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快 报

CS_2^+ 经由 $\widetilde{B}\,^2\Sigma_u^+ \leftarrow \widetilde{X}\,^2\Pi_{g,3/2}$ 跃迁的[1+1]光倒空和光碎片激发谱*

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摘 要： 用483.2 nm的电离激光使CS_2分子经由[3+1] REMPI制备出CS_2^+（$\widetilde{X}\,^2\Pi_{g,3/2}$）后，在270～285 nm扫描解离激光获得了$CS_2^+$经由$\widetilde{B}\,^2\Sigma_u^+ \leftarrow \widetilde{X}\,^2\Pi_{g,3/2}$跃迁的光倒空和光碎片激发谱，由此给出了$CS_2^+\,\widetilde{B}\,^2\Sigma_u^+$电子态的振动频率$\nu_1 = 613\ cm^{-1}$和$2\nu_2 = 707\ cm^{-1}$. 分析表明，正是$CS_2^+$的[1+1]双光子光激发解离过程导致了母体离子$CS_2^+$的光倒空和光解离成碎片离子$CS^+$和$S^+$，该过程中光碎片离子的分支比$CS^+/S^+$大约为3.

关键词： CS_2^+；光倒空；光碎片激发谱
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The [1+1] Photo-depletion and Photo-fragment Excitation Spectra of CS_2^+ via $\widetilde{B}\,^2\Sigma_u^+ \leftarrow \widetilde{X}\,^2\Pi_{g,3/2}$ Transitions*

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Key words CS_2^+, Photo-depletion, Photo-fragment excitation spectrum

As an important molecule astrophysics and atmospheric physics,[1] CS_2^+ has been the subject of extensive study[2-12]. For example, the predissociation via $\widetilde{C}\,^2\Sigma_g^+ \leftarrow \widetilde{B}\,^2\Sigma_u^+ \leftarrow \widetilde{X}\,^2\Pi_{g,3/2}$ transitions has been investigated by using an optical-optical resonance technique[8,9]. Recent studies[2,3] shows that the dissociation of CS_2^+ to produce $S^+ + CS$ and $CS^+ + S$ may proceed via the energy curve crossing between $\widetilde{B}\,^2\Sigma_u^+$ state and the repulsive $^4\Sigma^-$ state and/or $^2\Sigma^-$ state correlated with the first and the second dissociation limits. Hence, the $\widetilde{B}\,^2\Sigma_u^+$ state plays a very important role in the photochemistry of CS_2^+ and its spectral constants are mainly found in the photoelectron spectrum[4,5]. The aim of this work is to excite the $CS_2^+(\widetilde{B}\,^2\Sigma_u^+) \leftarrow CS_2^+(\widetilde{X}\,^2\Pi_{g,3/2})$ transition and to obtain the photo-depletion and photo-fragment excitation spectra by using laser in the range of 270–285 nm, as well as to investigate the related photodissociation mechanism.

The experimental setup[2,3] consists of (i) a pulsed molecular beam source to generate jet-cooled CS_2 molecules by the supersonic expansion of a CS_2/Ar

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gas mixture (CS_2/Ar at about 10%, around 3 atms) through a pulsed nozzle (General Valve), with a nozzle orifice diameter of 0.5 mm into a photoionization chamber, (ii) the ionization, dye laser (483.2 nm, about 1.5 mJ/pulse) focused perpendicularly to the molecular beam of CS_2 by a quartz lens with f = 150 mm to produce CS_2^+ via [3 + 1] resonance enhanced multi-photon ionization (REMPI) of CS_2 molecules[2,3], (iii) the dissociation dye laser (270 – 285 nm, about 0.02 mJ/pulse) coaxially counterpropagated and weakly focused by another quartz lens with f = 300 mm to excite CS_2^+, (iv) a home-made time-of-flight (TOF) mass spectrometer with a 70 cm long TOF tube and a microchannel plate (MCP) detector to obtained the mass selected photofragment excitation spectrum. Both dye lasers were temporally and spatially matched at the laser-molecular interaction point.

Fixing the wavelength of the ionization laser at 483.2 nm, we could certainly prepare exclusive CS_2^+ in the $\tilde{X}\ ^2\Pi_g$ state with a minimum amount of S^+ and CS^+ by using a lens with a middlefocal length of f = 150 mm and optimizing the laser pulse energy at about 1.5 mJ[2,3].

With the ionization laser fixed at 483.2 nm to produce CS_2^+ and the dissociation laser scanned in the range of 270 – 285 nm, there are evident signals of fragment ions S^+ and CS^+ in the TOF mass spectrum generated from the interaction of the dissociation laser on the parent CS_2^+. Using this approach, the photodissociation spectra via the $\tilde{B}\ ^2\Sigma_u^+(\nu_1\nu_2 0) \leftarrow \tilde{X}\ ^2\Pi_{g,3/2}(000)$ transition of CS_2^+ have been obtained. Figure 1 shows the depletion spectrum of the parent ion CS_2^+ and the enhancement spectrum of fragment ions CS^+ and S^+ obtained by minotoring CS_2^+, CS^+ and S^+, respectively. With the aid of the spectroscopic data obtained from previous studies of redundant CS_2^+[4,5,11,12], the photo-dissociation spectra could be assigned as the electronic transition $\tilde{B}\ ^2\Sigma_u^+(\nu_1\nu_2 0) \leftarrow \tilde{X}\ ^2\Pi_{g,3/2}(000)$ of CS_2^+. The assignments for the photodissociation spectra are given in Fig. 1 and Table 1. Also listed in Table 1 are the spectral data obtained by emission spectra[11] and the photoionization resonance spectra[12]. Although the photoexcitation of the $\tilde{B}\ ^2\Sigma_u^+(000) \leftarrow \tilde{X}\ ^2\Pi_{g,3/2}(000)$ transition was used in previous studies[8,9], the photoexcitation spectrum of the $\tilde{B}\ ^2\Sigma_u^+(\nu_1\nu_2 0) \leftarrow \tilde{X}\ ^2\Pi_{g,3/2}(000)$ transitions is not reported until now. From table 1 the symmetric stretching vibration frequency and bending vibration frequency are deduced, in this case, ν_1 = 613 cm^{-1} and $2\nu_2$ = 707 cm^{-1}.

The energy levels of $\tilde{B}\ ^2\Sigma_u^+$ corresponding to the resonance peaks in Fig. 1 are all less than the first dissociation limit (4.6 eV) to produce S^+ and the

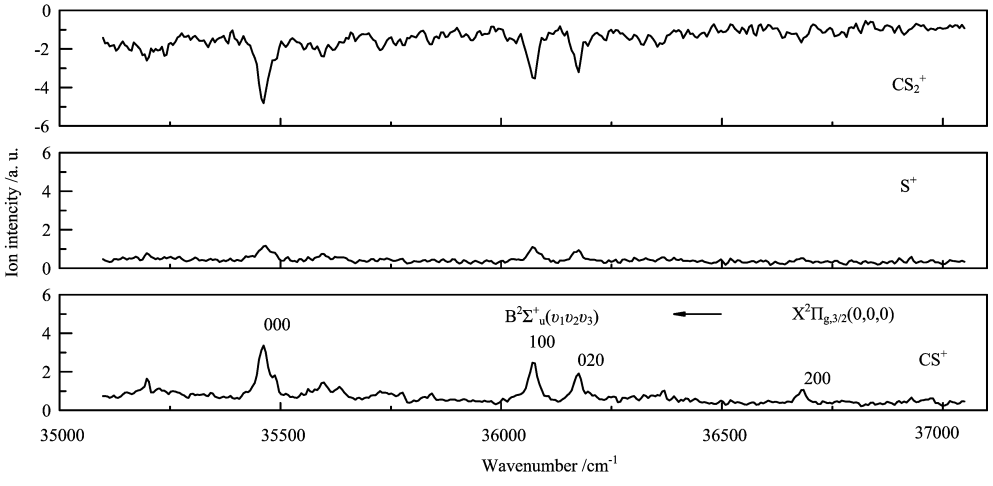

Fig. 1 The photodissociation spectra (the depletion spectrum of parent ion CS_2^+ and the enhanced spectra of fragment ions S^+ and CS^+) obtained by scanning the dissociation laser in the range of 270 – 285 nm
The spectra are assigned to the $\tilde{B}\ ^2\Sigma_u^+(\nu_1\nu_2\nu_3) \leftarrow \tilde{X}\ ^2\Pi_{g,3/2}(000)$ transitions of CS_2^+.

Table 1　Observed $\tilde{B}\,^2\Sigma_u^+(\nu_1\nu_20) \leftarrow \tilde{X}\,^2\Pi_{g,3/2}(000)$ transitions in 1 + 1 photodissociation spectra and the corresponding assignments

$\tilde{B}\,^2\Sigma_u^+$ $(\nu_1\nu_20) \leftarrow \tilde{X}\,^2\Pi_{g,3/2}(000)$	ν_{exp}/cm^{-1}	Refs. [8,9]	Ref. [11][a]	Ref. [12][b]	Spacing/cm^{-1}
000	35468	35460	35461	35507	0
100	36081		36063	36110	613
020	36175				707
200	36690				1222
120	36783				1315

a: These values are from the electronic emission spectra in Ref. [11].

b: These values are deduced from the photoionization resonance spectra of CS_2 in Ref. [12].

second dissociation limit 5. 852 eV to produce CS^+[3,6]. Accordingly two photons are needed in the dissociation of CS_2^+, that is, the dissociation process via the $\tilde{B}\,^2\Sigma_u^+ \leftarrow \tilde{X}\,^2\Pi_{g,3/2}$ transition of CS_2^+ to produce CS^+ and S^+ is a [1 + 1] process. It is shown in Figure 1 that the CS^+/S^+ branching ratio decreeses from about 3 for the $\tilde{B}\,^2\Sigma_u^+(000) \leftarrow \tilde{X}\,^2\Pi_{g,3/2}(000)$ transition to about 2.5 for the $\tilde{B}\,^2\Sigma_u^+(100) \leftarrow \tilde{X}\,^2\Pi_{g,3/2}$ (000) transition. The branching ratios of 2. 5 – 3 measured in this work are consistant with those given by the photoelectron-photon coincidence spectra of CS_2 in the same energy range reached by two photon excitation of CS_2^+[13]. This means that the [1 + 1] dissociation mechanism is indeed a reasonable presumption. Since the two photon excitation energy (8. 7 – 9. 2 eV) of a dissociation laser in the 270 – 285 nm is at Satellite 3[5] and beyond several dissociation limits of CS_2^+, it is hard to determine accurate dissociation paths to produce CS^+ and S^+. However, the TOF mass peaks widths of CS^+ and S^+ are observed to be nearly the same as that of CS_2^+, from this we conclude that the available energy in the dissociation process and the kinetic energy of fragment ions are small.

To check if there any disturbance from the ionization laser on the photodissociation of CS_2^+, we repeated the experiment with about a 60 ns delay and a slight separation in the direction of ion flight between the dissociation laser and the ionization laser in the laser-molecule interaction region. This result means that there is no temporal overlap between the ionization laser and the dissociation laser, when using roughly a 5 ns pulse width. The same result obtained indicates that the disturbance from the ionization laser can be negligible in the photodissociation experiment of CS_2^+. The 1 + 1 photodissociation process of CS_2^+ via the $\tilde{B}\,^2\Sigma_u^+ \leftarrow \tilde{X}\,^2\Pi_{g,3/2}$ transition can be expressed as follows

$$CS_2^+(\tilde{X}\,^2\Pi_g) \xrightarrow{h\nu} CS_2^+(\tilde{B}\,^2\Sigma_u^+)$$

$$CS_2^+(\tilde{B}\,^2\Sigma_u^+) \xrightarrow{h\nu} CS_2^+(\text{Statellite 3 or other repulsive states nearby}) \begin{cases} \longrightarrow CS + S^+ \\ \longrightarrow CS^+ + S \end{cases}$$

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