

Observation of vibronically excited thioformaldehyde at 62,000–72,000 cm⁻¹ by 1 + 1' + 1' resonance enhanced multiphoton ionization spectroscopy

Hsing-Chen Wu^{a,b}, Chun-Cing Chen^{a,b}, Yit-Tsong Chen^{a,b,*}

^a Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

^b Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan

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Abstract

Vibronically excited thioformaldehyde (H₂CS) has been studied by two-color 1 + 1' + 1' resonance enhanced multiphoton ionization (REMPI) spectroscopy, in which the $\tilde{C}^1B_2 0_0^0$ state of H₂CS was selected as an intermediate state for the resonant excitation to high-lying electronic states at 62,000–72,000 cm⁻¹. In light of the distinctive selection rules for the 1 + 1' + 1' REMPI and one-photon direct absorption transitions excited from the \tilde{C}^1B_2 and \tilde{X}^1A_1 states of H₂CS, respectively, we have been able to identify 1 valence state ($n\pi$, π^*), and 14 Rydberg states (n , 5s), (π , 4s), (n , 3d_{xz}), (n , 3d_{yz}), (n , 5p_x), (n , 5p_y), (n , 5p_z), (n , 4d_{xz}), (n , 4d_{yz}), (n , 4d_{xy}), (n , 6s), (π , 4p_y), (n , 6p_x), and (n , 6p_y), in this study.

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1. Introduction

Thioformaldehyde (H₂CS), unstable as a monomeric species under normal conditions, is the simplest molecule in the thio-carbonyl family [1]. It is also an important intermediate in organic synthesis [2,3], biological functions [4–6], photochemical reactions [7–10], and astronomical systems [11,12]. In early spectroscopic studies, the ionization energy (IE) and heat of formation of H₂CS were determined by Lossing and Jones using electron impact mass spectroscopy [7]. Callear et al. also recorded the absorption spectra of H₂CS at 210–220 nm with the molecules being generated by the flash photolysis of dimethylid-sulfide (CH₃SSCH₃) [13].

While considerable photodynamic and spectroscopic efforts were made for the two lowest-lying electronic states of H₂CS (\tilde{X}^1A_1 and \tilde{A}^1A_2), studies on the molecular higher excited electronic states are relatively few in number. Moule et al. have assigned rovibrational features in the (π , π^*), (n , 4s), (n , 4p_y),

and (n , 4p_z) transitions at 180–220 nm [1,14,15], in which the electronic identifications were facilitated with the calculation by Bruna et al. [16]. Recently, Kasatani et al. examined the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ (i.e. (n , 4s)) transition of H₂CS centered at 212 nm by 2 + 2 resonance-enhanced multiphoton ionization (REMPI) spectroscopy [17] and analyzed the spectral features with aid of a rotational simulation using the rotational constants determined by Moule's work [1,15]. For the theoretical studies of H₂CS, a wealth of calculations have been conducted for the low-lying electronic states, such as the ground state (\tilde{X}^1A_1) and the first excited singlet (\tilde{A}^1A_2) and triplet (\tilde{a}^3A_2) states [16,18,19]. Furthermore, Hachey and Grein investigated theoretically a series of high-lying electronic states with a multireference configuration interaction (MRCI) method [20–23].

The present experiment has been devoted to observing the excited valence and Rydberg states of H₂CS with excitation energies ranging from 62,000 cm⁻¹ to its first IE of 75,622 cm⁻¹ by two-color 1 + 1' + 1' REMPI spectroscopy. In the 1 + 1' + 1' REMPI spectroscopic scheme (as illustrated in Fig. 1), the $\tilde{C}^1B_2 0_0^0$ state of H₂CS was selected as an intermediate state for the first excitation ($\nu_{\text{exc}} = 47,110.8 \text{ cm}^{-1}$) [1,14]. A second laser was then scanned to search for high-lying electronic states at 62,000–75,622 cm⁻¹. Calculated excitation energies and vibrational frequencies of the electronically excited H₂CS

* Corresponding author at: Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan. Tel.: +886 2 2362 8250; fax: +886 2 2362 0200.

E-mail address: ytschen@pub.iams.sinica.edu.tw (Y.-T. Chen).

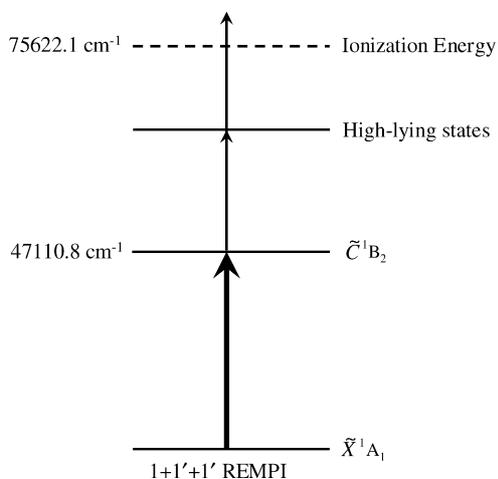


Fig. 1. An illustration of the electronic states involved in the $1 + 1' + 1'$ REMPI excitations. The bold arrow indicates the first excitation of H₂CS from \tilde{X}^1A_1 to \tilde{C}^1B_2 . The subsequent excitation and ionization, represented by the thin arrows, are enhanced when the high-lying Rydberg states of H₂CS are in resonance with the second laser excitation.

have also been applied to assist spectroscopic assignment for the observed $1 + 1' + 1'$ REMPI transitions. This experiment is complementary to a one-photon absorption spectroscopic study of the Rydberg states of H₂CS by Chiang and Lin [24]. Taking advantage of the different spectral selection rules in the $1 + 1' + 1'$ REMPI and one-photon direct absorption transitions, a few new electronic states of H₂CS have been identified by $1 + 1' + 1'$ REMPI spectroscopy in this study.

2. Experiment

Experimental details for two-color $1 + 1' + 1'$ REMPI spectroscopy in this work are similar to those of one-color $2 + 1$ REMPI spectroscopy used previously in our laboratory for the studies of molecular radicals and can be found in several earlier publications [25–27]. In this experiment, H₂CS were produced by the pyrolysis of trimethylene sulfide (TMS, (CH₂)₃S, Acros 97%) in a pyrolytic nozzle of supersonic-jet expansion. The pyrolytic nozzle was temperature-controlled to reach $\sim 700^\circ\text{C}$ to efficiently produce the H₂CS molecules. The molecular beam of H₂CS through the heated nozzle was expanded into a vacuum chamber and skimmed into the ionization region of an 80 cm long time-of-flight (TOF) tube.

In the $1 + 1' + 1'$ REMPI experiment, two tunable dye lasers were employed. The first dye laser (Lambda Physik, LPD3002), pumped by a XeCl excimer laser (Lambda Physik, LPX205i), was operated at 15 Hz with a pulse duration of ~ 20 ns. The second dye laser (Lambda Physik, Scanmate 2E), pumped by the second-harmonic (532 nm) or third-harmonic (355 nm) output of a Nd:YAG laser (Spectra Physics, GCR-190), was operated at 30 Hz with a pulse duration of ~ 7 ns. The double-frequency outputs of the dye lasers generated by a BBO crystal are typically 0.5–10 mJ/pulse at 235–360 nm.

Excitation of the H₂CS molecule to its rotational band-origin of the vibrationless state (0_0^0) in \tilde{C}^1B_2 was implemented by the first dye laser at a fixed frequency of 47,110.8 cm⁻¹. The excited

H₂CS was then pumped further upward by the second dye laser to reach the high-lying electronic states of total excitation energy ranging from 62,000 to 75,622 cm⁻¹. The two laser beams were collimated into the same optical path by a dichroic mirror and were focused with a spherical lens (f.l. = 15 cm) to the ionization region in a vacuum chamber. Time delay between the two lasers was controlled by a digital pulse/delay generator (Stanford Research, DG535) and monitored by a photodiode. The H₂CS⁺ ions, produced via the multiphoton ionization process, were repelled in an electric field [28] and were further collimated by a set of Einzel lenses [29,30] during their flight across the TOF tube. The H₂CS⁺ ions were finally detected by a microsphere plate (MSP, E1-Mul) at the end of the TOF tube. The $1 + 1' + 1'$ REMPI spectra of H₂CS were obtained by gating at $m/z = 46$ (H₂CS⁺) and monitoring the ion yield as a function of excitation laser frequency. The detected signal from the MSP was amplified by a preamplifier (EG&G, VT120), monitored by a digital oscilloscope (LeCroy, 9344), processed in a gated integrator (Stanford Research, SR250) with a repetition rate of 15 Hz, and finally converted to spectral data by an A/D converter. For each step in the frequency scan, signal was averaged for 60–150 laser shots to reduce the noise caused by laser fluctuation. An optogalvanic hollow-cathode lamp filled with Ne (Hamamatsu, L233-13NB) was employed simultaneously in the spectral scan for frequency calibration. Accuracy of this calibration is better than 2 cm⁻¹, and the frequency difference is estimated with a precision of ± 0.5 cm⁻¹.

3. Calculation

Following the extensive calculation of the excitation energies of H₂CS by Hachey and Grein [22], we have calculated the molecular geometries and vibrational frequencies of several electronically excited H₂CS states at 62,000–64,000 cm⁻¹ to assist spectroscopic assignment. The molecular geometries and vibrational frequencies of electronically excited H₂CS were computed with the CASSCF and B3LYP methods, respectively, with the same 6-311 ++ G (d, p) basis set. The adiabatic excitation energies were obtained with an internally contracted MRCI method including all single- and double-excitations from the occupied valence orbitals. The B3LYP calculation was performed using the GAUSSIAN 98 package [31]; the CASSCF and MRCI computation were carried out using the MOLPRO 2000 program [32]. The calculated excited electronic states of H₂CS at 62,000–70,000 cm⁻¹ by Refs. [22,24] together with the computed vibrational frequencies of several Rydberg states in this work are listed in Table 1.

4. Results and discussion

4.1. $1 + 1' + 1'$ REMPI spectrum

Fig. 2 shows the TOF mass spectra of H₂CS obtained by one-color $1 + 1$ resonance-enhanced ionization with the rotational band-origin of $\tilde{C}^1B_2 0_0^0$ (47,110.8 cm⁻¹) as an excitation intermediate state. The increase of H₂CS⁺ signals ($m/z = 46$, Fig. 2(b)) when the pyrolytic nozzle was heat-on, as compared

Table 1

Observed vibronic band positions and spectral assignment for H₂CS studied by 1 + 1' + 1' TREMPI and one-photon absorption spectroscopy (unit: cm⁻¹)

Experimental data					One-photon absorption ^a				Calculated data	
1 + 1' + 1' REMPI									Excitation energies	
Electronic identification	Vibrational assignment	Band position	Vibrational frequency ^b	δ	Electronic identification ^c	Vibrational assignment	Band position	Vibrational frequency ^b	Ref. [22]	Ref. [24]
$(n, 5s) \ ^1B_2$	0_0^0	62,421		2.117	$(n, 5s)$	0_0^0	62,386		62,104	60,491
					$(\pi, 4s) \ ^1B_1^\#$	0_0^0	63,156		64,362	
						3_0^1	63,908	752 (781)		
$(n, 3d_{xz}) \ ^1A_2$	0_0^0	62,630		0.104					61,136	
	0_0^0	63,692	1062 (1063)							
	0_0^0	63,998	1368 (1455)							
$(n\pi, \pi^{*2}) \ ^1A_2$	0_0^0	62,843							61,459	
	3_0^1	63,771	928 (878)							
	2_0^1	64,071	1228 (1439)							
$(n, 5p_z) \ ^1B_2$	0_0^0	64,805		1.815	$(n, 5p_z)$	0_0^0	64,841			64,766
	2_0^1	66,210	1405							
$(n, 3d_{yz}) \ ^1A_1$	0_0^0	65,476		0.289	$(n, 3d_{yz})^\#$		65,420		61,136	
$(n, 5p_x) \ ^1A_2$	0_0^0	65,755		1.665						64,604
$(n, 5p_y) \ ^1A_1$	0_0^0	66,023		1.619	$(n, 5p_y)$	0_0^0	66,004			65,967
$(n, 4d_{z^2}) \ ^1B_2$	0_0^0	67,212		0.388	$(n, 4d_{z^2})$	0_0^0	67,165			67,137
$(n, 4d_{xz}) \ ^1A_2$	0_0^0	67,594		0.303						
$(n, 4d_{yz}) \ ^1A_1$	0_0^0	67,662		0.287	$(n, 4d_{yz})^\#$	0_0^0	67,656			
$(n, 6s) \ ^1B_2$	0_0^0	68,530		2.066	$(n, 6s)$	0_0^0	68,508			68,315
$(\pi, 4p_y) \ ^1A_2$	0_0^0	69,025		1.787					71,299	
$(n, 6p_z) \ ^1B_2$	0_0^0	69,229		1.889	$(n, 6p_z)$	0_0^0	69,274	0_0^0		68,718
$(n, 6p_y) \ ^1A_1$	0_0^0	69,836		1.788	$(n, 6p_y)$	0_0^0	69,847	0_0^0		68,637

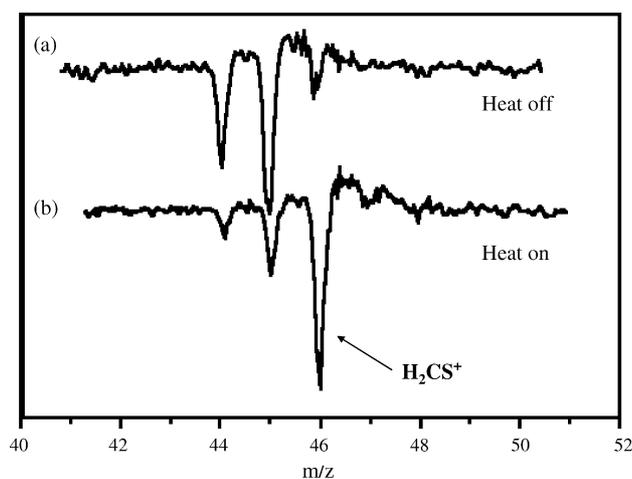
^a Ref. [24].^b Numbers in parentheses are the vibrational frequencies calculated by B3LYP/6-311++G (d, p) in this study.^c The new transitions identified by this study are marked with superscript symbol (#).

Fig. 2. Time-of-flight mass spectra of H₂CS⁺ under the (a) heat-off and (b) heat-on conditions in a flash-pyrolysis process. H₂CS⁺ ions were produced by one-color 1 + 1 resonance-enhanced ionization with the rotational band-origin of $\tilde{C}(\ ^1B_2) \ 0_0^0$ at 47,110.8 cm⁻¹ as an intermediate state for the excitation.

with that at the heat-off condition (Fig. 2(a)), has demonstrated the efficient pyrolysis of TMS to generate H₂CS. The jet-expansion condition of the pyrolytic nozzle to generate H₂CS is similar with that was used in the production of 2-methylallyl radicals in our previous study [27]. The residual H₂CS⁺ signal (*m/z* = 46) in Fig. 2(a), when the pyrolytic nozzle was heat-off, came from the dissociative ionization of the pyrolytic precursor of TMS which has the appearance energy for H₂CS⁺ at 10.4 eV [7]. A composite 1 + 1' + 1' REMPI spectrum of H₂CS, also taking the $\tilde{C}(\ ^1B_2) \ 0_0^0$ as an intermediate state, is shown in Fig. 3(a) with the total excitation energy ranging from 62,000 to 72,000 cm⁻¹. Signal intensity in the composite spectrum was not corrected for changes in the laser energy, but was normalized to the same value in the common wavelength regions of dyes. In the experiments, care was taken to adjust both lasers to have a moderate power level in order to avoid any multiphoton ionization of H₂CS by a single laser. As such, an increase of the H₂CS⁺ signal in 1 + 1' + 1' REMPI spectrum occurred when the two lasers were tuned in resonance with the H₂CS molecule. The observed electronic transitions of H₂CS by 1 + 1' + 1' REMPI spectroscopy are listed in Table 1. For comparison, a recently obtained one-photon absorption spectrum by

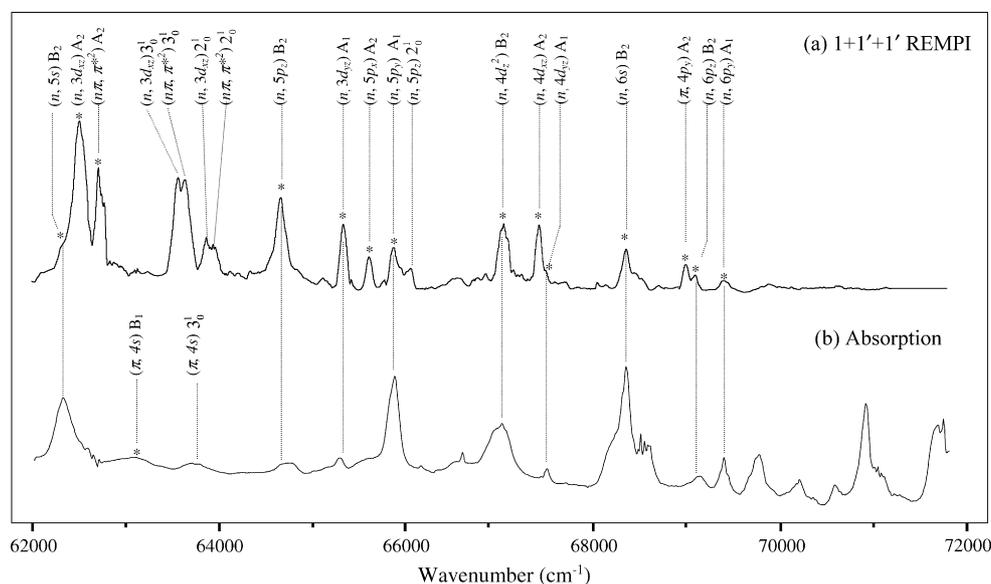


Fig. 3. (a) $1 + 1' + 1'$ REMPI and (b) one-photon direct absorption spectra of H_2CS at $62,000\text{--}72,000\text{ cm}^{-1}$. The 0_0^0 band for each identified excited electronic state is marked by an asterisk.

Chiang and Lin [24] with synchrotron-radiation facility is also conveyed in Fig. 3(b).

4.2. Spectroscopic assignment

Under a C_{2v} molecular symmetry of the H_2CS molecule, the spectral selection rules for one-photon direct absorption and $1 + 1' + 1'$ REMPI transitions are quite different. An excited electronic state of H_2CS with A_2 (B_1) symmetry can (cannot) be reached in the $1 + 1' + 1'$ REMPI transitions with \tilde{C}^1B_2 as an intermediate, but is forbidden (allowed) in the one-photon excitation from the \tilde{X}^1A_1 ground state. Accordingly, peaks present (absent) in the $1 + 1' + 1'$ REMPI excitation, but absent (present) in the one-photon absorption, should belong to the excited states of A_2 (B_1) symmetry. In line with the same reasoning, peaks that appear in both $1 + 1' + 1'$ REMPI and one-photon absorption spectra should correspond to excited states of either A_1 or B_2 symmetry.

Spectroscopic assignment for the Rydberg transitions of H_2CS can further be examined by fitting the band energies of the observed Rydberg states (Table 1) to Rydberg formula. For H_2CS , the Rydberg formula of

$$v = \text{IE} - \frac{R}{(n - \delta)^2} \quad (1)$$

was applied in the fitting, where $\text{IE} = 75,622.1 \pm 24\text{ cm}^{-1}$ is borrowed from the measured value by Ruscic and Berkowitz [33], $R = 109,735.9923\text{ cm}^{-1}$ the Rydberg constant taking the mass of H_2CS into account, n the principal quantum number, and δ is the quantum defect. Considering the uncertainties of IE ($\pm 24\text{ cm}^{-1}$) and measured transition frequencies ($\pm 5\text{ cm}^{-1}$), an uncertainty of ± 0.003 for the resultant quantum defects is estimated from the Rydberg-formula calculation. The fitted quantum defects for the observed Rydberg states of H_2CS by $1 + 1' + 1'$ REMPI spec-

troscopy are listed in Table 1. It is well-documented that the quantum-defect values for the s, p, and d Rydberg orbitals of a sulfur-containing molecule are typically $1 \sim 2$, $1 \sim 2$, and $0 \sim 1$, respectively [34].

Taking into consideration the spectral selection rules, the fitted quantum defects, and the calculated excitation energies of H_2CS by Hachey and Grein [22] and Chiang and Lin [24], we have made spectroscopic assignments for the observed $1 + 1' + 1'$ REMPI transitions of H_2CS as follows (Table 1). Transitions at $62,630$; $62,843$; $65,755$; $67,594$; and $69,025\text{ cm}^{-1}$ should have the excited electronic states of A_2 symmetry, because they are present in the $1 + 1' + 1'$ REMPI spectrum (Fig. 3(a)) and absent in the one-photon direct absorption (Fig. 3(b)). These transitions have been assigned to $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$, $(n, 5p_x)$, $(n, 4d_{xz})$, and $(\pi, 4p_y)$, respectively. The 0_0^0 bands of these assigned electronic transitions have been marked with asterisks in Fig. 3(a). The fitted quantum defects for the assigned $(n, 3d_{xz})$, $(n, 5p_x)$, $(n, 4d_{xz})$, and $(\pi, 4p_y)$ Rydberg states are 0.104, 1.665, 0.303, and 1.787, respectively, in good agreement with the typical quantum-defect values for the p- and d-orbitals of a sulfur-containing molecule.

Peaks at $65,476$; $66,023$; $67,662$; and $69,836\text{ cm}^{-1}$ are assigned to $(n, 3d_{yz})$, $(n, 5p_y)$, $(n, 4d_{yz})$, and $(n, 6p_y)$, respectively, with corresponding quantum defects of 0.289, 1.619, 0.287, and 1.788. These transitions with the final states corresponding to the Rydberg states of A_1 symmetry indeed appear in both $1 + 1' + 1'$ REMPI and one-photon absorption spectra, in accordance with the selection rules mentioned earlier. It is noted that the $(n, 3d_{yz})$ and $(n, 4d_{yz})$ states were observed, yet without assignments, in the one-photon absorption spectrum studied previously by Chiang and Lin [24].

We have assigned the transitions at $62,421$; $64,805$; $67,212$; $68,530$; and $69,229\text{ cm}^{-1}$ to $(n, 5s)$, $(n, 5p_z)$, $(n, 4d_z)$, $(n, 6s)$, and $(n, 6p_z)$, which also render the fitted quantum defects of 2.117, 1.815, 0.388, 2.066, 1.889, respectively. These Ryd-

berg states of B_2 symmetry again show up in both $1 + 1' + 1'$ REMPI and one-photon absorption spectra, as can be seen in Fig. 3(a and b), and comply with the selection rules discussed above.

Finally, electronic transitions appear only in the one-photon absorption spectrum but absent in the $1 + 1' + 1'$ REMPI one should have the excited electronic states of B_1 symmetry. In one-photon absorption spectrum, the broad band at $63,156\text{ cm}^{-1}$ has been assigned to $(\pi, 4s)$ with B_1 symmetry. The identification of $(\pi, 4s)$ is also supported by the calculated excitation energy of $64,362\text{ cm}^{-1}$ for this state predicted by Hachey and Grein [22] within the generally accepted theoretical uncertainty of $\sim 1600\text{ cm}^{-1}$ (0.2 eV). In addition, the observed vibrational frequency of $\nu_3 = 752\text{ cm}^{-1}$ for the C=S stretching mode in the $(\pi, 4s)$ state agrees well with the theoretical value of 781 cm^{-1} calculated by us in this study (Table 1).

As listed in Table 1, the measured band energies of the $(n, 5s)$, $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$, $(n, 5p_z)$, $(n, 5p_x)$, $(n, 5p_y)$, $(n, 4d_{z^2})$, $(n, 4d_{xy})$, $(n, 4d_{yz})$, $(n, 6s)$, $(n, 6p_z)$, $(n, 6p_y)$, and $(\pi, 4s)$ states are in satisfactory consistence with those calculated by Hachey and Grein [22] or Chiang and Lin [22] within the theoretical uncertainty of $\sim 1600\text{ cm}^{-1}$ (0.2 eV), while larger energy discrepancies of 2274 cm^{-1} (0.28 eV) and 4340 cm^{-1} (0.53 eV) were found for $(\pi, 4p_y)$ and $(n, 3d_{yz})$, respectively. In total, eight new electronic states of H_2CS have been identified in this study, five of which $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$, $(n, 5p_x)$, $(n, 4d_{xz})$, and $(\pi, 4p_y)$, have been observed in the $1 + 1' + 1'$ REMPI spectrum and the other three transitions, $(\pi, 4s)$, $(n, 3d_{yz})$ and $(n, 4d_{yz})$, in the one-photon absorption spectrum. The five new excited electronic states of H_2CS observed by $1 + 1' + 1'$ REMPI spectroscopy are of A_2 symmetry, which cannot be reached by one-photon absorption spectroscopy. Some common states observed by both $1 + 1' + 1'$ REMPI and one-photon absorption [24] spectroscopies have energy deviations of $\sim 50\text{ cm}^{-1}$, which could come from the uncertainties of $1 + 1' + 1'$ REMPI ($\pm 5\text{ cm}^{-1}$) and one-photon absorption spectroscopy ($0.04\text{ nm} \approx \pm 20\text{ cm}^{-1}$).

In this study, the Rydberg transitions observed in the $1 + 1' + 1'$ REMPI spectrum have relatively strong 0_0^0 bands with only very short (or without) companion vibrational progressions. Taking into account the Franck-Condon factors, this outcome indicates the geometric similarity between the \tilde{C}^1B_2 intermediate state and the high-lying Rydberg states of H_2CS . In the $1 + 1' + 1'$ REMPI spectrum, several electronic transitions accompany with vibrational progressions, such as the ν_3 mode (C=S stretching) showing up in the $(n, 3d_{xz})$ and $(n\pi, \pi^{*2})$ states and the ν_2 mode (CH_2 bending) presenting in $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$ and $(n, 5p_z)$. The appearances of the ν_3 and ν_2 vibrational modes have suggested substantial geometric changes in the bond length of r_{CS} and the bond angle of \angle_{HCH} , respectively, when the H_2CS molecule was excited from \tilde{C}^1B_2 to high-lying electronic states. The observed large changes in the C=S stretching frequency from the \tilde{X}^1A_1 ground state ($\nu_3 = 1059.2\text{ cm}^{-1}$) [35,36] to the excited states of $(n\pi, \pi^{*2})$ and $(\pi, 4s)$ ($\nu_3 = 928$ and 752 cm^{-1} , respectively) can also be rationalized by the weakening of the C=S bond strength after the n/π electronic excitations to the π^* anti-bonding or $4s$ Rydberg states.

5. Conclusions

We have observed the high-lying vibronic states of H_2CS at $62,000\text{--}72,000\text{ cm}^{-1}$ by $1 + 1' + 1'$ REMPI spectroscopy. In total, we have identified fourteen electronic states in the $1 + 1' + 1'$ REMPI spectrum, i.e. $(n, 5s)$, $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$, $(n, 5p_z)$, $(n, 3d_{yz})$, $(n, 5p_x)$, $(n, 5p_y)$, $(n, 4d_{z^2})$, $(n, 4d_{xz})$, $(n, 4d_{yz})$, $(n, 6s)$, $(\pi, 4p_y)$, $(n, 6p_z)$, and $(n, 6p_y)$. Distinctive selection rules for the $1 + 1' + 1'$ REMPI and one-photon direct absorption transitions have allowed us to identify five new electronic states of A_2 symmetry in H_2CS , including $(n, 3d_{xz})$, $(n\pi, \pi^{*2})$, $(n, 5p_x)$, $(n, 4d_{xz})$, and $(\pi, 4p_y)$. In addition, three states of $(\pi, 4s)$, $(n, 3d_{yz})$, and $(n, 4d_{yz})$ observed previously by one-photon absorption spectroscopy have also been identified in this study.

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