Multi-reference configuration-interaction calculations on multiply charged ions of carbon monosulfide*

Yan Bing(闫 冰)[a)†] and Zhang Yu-Juan(张玉娟)[b)]

[a)] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China
[b)] Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China

(Received 1 June 2012; revised manuscript received 28 June 2012)

The potential energy curves for neutrals and multiply charged ions of carbon monosulfide are computed with highly correlated multi-reference configuration interaction wavefunctions. The correlations of inner-shell electrons with the scalar relativistic effects are included in the present computations. The spectroscopic constants, dissociation energies, ionization energies for ground and low-lying excited states together with corresponding electronic configurations of ions are obtained, and a good agreement between the present work and existing experiments is found. No theoretical evidence is found for the adiabatically stable CS^{q+} ($q > 2$) ions according to the present *ab initio* calculations. The calculated values for 1st–6th ionization energies are 11.25, 32.66, 64.82, 106.25, 159.75, and 224.64 eV, respectively. The kinetic energy release data of fragments are provided by the present work for further experimental comparisons.

Keywords: potential energy curve, spectroscopic constants, multi-reference configuration interaction, kinetic energy release

PACS: 31.15.ae, 31.50.Df, 33.15.Fm **DOI:** 10.1088/1674-1056/22/2/023103

1. Introduction

The growing research interests in multiply charged molecular ions are arising from their physicochemical properties and their important roles in the dynamical process in plasma, ionosphere chemistry, strong-field physics and astrophysics.[1–6] The characteristics of electronic states of ions such as bound or repulse along potential energy curves (PECs), positions of minima, the dissociation energies or barrier height for bound or quasibound states, the vertical and adiabatic ionization energies are of great importance for experimental and theoretical research.

The neutral carbon monosulfide molecule naturally exists in the interstellar medium.[7] The multiply charged ions of CS generated through Coulomb explosions were observed in intense laser fields,[8–10] and subsequently became the subject of experimental and theoretical efforts.[11,12] The monocation and dication of CS were experimentally investigated with ion translational energy spectrometry[11] and synchrotron radiation photoelectron spectroscopy,[13] and the ground state and some low-lying excited states were characterized. Nobumitsu[14] studied the lowest 1-$5^2\Sigma^+$ and 1-$3^2\Pi$ states of CS^+ with the configuration interaction (CI) method, and then used molecular vibrations based on accurate potential energy functions of $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, and $C^2\Sigma^+$ to explain the vibrational structure of the observed photoelectron band of CS.[15] The lowest eleven electronic states of CS^{2+} were calculated with multi-reference CI method by Šedivcová *et al.*,[12] and the pathways of a three-body Coulomb explosion process of CS_2^{3+} ion were determined. It is obvious that the theoretical calculations on multiply charged ions, especially on CS^{q+} ($q > 2$), are not enough to understand the physicochemical natures of these species. Another motivation of present computation is driven by the studies on triple ionization of carbon monoxide: up to now, experimental and theoretical work gives no evidence for metastable CO^{3+}.[16] However, recent time-of-flight mass spectroscopy hints at the existence of possible metastable states for CO^{4+} and CO^{5+} ions.[17] Since the $n = 2$ shell electrons of the sulfur atom contribute more significant shielding than those of the carbon atom, whether a low-lying metastable state of CS^{q+} ($q > 3$) exists is an interesting question, which will also provide new insights into the understanding of the ionization process of CS.

In this work, we perform theoretical computations on a large set of electronic states for CS^{q+} ($q = 0 \sim 6$) with highly correlated wavefunctions. In addition, the scalar relativistic (mass-velocity term and Darwin term) corrections and the correlation energies of inner-shell electrons, which are both excluded in previous calculations, are considered in the present computations. We subsequently calculate the potential energy curves for low-lying states of CS^{q+} ($q = 0 \sim 6$), and evaluate theoretically (i) the spectroscopic constants of bound and quasibound states, (ii) dissociation energies for bound states and dissociation barriers for metastable states, (iii) vertical and adiabatic ionization energies for each species, and (iv) kinetic energy release (KER) data for different dissociation channels. We believe that the results of the present study are helpful

*Project supported by the National Magnetic Confinement Fusion Science Program of China (Grant No. 2010GB104003) and the Fundamental Research Funds for the Central Universities, China (Grant No. 450060481375).

†Corresponding author. E-mail: yanbing@jlu.edu.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

for understanding existing and further experiments concerning multiply charged ions of carbon monosulfide.

2. Methods and computational details

The electronic structure computations are performed with Molpro2010 package.[18] The state-averaged complete active space self-consistent field (SA-CASSCF) calculations are carried out to construct the reference orbital, followed by computations with internal contracted multi-reference configuration interaction method with Davidson correction (icMRCI+Q) to evaluate dynamical correlations. The active space is composed of 5-8σ and 2-3π (5-8a_1, 2-3b_1, and 2-3b_2 in C_{2v} symmetry) orbitals. The core molecular orbitals 1-4σ and 1π are constrained to be doubly occupied but optimized in SA-CASSCF calculations. In the icMRCI treatment of CS^{q+} ($q = 0 \sim 6$), only the correlations of 1-2σ orbitals (the 1s core orbitals for C and S atoms) are excluded, that is, the electron correlations of 3-8σ and 1-3π orbitals including the $n = 2$ inner shells of sulfur are considered in this work. We use the one-electron second order transformation of the Douglas–Kroll–Hess (DKH2) approach[19–21] to evaluate the scalar relativistic energy corrections. The uncontracted correlation-consistent aug-cc-pV5Z basis set of Dunning and co-workers[22,23] is used throughout this work, and several millions of configuration state functions are used to describe each state in icMRCI calculations.

The spectroscopic constants are obtained by solving the one-dimensional Schrödinger equation based on calculated PECs,[24] and the tunneling lifetimes of quasibound levels are evaluated by the uncertainty principle with calculated level widths using the method developed by Le Roy and Liu.[25]

3. Results and discussion

3.1. Potential energy curves and spectroscopic constants

The computed PECs for considered electronic states of CS^{q+} ($q = 0, 1, 2$) are illustrated in Figs. 1 and 2. The spectroscopic constants of bound states are listed in Table 1 with other theoretical and experimental values listed for comparison. The PEC for ground state $X^1\Sigma^+$ of neutral CS is first computed to probe the accuracy of theoretical method used in this work. We compare the computed spectroscopic constants of $CS(X^1\Sigma^+)$ with the experimental values summarized in a previous review,[26] and find excellent agreement between theory and experiment. The theoretical equilibrium bond distance deviates from the experimental value by less than 0.001 Å (1 Å=0.1 nm). The harmonic frequency ω_e is overestimated by one percent (14 cm^{-1}), the calculated anharmonic frequency $\omega_e x_e$ and rotational constant B_e are both in good accordance with experimental results. The theoretical dissociation energy D_e falls exactly into the error bar in experimental values. The calculated results reveal that the present theoretical method used is very accurate to describe the CS molecular system.

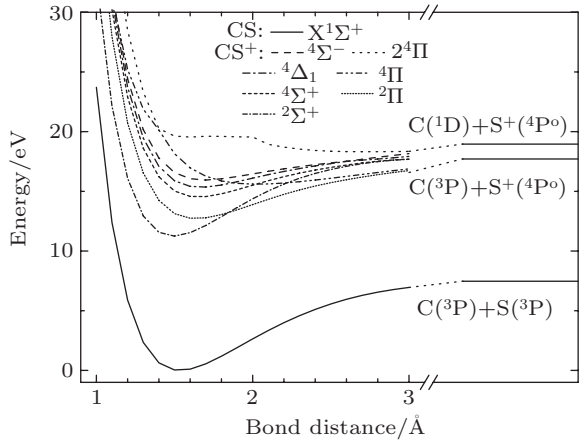


Fig. 1. Potential energy curves of CS and CS^+.

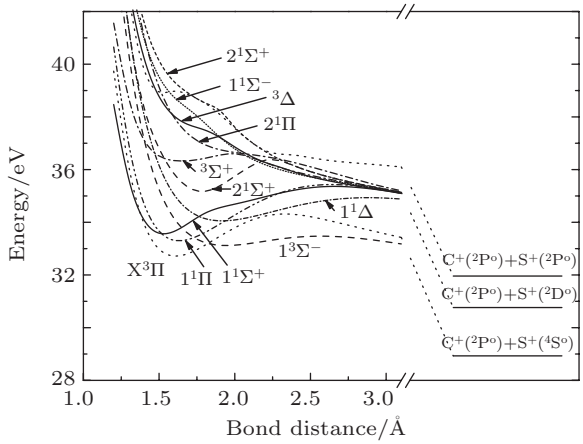


Fig. 2. Potential energy curves of low-lying states of CS^{2+}.

The calculated equilibrium bond distance of singly ionized $CS^+(X^2\Sigma^+)$ is 1.490 Å, which is underestimated by 0.003 Å compared with experimental value.[28] The calculated values of ω_e and $\omega_e x_e$ are in the same accuracy as those of neutral CS. The calculated relative energy T_e above $CS(X^1\Sigma^+)$ is 11.25 eV, which is only 0.08 eV smaller than the adiabatic ionization energy of CS, (11.33±0.02) eV. The dissociation energy D_e for $CS^+(X^2\Sigma^+)$ is calculated to be 6.46 eV. The $A^2\Pi$ state of singly ionized CS is 1.42 eV above its ground state, and the energy gap accords with the experimental $A^2\Pi$–$X^2\Sigma^+$ transition energy of 1.486 eV. The dissociation energy of $CS^+(A^2\Pi)$ is determined to be 4.99 eV at the icMRCI+Q level. The lowest four quartet electronic states are typical bound states with dissociation energy in a range of 2 eV∼4eV. The first quartet state $^4\Sigma^+$ originates from 5-7$\sigma^2 2\pi^2 3\pi^1$ configuration, which lies 3.28 eV above the ground states with an energy minimum at 1.6520 Å. The values of ω_e for the lowest $^4\Sigma^+$, $^4\Delta$, and $^4\Sigma^-$ states are all approximately 1000 cm^{-1} in magnitude, and about one third smaller than that of the ground state. The potential of first quartet Π state is rather flat, and the dissociation energy is reduced to one third of that for the ground state. The energy minimum point of $^4\Pi$ state is

shifted to a longer bond distance at 2.035 Å. The $2^4\Pi$ state is a metastable one with a barrier of 0.08 eV along the dissociation path adiabatically correlating to ground state $S^+(^4P^o)$ ion and excited neutral $C(^1D)$.

Table 1. Spectroscopic constants for bound states of CS^{q+} ($q = 0, 1, 2$).

Species	States	Reference	r_e/Å	ω_e/cm^{-1}	$\omega_e x_e$/cm^{-1}	B_e/cm^{-1}	T_e/eV	D_e[a]/eV
CS	$X^1\Sigma^+$		1.5350	1298.60	6.73	0.821	0	7.47
		expt. [26]	1.53496	1285.15	6.50	0.8200	0	7.46±0.02
								7.49±0.04
CS^+			1.4901	1387.10	7.64	0.868	11.25	6.46
	$X^2\Sigma^+$	expt. [26]	1.493	1376.6	7.8	–		
		expt. [27]					11.33±0.02 (T1)	
			1.6373	1025.9	6.75		12.72	
	$A^2\Pi$	expt. [26]	1.640	1013.7	6.7	0.721	T_1+1.486	4.99
	$^4\Sigma^+$		1.6520	997.7	8.36	0.708	14.53	3.18
	$^4\Delta$		1.6650	924.1	9.98	0.696	15.34	3.61
	$^4\Pi$		2.0253	490.3	2.64	0.472	15.60	2.11
	$^4\Sigma^-$		1.6880	817.1	10.96	0.676	15.95	3.01
	$2^4\Pi$		1.5737	$G_{1/2} = 668.5$	–	0.494	17.10	(0.08)
CS^{2+}	$X^3\Pi$		1.5928	1043.8	11.73	0.758	32.66	(1.67)
		theory [12]	1.607	1032.6	10.6	0.748	32.76(T2)	
	$A^3\Sigma^t$		1.9350	553.9	17.09	0.517	33.10	(0.38)
		theory [12]	1.953	515.8	13.8	0.505	T2+0.385	
	$a^1\Pi$		1.6226	991.6	9.72	0.735	33.24402	(2.19)
		theory [12]	1.629	975.3	9.6	0.728	T2+0.624	
	$b^1\Sigma^r$		1.5204	1319.4	34.49	0.837	33.4839	(1.88)
		theory [12]	1.525	1170.5	22.4	0.825	T2+0.874	
	$c^1\Delta$		1.9091	596.2	7.46	0.532	34.03545	(0.90)
		theory [12]	1.919	575.0	5.8	0.524	T2+1.374	
	$d^1\Sigma^r$		1.7844	1120.1	17.24	0.609	35.10567	(1.32)
		theory [12]	1.791	1118.2	19.8	0.604	T2+2.440	
	$B^3\Sigma^r$		1.6444	599.8	6.94	0.718	36.31	(0.33)
		theory [12]	1.651	575.0	6.4	0.718	T2+3.570	

[a] The values in parentheses are barrier heights for metastable states.

The ground state and low-lying electronic excited states of CS^{2+} dication are metastable, and the barrier heights along adiabatic PECs are in a range of 2 eV–3 eV. In a region of $R > 2.5$ Å, the PECs of most states obviously exhibit the nature of Coulomb repulsive interaction. The ground state of dication CS^{2+} is determined as triplet Π state originating from $5\sigma^2 6\sigma^2 2\pi^3 7\sigma^1$ configuration. Comparing with previous *ab initio* work, we find that the additional corrections to scalar relativistic effect and inner-shell correlation lead to the decrease of bond distance by ~ 0.01 Å and the slight increase of ω_e, $\omega_e x_e$, and B_e for $X^3\Pi$ state. The icMRCI+Q value for adiabatic double ionization energy of CS is 32.66 eV, which is close to the calculated value 32.76 eV[12] with couple-cluster theory. The potential energy maximum of $CS^{2+}(X^3\Pi)$ state is at a bond distance of 2.3238 Å with a barrier height of 2.32 eV. The first electronic excited state of CS^{2+} is $A^3\Sigma^-$, and the energy gap for A–X is 0.34 eV, which is close to the previous theoretical value 0.385 eV. It is found that the additional scalar relativistic and inner-shell correlation correction lead to more significant change for PECs of excited states than those of ground state by comparing the spectroscopic constants calculated in the present work and Ref. [12]. For instance, the bond distance of $A^3\Sigma^-$ state is reduced by ~ 0.02 Å, while ω_e of the $b^1\Sigma^+$ state is overestimated by $\sim 12\%$ (150 cm^{-1}), with additional corrections taken into account. Briefly, the main features of PECs for dication CS^{2+} are in agreement with previous theoretical results, while for excited states, the additional corrections in this work, including to scalar relativistic effect and correlations of inner-shell electrons, tend to lead to more prominent changes for CS^{2+}.

The calculated PECs of low-lying electronic states of CS^{q+} ($q = 3 \sim 6$) ions are shown in Fig. 3. The lowest four doublet electronic states $^2\Delta$, 1-$2^2\Pi$, and $^2\Sigma^+$ correlated to $C^+(^2P^o)$+$S^{2+}(^3P)$ are investigated with icMRCI+Q theory. The $^2\Delta$ state which originates from configuration $5\sigma^2 6\sigma^2 7\sigma^1 2\pi^2$ is the lowest electronic state for CS^{3+}. The potentials for these four states are rather flat in a short-range bond distance and an avoided crossing point is found in 1-$2^2\Pi$ states. The avoided crossing point is located at 1.8 Å, which will lead to a diabatic energy minimum, while according to the present *ab initio* calculations, no obvious minima are found for adiabatic potentials of triply ionized CS. For highly charged ions CS^{q+} ($q = 4 \sim 6$), the potentials are repulsive even at a short-range bond distance. In a range of $R = 1.3$ Å~ 1.4 Å ,

crossing points along adiabatic PECs are found in CS^{6+} ion, and the $^1\Sigma^+$ state correlated to the lowest dissociation limit $C^{2+}(^1S)$+$S^{4+}(^1S)$ crosses with the $^{1,3}\Pi$ states which are correlated to a higher dissociation limit. For a low-lying electronic state, strong repulsive interactions are found to be dominant in CS^{q+} $(q = 4 \sim 6)$ ions.

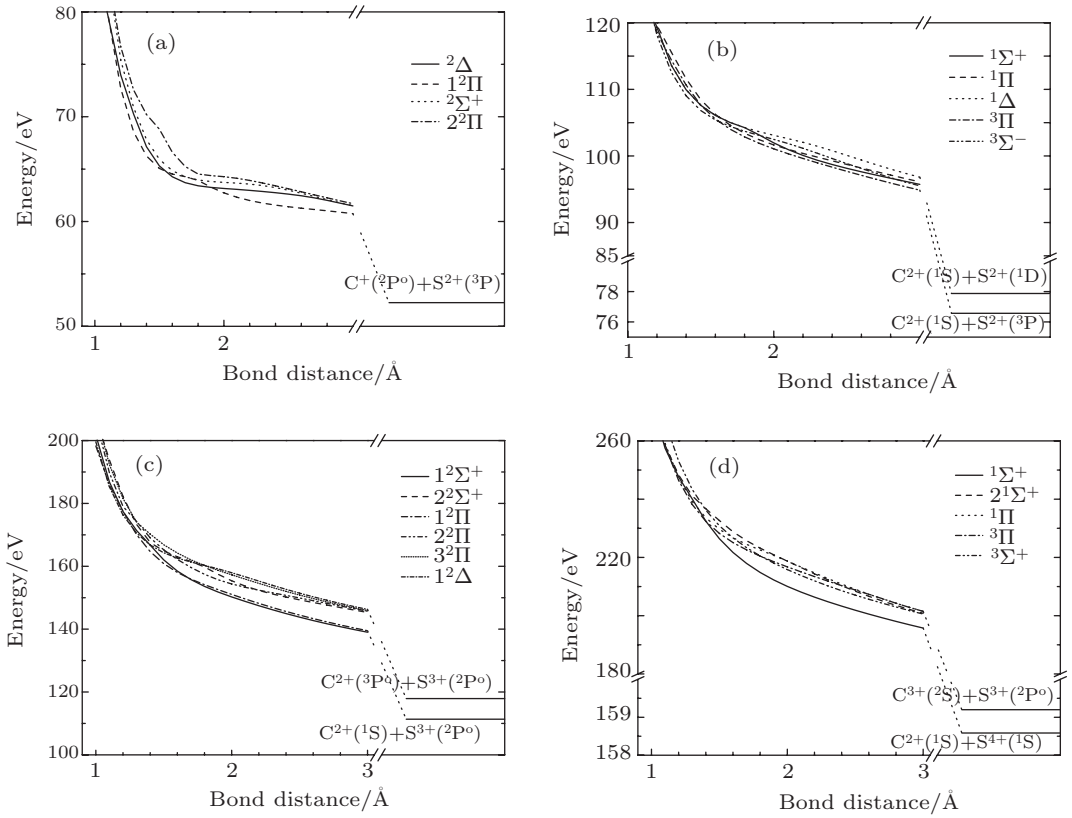


Fig. 3. Potential energy curves of low-lying electronic states for (a) CS^{3+}, (b) CS^{4+}, (c) CS^{5+}, and (d) CS^{6+}.

3.2. Vertical and adiabatic ionization energy

The vertical and adiabatic ionization energies of CS evaluated with icMRCI+Q method together with dominant configurations are listed in Table 2. The photoelectron spectrum of CS was observed early in 1972,[27] and the theoretical calculations[14] were performed to explain the vibrational structure of the first four bands. The first ionization of CS originates from the loss of one electron from the doubly occupied 7σ orbital. The first adiabatic ionization energy has been measured experimentally by numerous investigators, and the experimental values range from 11.0 eV to 11.71 eV, while most of them concentrate at 11.33 eV.[27,28] The present vertical and adiabatic ionization energies are calculated to be 11.30 eV and 11.25 eV, respectively, which indicates that the diagonal v'–v'' ionization is preferred more in $CS(X^2\Sigma^+)$–$CS^+(X(1)^3\Pi)$ ionization. Both of the ionization energy values are in good agreement with experimental results. The second band in the ionization spectrum is assigned to $A^2\Pi$ state of CS^+, the adiabatic ionization energy is determined to be 12.79 eV.[27] The $A^2\Pi$ band comes from the $5\text{-}7\sigma^2 2\pi^3$ configuration with one electron stripped from 2π orbital. Our calculated adiabatic ionization energy is 12.72 eV, which is underestimated by only 0.07 eV. Our calculated vertical ionization energy is 12.93 eV. Four bands corresponding $^4\Sigma^+$, $^4\Delta$, $^4\Pi$, and $^4\Sigma^-$ states are found to be in a range of 14 eV∼18 eV. The $2^4\Pi$ state of CS^+ is a metastable state with only one vibrational level contained in its potential, so the $2^4\Pi$ band in ionization spectrum should be near continuum.

The adiabatic ionization energy of CS^+ ion is 32.73–11.25=21.48 eV, which is close to previous theoretical values in a range of 21.48 eV–21.64 eV, and also in good agreement with experimental value (22.0±0.9) eV. The present vertical double ionization energy of neutral CS is calculated to be 32.66 eV, which falls exactly into the error bar of experimental value (33.3±1.1) eV. In a range of 33 eV–40 eV, massive photoelectron bands of CS^+ can be expected to correspond to the excited states of CS^{2+}. The dominant configuration of CS^{2+} is $5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3$, and it is found that one additional electron in 2π orbital is stripped from the ground-state CS^+ ion. The vibrational structures of some ionization bands are heavily overlapped due to small energy gaps between them (e.g. only 0.1 eV between $a^1\Pi$ and $b^1\Sigma^+$ state), which are difficult to distinguish in experiment. Other calculated double ionization energy data of CS and corresponding electronic configurations of ionic states are listed in Table 2 for further comparison.

Table 2. Vertical and adiabatic energies (in eV) for CS^{q+} and the leading configurations of ionic states.

Species	States	Dominant configuration	Vertical energy/eV	Adiabatic energy/eV	Species	States	Dominant configuration	Vertical energy/eV
CS^+	$X(1)^2\Sigma^+$	$5\sigma^2 6\sigma^2 2\pi^4 7\sigma^1$	11.30	11.25 11.33±0.01[27]	CS^{3+}	$1^2\Sigma^+$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^2$	65.48
	$A(1)^2\Pi$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^3$	12.93	12.72		$1^2\Pi$	$5\sigma^2 6\sigma^2 2\pi^3$	64.82
	$1^4\Sigma^+$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3 3\pi^1$	14.80	14.53		$1^2\Delta$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^2$	64.86
	$1^4\Delta$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3 3\pi^1$	15.66	15.34		$2^2\Pi$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^1$	68.04
	$1^4\Sigma^-$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3 3\pi^1$	16.33	15.95	CS^{4+}	$1^1\Delta$	$5\sigma^2 6\sigma^2 2\pi^2$	107.00
	$1^4\Pi$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^2 3\pi^1$	17.66	15.60		$1^1\Pi$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^1$	107.59
	$2^4\Pi$	$5\sigma^2 6\sigma^1 7\sigma^1 2\pi^4 3\pi^1$	19.56	18.32		$1^1\Sigma^+$	$5\sigma^2 6\sigma^2 2\pi^2$	106.99
						$1^3\Pi$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^1$	106.81
CS^{2+}	$X(1)^3\Pi$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3$	32.73	32.66		$X^3\Sigma^-$	$5\sigma^2 6\sigma^2 2\pi^2$	106.25
	$a(1)^1\Pi$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^3$	33.38	33.25	CS^{5+}	$1^2\Delta$	$5\sigma^2 6\sigma^1 2\pi^2$	163.62
	$A(1)^3\Sigma^-$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^2$	34.67	33.10		$X^2\Pi$	$5\sigma^2 6\sigma^2 2\pi^1$	159.75
	$b(1)^1\Sigma^+$	$5\sigma^2 6\sigma^2 2\pi^4$	33.49	33.49		$2^2\Sigma^+$	$5\sigma^2 6\sigma^1 2\pi^2$	164.15
	$B(1)^3\Sigma^+$	$5\sigma^2 6\sigma^2 2\pi^3 3\pi^1$	36.37	36.31		$2^2\Pi$	$5\sigma^2 6\sigma^2 3\pi^1$	164.09
							$5\sigma^2 6\sigma^1 7\sigma^1 2\pi^1$	
	$c(1)^1\Delta$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^2$	35.58	34.04		$1^2\Sigma^+$	$5\sigma^2 6\sigma^2 7\sigma^1$	160.66
	$d(2)^1\Sigma^+$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^2$	36.34	35.11		$3^2\Pi$	$5\sigma^2 6\sigma^2 3\pi^1$	165.85
							$5\sigma^2 6\sigma^1 7\sigma^1 2\pi^1$	
	$1^1\Sigma^-$	$5\sigma^2 6\sigma^2 7\sigma^2 2\pi^2$	34.67	33.10	CS^{6+}	$1^3\Sigma^+$	$5\sigma^2 6\sigma^1 7\sigma^1$	229.30
	$1^3\Delta$	$5\sigma^2 6\sigma^2 2\pi^3 3\pi^1$	38.35	–		$1^3\Pi$	$5\sigma^2 6\sigma^1 2\pi^1$	227.04
	$2^1\Pi$	$5\sigma^2 6\sigma^2 7\sigma^1 2\pi^2 3\pi^1$	38.54	–		$X^1\Sigma^+$	$5\sigma^2 6\sigma^2$	224.64
	$3^1\Sigma^+$	$5\sigma^2 6\sigma^1 7\sigma^1 2\pi^4$	38.85	–		$1^1\Pi$	$5\sigma^2 6\sigma^1 2\pi^1$	228.58
	$2^1\Sigma^-$	$5\sigma^2 6\sigma^2 2\pi^3 3\pi^1$	39.71	–		$2^1\Sigma^+$	$5\sigma^2 6\sigma^1 7\sigma^1$	231.26

The main configuration of the electronic ground state for CS^{3+} is $5\sigma^2 6\sigma^2 2\pi^3$, in which three π electrons are coupled into $X^2\Pi$ state. For the triple ionization of CS, following the loss of two electrons in 7σ orbital, an additional electron in 2π is stripped. The second doublet state is $A^2\Delta$ state originating from $5\sigma^2 6\sigma^2 7\sigma^1 2\pi^2$ configuration, another electronic state with the same configuration but different coupling schemes is $B^2\Sigma^+$ state, which is 0.66 eV above the $X^2\Pi$ state. The vertical triple ionization energy is in a range of 64.8 eV–65.5 eV according to the present *ab initio* calculations.

The quadruple ionization energy for $X^3\Sigma^-$ state of CS^{4+} is calculated to be 106.25 eV with ic-MRCI+Q method. The dominant configuration of $CS^{4+}(X^3\Sigma^-)$ is $5\sigma^2 6\sigma^2 2\pi^2$, that is, all electrons in 7σ orbital are stripped while 2π orbital is kept half occupied for the lowest state of CS^{4+}. The other main configuration for low-lying electronic state is $5\sigma^2 6\sigma^2 7\sigma^1 2\pi^1$, which leads to $A^3\Pi$ and $^1\Pi$ states. The quadruply ionized energies for low-lying states of CS^{4+} are in a range of 106 eV∼107 eV. The quintuple ionization energy for $X^2\Pi$ state of CS^{6+} is 159.75 eV. The dominant configuration of $X^2\Pi$ state is $5\sigma^2 6\sigma^2 2\pi^1$. The leading configurations for other low-lying states of CS^{6+} are presented in Table 2, and the ionization energies are in a range of 159 eV–165 eV. The sextuple ionization energy for $CS^{6+}(X^1\Sigma^+)$ state is determined to be 224.64 eV. The $CS^{6+}(X^1\Sigma^+)$ state comes from $5\sigma^2 6\sigma^2$ configuration, in which all outer valence electrons in atomic p shell are stripped. Higher ionization energies for excited states, such as $A^1\Pi$, $a^3\Pi$, and others, arise from excitation of electrons in atomic outer valence orbitals into p orbitals.

3.3. Dissociation channels and KER

The dissociation channels and corresponding KER obtained with icMRCI+Q method are listed in Table 3. Compared with *J*-averaged atom ionization energies of S and C, the relative energy of dissociation limits is under-estimated by ∼1%. It is found that the average KER value of S^++C channel is 0.3 eV in ion-collision experiment, which is close to the present calculated value 0.6 eV in the $C(^1D)+S^+(^4S^o)$ channel. The ion translational energy spectrum yields two KER values for dissociation of CS^{2+}, i.e., 2.80 eV and 5.20 eV, respectively, in $CS^{2+}+N_2$ collision experiment. As shown in Fig. 2 and Table 3, obviously, the KER values (7.7 eV∼9.0 eV) along repulsive $2^1\Pi$, $2^1\Sigma^-$, and $^3\Delta$ potentials are higher than experimental values, so the observed fragments are not produced directly through these repulsive dissociation channels. The $X^3\Pi$ and $1^3\Sigma^-$ states are correlated to the lowest dissociation channel $C^+(^2P^o)+S^+(^4S^o)$, and are 3.73 eV and 4.17 eV, respectively, above the dissociated atomic limit. Since the $X^3\Pi$ and $1^3\Sigma^-$ states are quasibound, tunneling effects are prominent in high vibrational levels, and the dissociation into $C^+(^2P^o)+S^+(^4S^o)$ atomic product by tunneling is possible. Thus, according to our calculated vibra-

tional spectrum, the KER data for the lowest channel should be in ranges of 3.73 eV–6.05 eV and 4.17 eV–4.55 eV for $^3\Pi$ and $^3\Sigma^-$, respectively. A total of 16 vibrational levels are found in $X^3\Pi$ potential well, the highest four levels are 5.11, 5.20, 5.28, and 5.35 eV, respectively, above the dissociation limit $C^+(^2P^o)+S^+(^4S^o)$. The corresponding tunneling lifetimes calculated in the present work are 39, 0.004, 1.1×10^{-6}, and 1.1×10^{-9} s, respectively, for $v = 12$, 13, 14, 15 vibrational levels of $X^2\Pi$ state. According to the present computational work, the observed dissociation channel with 5.20 eV of KER value originate from $X^2\Pi$ state correlated to $C^+(^2P^o)+S^+(^4S^o)$. Considering the bound state correlated to $C^+(^2P^o)+S^+(^2D^o)$ dissociation limit, the energies of $1^1\Sigma^+$, $1^1\Pi$, and $1^1\Delta$ states are in a range of 2.5 eV–4.5 eV above this atomic limit. Though the highest vibrational levels of these electronic states are in ns magnitude, the KER data induced by these states are in a range of 4.1 eV–4.7 eV, while no experimental KER data are observed in this range.

Table 3. Dissociation channels of CS^{q+} ($q = 1 \sim 6$) and kinetic energy release (KER) data (in eV).

Species	Electronic state	Dissociation channel	KER
CS	$^1\Sigma^+$	$C(^3P)+S(^3P)$	–
CS^+	$^2\Sigma^+$	$C(^3P) + S^+(^4S^o)$	–
CS^+	$^4\Delta$	$C(^1D) + S^+(^4S^o)$	–
CS^+	$2^2\Pi$	$C(^1D) + S^+(^4S^o)$	0.6
CS^{2+}	$^3\Pi$	$C^+(^2P^o)+S^+(^4S^o)$	3.73
	$2^1\Pi$	$C^+(^2P^o)+S^+(^2D^o)$	7.77
	$2^1\Sigma^-$		8.94
	$^3\Delta$		8.09
CS^{3+}	$1^2\Pi$	$C^+(^2P^o)+S^{2+}(^3P)$	12.56
	$1^2\Delta$		12.61
	$^2\Sigma^+$		13.22
	$2^2\Pi$		15.79
CS^{4+}	$^3\Pi$	$C^{2+}(^1S)+S^{2+}(^3P)$	30.24
	$^3\Sigma^-$		29.68
	$^1\Delta$	$C^{2+}(^1S)+S^{2+}(^1D)$	29.14
	$^1\Pi$	29.72	
	$^1\Sigma$		29.13
CS^{5+}	$^2\Pi$	$C^{2+}(^1S)+S^{3+}(^2P^o)$	48.41
	$1^2\Sigma^+$		49.33
	$^2\Delta$	$C^{2+}(^3P^o)+S^{3+}(^2P^o)$	45.73
	$2^2\Sigma^+$		46.26
	$2^2\Pi$		46.19
	$3^2\Pi$		47.95
CS^{6+}	$^1\Sigma^+$	$C^{2+}(^1S)+S^{4+}(^1S)$	66.07
	$^3\Sigma^+$	$C^{3+}(^2S)+S^{3+}(^2P^o)$	70.12
	$^3\Pi$		67.86
	$^1\Pi$		69.40
	$2^1\Sigma^+$		72.08

For highly charged CS^{q+} ($q > 2$), direct dissociations along these repulsive potentials are the dominant pathways for the low-lying states. The appearance potential for $C^+(^2P^o)+S^{2+}(^3P)$ pair is 12.56 eV, and the KER data for dissociation of CS^{3+} are in a range of 12.36 eV–15.79 eV. Symmetrical dissociation is preferred in CS^{4+}, and the KERs for $C^{2+}(^1S)+S^{2+}(^3P,^1D)$ ion pairs are centered at 30 eV. The yields of $C^{2+}(^1S,^3P)+S^{3+}(^2P^o)$ ion pairs are preferred in CS^{5+} dissociation, the KER data are in a range of 45 eV–50 eV. It is very interesting that the unsymmetrical dissociation is preferred in CS^{6+} with an appearance potential of 66.07 eV for $C^{2+}(^1S)+S^{4+}(^1S)$ ions pair. The appearance potential of symmetrical dissociation is 67.86 eV for $C^{3+}(^2S)+S^{3+}(^2P^o)$ yield, which is 1.8 eV higher than the one of unsymmetrical dissociation. Other KER peaks around 70 eV are also found, which yield symmetrical ions pair $C^{3+}(^2S)+S^{3+}(^2P^o)$.

4. Conclusion

In the present computational work, we investigated the multiply charged ions CS^{q+} ($q = 0 \sim 6$) with highly-correlated multi-reference interaction wavefunctions. The low-lying bound states of CS ions are characterized by the *ab initio* calculations. The spectroscopic constants, dissociation energies, barrier heights, and transition energies of ionic states are obtained, and good accordance between the present results and existing theoretical and experimental values are found. No adiabatic potential energy minimum is found in low-lying electronic states of CS^{q+} ($q = 3 \sim 6$) ions in our computational work. The adiabatic and vertical ionization energies of neutral CS to CS^{q+} ($q = 1 \sim 6$) cations are found in this work. The symmetrical and unsymmetrical dissociation channels and corresponding KER are obtained through potential energy curves by the *ab initio* calculations for further experimental comparisons.

References

[1] Mathur D 2004 *Phys. Rep.* **391** 1
[2] Böhme D K 2011 *Phys. Chem. Chem. Phys.* **13** 18253
[3] Thissen R, Witasse O, Dutuit O, Wedlund C S, Gronoff G and Lilensten J 2011 *Phys. Chem. Chem. Phys.* **13** 18264
[4] Zhang D D 2011 *Research of Dissociation and Ionization of Molecules in Femosecond Laser Field and Rotational State Selection of Molecules in Static Electric Hexapole Field* (Ph D. Dissertation) (Changchun: Jilin University) (in Chinese)
[5] Cheng X L, Yang J H and Zhang H 2012 *Chin. Phys.* B **19** 063201
[6] Zhang C J, Hu B T and Luo X W 2012 *Chin. Phys.* B **21** 053601
[7] Wilson R W, Penzias A A, Wannier P G and Linke R A 1976 *Astrophys. J.* **204** L135
[8] Hishikawa A, Hasegawa H and Yamanouchi K 2004 *Chem. Phys. Lett.* **388** 1
[9] Taylor S, Eland J H D and Hochlaf M 2006 *Chem. Phys.* **330** 16
[10] Kanamori H and Hirota E 1987 *J. Chem. Phys.* **86** 3901
[11] Krishnamurthi V, Krishamurthy M, Marathe V R and Mathur D 1992 *J. Phys.* B **25** 5149
[12] Šedivcová T, Špirko V and Fišer J 2006 *J. Chem. Phys.* **125** 164308
[13] West J, Dyke J, Morris A, Wright T and Gamblin S 1999 *J. Phys.* B **32** 2763
[14] Nobumitsu H 2008 *Chem. Phys.* **344** 128
[15] Nobumitsu H 2006 *Chem. Phys.* **324** 413
[16] Handke G, Tarantelli F and Cederbaum L 1996 *Phys. Rev. Lett.* **76** 896
[17] Rajput J and Safvan C P 2007 *Phys. Rev.* A **75** 062709

[18] Werner H J, Knowles P J, Knizia G, Manby F R and Schütz M 2012 *WIREs Comput. Mol. Sci.* **2** 242
[19] Wolf A, Reiher M and Hess B A 2002 *J. Chem. Phys.* **117** 9215
[20] Reiher M and Wolf A 2004 *J. Chem. Phys.* **121** 10945
[21] Reiher M and Wolf A 2004 *J. Chem. Phys.* **121** 2037
[22] Woon D E and Dunning T H 1993 *J. Chem. Phys.* **98** 1358
[23] Dunning T H 1989 *J. Chem. Phys.* **90** 1007
[24] Le Roy R J 2002 *University of Waterloo Chemical Physics Research Report* CP-655
[25] Le Roy R J and Liu W 1978 *J. Chem. Phys.* **69** 3622
[26] Moltzen E K, Klabunde K J and Senning S 1988 *Chem. Rev.* **88** 391
[27] Jonathan N, Morris A, Okuda M, Ross K J and Smith D J 1972 *Faraday Discuss. Chem. Soc.* **54** 48
[28] Dyke J M, Gamblin S D, Haggerston D, Morris A, Stranges S, West J B, Wright T G and Wright A E 1998 *J. Chem. Phys.* **108** 6258