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Electron impact excitation of tetrasulfur S_4 molecule*

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Electron impact excitation of tetrasulfur S_4 molecule is investigated in this work using R-matrix method. The twelve low-lying electronic states are used in close-coupling expansion to represent the target states, and the integral cross sections for elastic scattering and excitation into the six lowest electronic states are calculated.

Keywords: cross section, S_4 molecule, scattering
PACC: 3480G, 3480B

1. Introduction

The sulfur dimer S_2 is one of most efficient irradiancy materials,[1] and the transition of $S_2(B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-)$ has been proposed as tunable laser with wide wavelength range (300–600 nm).[2] Experimental works focused on sulfur laser pumped by electron collision are in progress.[3] The sulfur dimer is produced by the pyrogenation of solid sulfur in experiments, and simultaneously other polysulfur $S_n(n = 3 - 8)$ is produced. The tetrasulfur S_4 exists in sulfur vapour as observed by mass spectroscopy and other techniques, which is mixed with other polysulfurs[4–8] and has never been prepared experimentally in pure state. To increase the abundance of sulfur dimer, more polysulfur is needed to dissociate into sulfur dimer in the electron collision process. We wish to study theoretically the electron impact with S_4 molecule in this work.

Electron–molecule collision is one of important methods to determine optical oscillator strengths and scattering cross sections experimentally.[9,10] The R-matrix method is accurate and reliable in dealing with the electron–molecule process in the low energy range theoretically.[11] In this work we report the electron collision calculations on S_4 molecule. The calculations are performed using the R-matrix code.[12]

2. Methods

The R-matrix method divides the configuration space into two regions. In the inner region, here defined as a sphere of radius 10 Bohr radii centred at the centre of mass of S_4 molecule, the scattering electron passes through the electronic cloud of target, and the coulomb interaction and electron–electron exchange interaction are important. In the outer region, all the interactions except the long-range multipolar interaction between scattering electron and target are negligible. The trial wavefunctions in the inner region are in the configuration interaction (CI) form:

$$\Psi_k = \hat{A} \sum_{ij} a_{ijk} \phi_i^N \eta_{ij} + \sum_j b_{jk} \phi_j^{N+1}, \qquad (1)$$

where $\hat{A}$ is the antisymmetrization operator, ϕ_i^N represents the ith state and η_{ij} represents the continuum states, coefficients a_{ijk} and b_{jk} are determined by the variational method.

The 64 electrons of S_4 molecule fill the $1-13a_1, 1-4b_1, 1-12b_2, 1-3a_2$ orbitals in the self-consistent-field (SCF) ground state. The $13a_1, 4b_1, 12b_2, 3a_2$ orbitals, whose SCF binding energy is less than 10 eV, are included in CI calculations combined with SCF virtual orbitals $4a_2, 14a_1, 13 - 14b_2$. All singlet and triplet $1A_1, 1B_1, 1B_2, 1A_2$ states have dominant configurations corresponding to the excitation to the lowest unoccupied molecular orbital $4a_2$; the $2^{1,3}B_1$ states corresponding to the excitation $4b_1$ to $14a_1$ and 2^3A_1 states are energetically allowed and should not be neglected. The vertical excitation energies for the 12 lowest electronic states considered in the close-coupling calculation are listed in Table 1. The scattering calculations are performed for doublet states with A_1, B_1, B_2, A_2 symmetries. In all calculations,

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the continuum orbitals used are up to f($l \leq 3$). The unit for cross section is the square of Bohr radius a_0^2.

Table 1. Vertical excitation energies (in eV) for tetrasulfur target states.

State	Vertical excitation energy
1^1A_1	0
1^3B_2	0.99
1^3A_2	2.17
1^1A_2	2.34
1^3B_1	2.53
1^1B_1	2.66
1^1B_2	3.33
2^3B_1	3.62
2^1B_1	3.98
1^3A_1	4.07
2^3A_1	4.16
2^1A_1	4.18

3. Results and discussion

In Fig.1, the elastic cross section of S_4 molecule is shown. Two shape resonance positions are located: the first is $^2B_1$ and $^2B_2$ resonance at 1.28 eV, the second is due to $^2A_2$ symmetry at 2.73 eV.

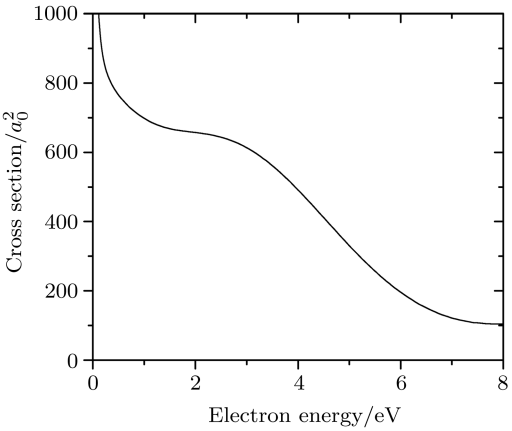


Fig.1. The elastic cross section of S_4.

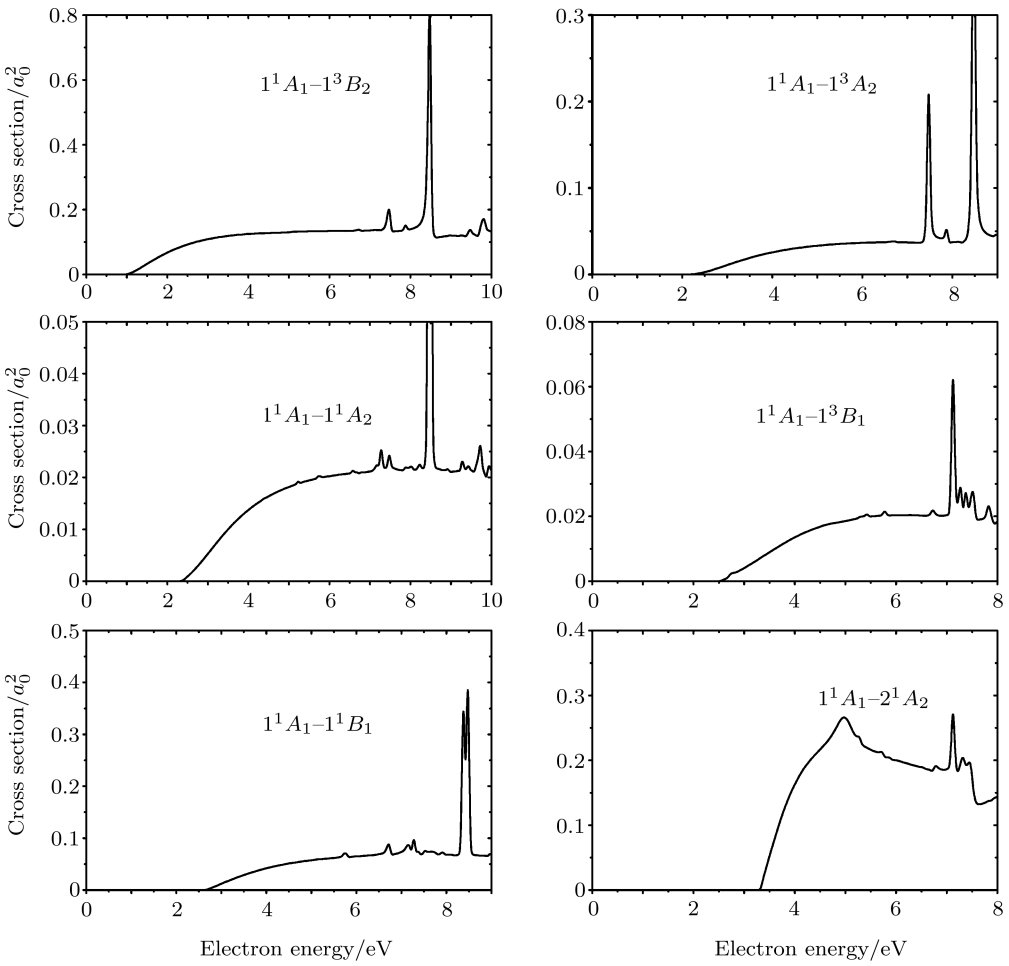


Fig.2. Electron-impact electronic excitation cross section for S_4 of the transition: 1^1A_1–1^3B_2; 1^1A_1–1^3A_2; 1^1A_1–1^1A_2; 1^1A_1–1^3B_1; 1^1A_1–1^1B_1; 1^1A_1–2^1A_2.

The cross sections for excitation into six low-lying electronic excited states are illustrated in Fig.2. The $^2A_2$ Feshbach resonances are located around 7.50 eV and 8.50 eV in the $1^1A_1 \rightarrow 1^3B_2$, $1^1A_1 \rightarrow 1^3A_2$, $1^1A_1 \rightarrow 1^1A_2$ and $1^1A_1 \rightarrow 1^1B_1$ transitions. The $^2A_2$ symmetry gives average and large contributions for the integral cross section of $1^1A_1 \rightarrow 1^3B_2$ transition below 10 eV, and $^2B_2$ symmetry contributes much to the cross section of $1^1A_1 \rightarrow 1^3A_2$ transition; similar cases are also found in $1^1A_1 \rightarrow 1^1A_2$ transition due to the $^2A_1$ and $^2B_1$ symmetry, and in $1^1A_1 \rightarrow 1^1B_1$ transition due to the $^2A_1$ symmetry. In $1^1A_1 \rightarrow 1^3B_1$ transition, one $^2A_1$ Feshbach resonance is located at 7.10 eV. The $^2A_1$ shape resonance is found in the $1^1A_1 \rightarrow 2^1A_2$ transition at 5.03 eV.

4. Summary

In summary, this is an initiative study of electron impact on tetrasulfur S_4 molecule. The integral cross sections of electron-impact S_4 molecule are calculated, and the main resonance contributions to the cross sections are discussed.

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