the TPES. All the ionization thresholds given in this paper have been corrected by this field-induced shift.

At each photon energy of the scans, the recorded images were inverted [37] so the electron signal detected in coincidence with $S_2$ can be obtained as a function of electron kinetic energy and photon energy in a two-dimensional matrix representation (see below). Therein, diagonal signals correspond to direct ionizations into a cationic state where the kinetic energy of the produced photoelectrons increases linearly with excess energy. Vertical lines, however, evidence excitations to Rydberg states that are resonant with the photon energy, which autoionize according to the different couplings to the cation states.

The threshold photoelectron spectrum (TPES) is obtained by integrating the intensities along the diagonal lines (constant ionization states) up to a relatively small value of kinetic energy [38,39]. For this experiment, the best signal to background ratio was found for an electron kinetic energy cut-off (Ele KE$_\text{max}$) value of 5 meV.

Mass signals corresponding to $m/z = 65$ ($^{32}$S$^{32}$S) and $m/z = 66$ ($^{33}$S$^{32}$S, $^{32}$S$^{33}$S) are the $S_2$ contribution is negligible were clearly visible [36] and the TPES from these mass channels are analyzed for the X$^2\Pi_{\Omega_3}$ ground state. As for the excited ionic states, the observed peak positions in the recorded TPES are indistinguishable in all mass channels which forbids any differentiation in the analysis of the ionic states of $^{32}$S$^{32}$S and $^{33}$S$^{32}$S, and in $S_2$. Furthermore, as the $^{33}$S$^{32}$S and $^{32}$S$^{33}$S signals were significantly weaker than that of the $m/z = 64$ channel, their TPES were created with larger Ele KE$_\text{max}$ values, namely 10 meV which also results in larger errors of their spectroscopic parameters as will be discussed in Section 3.2.

3. Results and discussion

3.1. Valence electron configurations of $S_2$ and $S_2^+$

Photoionization of homonuclear chalcogens (O$_2$, S$_2$, etc.) gives rise to multiplex photodynamics which can be attributed to the nature of being open shell triplet molecular systems. Here we present the electron configurations of the neutral and ionized $S_2$ to assist the reader through the assignments of the total ion yield curve (Section 3.2) and the TPES (Section 3.3).

The electron configuration of neutral $S_2$ in the ground state ($X^2\Sigma^{-}_g$) is the following:

$$[S_2]: \ (\sigma_g)^2 (\pi_g)^2 (\pi_u)^2$$

and for the ground state ($X^2\Pi_{\Omega_3}$) of the $S_2^+$ cation, the electron configuration is obtained by removing an electron from the $\pi_g$ orbital:

$$[S_2^+]: \ (\sigma_g)^2 (\pi_g)^2 (\pi_u)^2$$

The first two excited states of the $S_2^+$ cation, namely $\alpha^2\Pi_{\Omega_2}$ and $\alpha^2\Pi_{\Omega_1}$ are obtained by removing an electron from the $\pi_g$ orbital, spin down and spin up, respectively. As seen in Table 1, four different Rydberg series converging to each of the $\alpha^2\Pi_{\Omega_3}$ and $\alpha^2\Pi_{\Omega_1}$ states are obtained by promoting an electron from a $p$ orbital, to either $s$ ($\sigma_p$) or $d$ ($\pi_p$, $\delta_p$) Rydberg orbitals.

We note that the approximate quantum defects in the Rydberg series of free atomic sulfur are $\delta = 2.0$ for $ns$, 1.6 for $np$, and 0.3 for $nd$ orbitals [40] so that it is not unreasonable to expect similar trends for $S_2$ as has been done previously [26].

The next two excited states of $S_2^+$ are $b^2\Sigma^+_g$ and $b^2\Sigma^-_g$. Their electron configurations result from removing an electron from the $\pi_g$ orbital, spin down and spin up respectively, meaning that the Rydberg states converging to the $b^2\Sigma^+_g$ and $b^2\Sigma^-_g$ states can have two possible electron configurations (Table 1). Apart from the cationic states presented in Table 1, there are several other states that have been predicted by Yu et al. [27], namely, $1\Sigma^+_u$, $1\Sigma^-_g$, $1\Pi^-_u$, $1\Pi^+_g$, $1\Delta^-_u$, $1\Delta^+_g$, $1\Sigma^+_g$, $1\Delta^-_g$, $2\Pi^-_u$, $1\Sigma^-_g$, and $2\Pi^-_g$. The spectroscopic parameters of these states were calculated with onsets ranging from 31854 cm$^{-1}$ (3.9 eV) to 50531 cm$^{-1}$ (6.3 eV) above the X$^2\Pi_{\Omega_3}$ ground state, i.e., above the $B^2\Sigma^-_g$ state.

3.2. Total ion yield

The 2D matrices displaying the mass-filtered electron–ion coincidence signals pertaining to $m/z = 64$ are presented in Fig. 1. In the first scan from 9.2 to 12.0 eV, the X$^2\Pi_{\Omega_3}$ is the ground state and the first excited state, $\alpha^2\Pi_{\Omega_2}$ is seen with an onset of 11.58 eV. The second scan which covers 11.9–15.0 eV, unveils three additional excited states, namely $\alpha^2\Pi_{\Omega_1}$, $b^2\Sigma^+_g$, and $b^2\Sigma^-_g$.

The 2D matrix in the upper panel of Fig. 1 exhibits clear signs of autoionizing resonances that contribute to the ionization signals pertaining to the parent. These appear as vertical lines in the 2D matrix.

Table 1

| State | X$^2\Pi_{\Omega_3}$ (\(\Omega = 1/2, 3/2\)) | X$^2\Sigma^-_g$ |
|-------|-----------------|----------------|
| $\alpha^2\Pi_{\Omega_2}$ | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) |
| $\alpha^2\Pi_{\Omega_1}$ | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) |
| $b^2\Sigma^+_g$ | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) |
| $b^2\Sigma^-_g$ | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) | (\(\sigma_g)^2(\pi_g)^2(\pi_u)^2\)) |
whereas direct ionization is observed as diagonal lines. Between 10.0 and 10.5 eV, vertical lines are apparent in the 2D matrix. Above 10.5 eV, these signals seem to partly continue as tendrils dangling down from the direct ionization signal, whose shape resembles that of a diagonal cloud. Around 11.0 eV, the vertical lines become apparent again, albeit very weakly.

The sum of all of the ionic signals as a function of the photon energy in Fig. 1 gives the total ion yield. The first attempt at assigning the autoionizing features in the rich total ion yield of $S_2$ was made by Liao & Ng [26]. They assigned two Rydberg series converging to the $b^4Σ_g^-$ state with average quantum defects of 1.64 and 2.13 which would correspond to the $[b^4Σ_g^-]npσ_u$ and $[b^4Σ_g^-]np σ_u$ Rydberg series, respectively, as outlined in Section 3.1. They observed a plethora of other spectral structures but ultimately, their resolution forbade further assignments despite identifying structures relevant to Rydberg series converging to the ionic states of $S_2^-$.

Here, the recorded TPES (see Section 3.3) can be used to guide the assignments and identify vibrational features in autoionizing Rydberg series converging to the corresponding ionic states.

Our total ion yield curve along with all of the relevant assignments is shown in Fig. 2 and Table 2 presents the assignments of the onsets of the Rydberg series detailed in Fig. 2 along with the calculated quantum defects which are representative of the Rydberg assignments. Assignments labeled with an asterisk in Table 2 (*) denote blended lines whose energy is best estimated from the calculated quantum defect. The most notable is that of the $[A^2Π_u]nsσ_g$ Rydberg series whose $n = 5–8$ components are all blended with other series and hence their assignment should be regarded as tentative despite the quantum defects being comparable.

Sharp dips in the TIY are observed at 10.03 and 10.64 eV which correspond to krypton absorption lines (4p$^5$4s(3/2)$^1S_0$ ← 4p$^6$, 1S$^0$ and 4p$^5$4s(1/2)$^3S_0$ → 4p$^6$1S$^0$ series, respectively [41]. For the scan up to 12 eV, krypton was used in the gas filter that was used to filter out higher harmonics coming from the undulator. Argon was used in the gas filter for the second scan up to 15 eV which is evidenced by several argon absorption lines, perhaps the most obvious one at 14.30 eV (3p$^13d'(3/2)$ ← 3p$^31S_0$ [42]).

The assignments made by Liao & Ng to the two Rydberg series converging to the $b^4Σ_g^-$ state principally occurred in the spectral region above 12.0 eV. Our assignment completely reevaluates their assignment for two notable reasons. Firstly, the enhanced resolution allows us to observe more structures in the TIY. Secondly, the recorded TPES allows us to more accurately determine the appearance energies of the ionic states than in the PES study of $S_2$ by Dyke et al. [17] (Section 3.3). This greatly influences the calculation of the quantum defects which we used...
Table 2

Rydberg series of $S_2$ observed in the region 9.2 – 15.0 eV. Blended lines or tentative assignments are denoted with an asterisk. We estimate that the uncertainty of other lines is equal or better than 10 meV. Due to the broadened nature of the autoionizing lines, greater accuracy cannot be expected in this case. Below each Rydberg series we present the corresponding average quantum defect.

| Energy (eV) | Principal quantum number | Experimental determined quantum defect (Å) |
|------------|--------------------------|------------------------------------------|
| 10.96      | 81431                    | 1.99 [a$^1\tilde{\Pi}$3s$_g$]            |
| 10.66      | 86028                    | 2.17 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.00      | 88730                    | 2.21 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.18      | 90182                    | 2.27 [a$^1\tilde{\Pi}$3s$_g$]            |
| Average $\delta$ = 2.16 ± 0.12 |
| 10.43*     | 84116                    | 2.08 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.16*     | 90028                    | 2.02 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.48      | 92569                    | 1.99 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.64      | 93900                    | 2.00 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.741     | 94698                    | 2.02 [a$^1\tilde{\Pi}$3s$_g$]            |
| 11.806     | 95222                    | 2.02 [a$^1\tilde{\Pi}$3s$_g$]            |
| Average $\delta$ = 2.02 ± 0.03 |

To guide our assignment to best fit with the recorded TIY.

Though densely populated, we identify a number of Rydberg states in the spectral region between 10 and 11 eV. First of which is the vibrational progression of the [a$^4\Pi_4$]5σ$_g$ and [a$^4\Pi_4$]6σ$_g$ states which have a very similar structure and vibrational progression as that of the a$^1\Pi$ state. Higher components of the [a$^4\Pi_4$]nσ$_g$ states can be identified but they are significantly weaker.

The [a$^4\Pi_4$]4σ$_g$ and [A$^4\Pi_4$]4σ$_g$ states are not observed in our total ion yield curve and if we use the average quantum defects of both of these series ($\delta = 2.16 ± 0.12$ and $2.02 ± 0.03$, respectively), we can estimate the appearance energies of both components. This would lead the [a$^4\Pi_4$]4σ$_g$ state to appear between 7.00 and 8.05 eV ($56500-64900$ cm$^{-1}$) and the [A$^4\Pi_4$]4σ$_g$ state between 8.44 and 8.65 eV ($68100-69800$ cm$^{-1}$), well below the S$_2$ ionization energy located at $\sim 9.37$ eV. These energies are significantly lower than the B and B' states of S$_2$ [43] and the closest assignment (to our knowledge) of assigned Rydberg states in this region for S$_2$ pertain to the C$^2\Sigma^+$ Rydberg state but it was theorized by Cooper & Western that a quintet ion-pair state with an a$^1\Pi_4$ ion core should lie around 72620 cm$^{-1}$ [43]. For the moment, the whereabouts of the n = 4 components of the [a$^1\Pi_4$]nσ$_g$ and [A$^4\Pi_4$]nσ$_g$ Rydberg series remain up for discussion.

There are some Rydberg series that have been intentionally left out of the assignment which are those of the three Rydberg series corresponding to an excitation to a d Rydberg orbital, namely [a$^1\Pi_4$]3d$_g$, [a$^1\Pi_4$]3d$_g$, and [a$^1\Pi_4$]3d$_g$, and 10.15 and 10.51 eV in the case of [a$^1\Pi_4$]3d$_g$. The 9.73 – 10.80 eV region in the TIY does exhibit some structure, but it is too weak for a definitive assignment of the onsets of the [a$^1\Pi_4$]3d$_g$, [a$^1\Pi_4$]3d$_g$, and [a$^1\Pi_4$]3d$_g$ states. The 10.15 – 10.51 eV region on the other hand coincides with the vibrational progression of the [a$^1\Pi_4$]3σ$_g$ state, which forbids any further assignment of the d Rydberg series.

3.3. Threshold photoelectron spectrum (TPES)

3.3.1. $X^2\Pi_{2g}$ ground state

The TPES of $32S_2$ is presented in Fig. 3 from its first ionization threshold up to 11.5 eV. The transitions assigned in Fig. 3 are labeled by the final vibrational states of the cation (starting from the neutral S$_2$ ground state). The TPES of $32S_2$ and $34S_2$ are provided in Fig. S1 of the SI. The vibrational assignments of all isotopologues are given in Table 3.

On average, the observed spin-orbit (SO) splitting in the ground state is 463 ± 17 cm$^{-1}$. This value compares well with that observed by Dyke et al. (470 ± 25 cm$^{-1}$) [17].

By assigning the vibrational energy levels of the X$^2\Pi_{2g}$ ground state in the TPES, we can derive the ground state spectroscopic constants, namely $T_0$, $\omega_0$, and $\omega_0\chi_0$. To do this, we fit the observed energy levels to obtain the values of $T_0$, $\omega_0$, and $\omega_0\chi_0$ we present in Table 4. We could not include the $\omega_0\chi_0$ parameter in the fit without degrading the uncertainty of the other parameters.

In Fig. 4 we compare the measured energy level spacing between adjacent spin-orbit ladders of the X$^2\Pi_{2g}$ ground state and the same energy level spacing using the fitted parameters in Table 3. The agreement is good between $\nu = 0$ – 7, but the highest energy levels appear to suffer from perturbation effects from an unknown ionic state. However, since the uncertainties still overlap where the deviation in the energy level spacing is at its greatest, we cannot conclude such a perturbation is present. Furthermore, the additional ionic states predicted by Yu et al. [27] would have their onsets at least 32000 cm$^{-1}$ above the onset of the ground state, i.e., around 108000 cm$^{-1}$, which is still approximately 20000 cm$^{-1}$ higher than the alleged perturbation effects. We can thus not conclude that the ground state is suffering from perturbation effects from a hidden state.

As the TPES of these isotopologues were much weaker than that of $2^2S_2$, their fitted parameters suffer from larger uncertainties which make any discussion of supposed perturbations mute.

The unassigned peaks at 10.894 eV, 11.005 eV and 11.065 eV from Fig. 3 can now be tentatively assigned by using the derived spectroscopic parameters from the TPES as presented in Table 4. By extrapolating the fitted values to higher $\nu$ levels, we can tentatively estimate that these peaks belong to the X$^2\Pi_{2g}(\nu = 16)$, X$^2\Pi_{2g}(\nu = 18)$ and X$^2\Pi_{2g}(\nu = 18)$ levels, respectively. This comes with the assumption that these levels are reasonably unperturbed.

Regarding the peak intensities in the X$^2\Pi_{2g}$ ground state, they do not follow a definite Franck-Condon intensity trend. Between 10.0 and 10.6 eV, rather than decreasing monotonously, the signals increase in intensity before decreasing and disappearing above 10.6 eV. This is due to the presence of autoionizing states that can enhance weak direct transitions by indirect processes, because the vibrational overlap between the intermediate autoionizing state and the final cation state may be
more favorable for different cation equilibrium distances, as seen in other systems [44]. Indeed, the first autoionization features—converging towards the $a^3\Pi_u$ ionic state—are seen in Fig. 2 to begin at 10.1 eV, which coincides with the departure from the Franck-Condon behavior observed in the TPES of Fig. 3. This explanation likewise applies to the appearance of peaks belonging to the $X^3\Pi_u(v = 16), X^3\Pi_u(v = 18)$ and $X^3\Pi_u(v = 18)$ levels between 10.9 and 11.1 eV in the TPES, which coincides with the first autoionizing feature converging to the $b^3\Sigma_u^+$ ionic state.

### 3.3.2. $S_2^+$ excited states

The TPES of $S_2$ from 11.5 to 15.0 eV is presented in Figs. 5 and 6 along with assignments corresponding to the final cationic states of $S_2^+$. The assigned spectroscopic parameters are presented in Table 5. Above 12.0 eV, we expected to see the spectral fingerprints of the $A^3\Pi_u$ state (akin to Dyke et al.) but the threshold electron signal used to make up the TPES was not strong enough to resolve it and thus our TPES forbids vibrational assignment of the $A^3\Pi_u$ state.

Further comparison with the recorded PES from Dyke et al. does...
show the significantly improved resolution on the $a^4\Pi_u$ state as the quartet splitting of the $a^4\Pi_u$ state ($\Omega = 1/2, 3/2, 5/2$) is clearly visible. Dyke et al. predicted a spin–orbit splitting of approximately 160 cm$^{-1}$ or 20 meV. Here, we observe an average splitting of $98^{\pm 26}$ cm$^{-1}$ ($12.1^{\pm 3.2}$ meV) which is well below the resolution of the apparatus used by Dyke et al.

In Fig. 6, we see clear signatures of the $b^4\Sigma_g^+$, and $B^2\Sigma_g^+$ states. Between the $b^4\Sigma_g^+$, and $B^2\Sigma_g^+$ states there are several weak peaks that remain unassigned. In the case $O_2^+$, there are two ionic states found between the $2^2\Sigma_g^+$ and the $2^2\Sigma_u^+$, namely $2^2\Phi_u$ and $2^2\Delta_g$ [45]. Indeed, some states are expected to have small oscillator strength coefficients ($f >$

### Table 4

Spectroscopic parameters pertaining to the two SO components of the $X^2\Pi_{\Omega, g}$ ground state of $S_2^+$ and its isotopologues as obtained by including all of the observed vibrational levels.

| $X^2\Pi_g$ | $T_e$ [cm$^{-1}$] | $\omega_e$ [cm$^{-1}$] | $\omega_e$ [cm$^{-1}$] | Ref. |
|------------|-----------------|-----------------|-----------------|-----|
| $^{32}\text{S}_2$ | 75400 ± 30 | 807 ± 5 | 3.88 ± 0.03 | This work |
| $^{34}\text{S}_2$ | 806.099 | 3.3971 | [23] |
| $^{32\text{S}}^{32}\text{S}$ | 805.9 | 3.38 | [21] |
| $^{34}\text{S}^{32}\text{S}$ | 75410 ± 35 | 797 ± 7 | 3.5 ± 0.3 | This work |

Fig. 4. Vibrational energy level spacings for the $X^2\Pi_{\Omega, g}$ ground state are plotted in black. The red line represents the energy level spacing calculated from the fitted parameters presented in Table 3. Shaded regions denote the propagated uncertainties from the TPES for the measurement (black), and the propagated uncertainties from the fitted parameters (red).

Fig. 5. TPES of $S_2$ from 11.4 eV up to 12.9 eV. Up to 12.0 eV the step size of the TPES is 3 meV, changing to 10 meV above 12.0. Band assignments of the $a^4\Pi_u$, $A^2\Pi_u$ states are depicted as well as comparison with the PES from Dyke et al. [17]
4. Summary and conclusions

In light of recent progress on explaining the abundances (or lack thereof) of observed sulfur in the universe, we have investigated the photoionization spectroscopy and dynamics of the sulfur dimer, S₂. These include the first threshold photoelectron spectrum of S₂ whose resolution is significantly improved as compared with previous photoelectron spectra [17]. We also collected the total ion yield of S₂⁺ with significantly higher resolution than previous measurements [26]. The high-resolution TPES allows us to fit spectroscopic constants to the ionic states of S₂⁺ with higher accuracy and, in turn, guides the assignment of the very rich total ion yield curve exhibiting numerous autoionization features. Interestingly, these autoionization processes also lead to a more precise mapping of the potential energy surface of the X²Σ₉g ground cation state because highly excited vibrational states on the cation can now be accessed indirectly via Rydberg states.

Some unexplored features in the TPES are still observed around the b⁴Σₓ⁻ ; and B²Σᵧ⁻ states. These could be due to e.g., other excited states that have been predicted at higher energies [27], hot bands or even ionization of metastable states of neutral S₂.

CRediT authorship contribution statement

Helgi Rafn Hrodmarsson: Data curation, Formal analysis, Investigation, Writing – review & editing. Gustavo A. Garcia: Data curation, Methodology, Investigation. Laurent Nahon: Project administration, Investigation. Jean-Christophe Loison: Data curation, Methodology, Investigation. Bérenger Gans: Data curation, Formal analysis, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jms.2021.111533.

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