Electron impact excitations of $S_2$ molecules

Motomichi Tashiro$^1$

Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishihiraki-cho 34-4, Sakyo-ku, Kyoto 606-8103, Japan

Abstract

Low-energy electron impact excitations of $S_2$ molecules are studied using the fixed-nuclei R-matrix method based on state-averaged complete active space SCF orbitals. Integral cross sections are calculated for elastic electron collision as well as impact excitation of the 7 lowest excited electronic states. Also, differential cross sections are obtained for elastic collision and excitation of the $a^1\Delta_g$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$ states. The integrated cross section of optically allowed excitation of the $B^3\Sigma_u^-$ state agrees reasonably well with the available theoretical result.

Key words: Electron-molecule collision, R-matrix method, Diatomic sulfur
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1 Introduction

Diatomic sulfur, $S_2$, has been subject of many theoretical and spectroscopic investigations for long time [1,2,3]. We can find $S_2$ molecules at various natural and industrial plasmas containing sulfur compounds. For example, emissions and absorptions of $S_2$ molecules have been observed in the atmospheres of Jupiter [4] and its satellite Io [5]. They are also observed in the atmospheres of some comets [6]. In industrial condition, $S_2$ molecules can be seen in reactive ion etching process using SF$_6$ molecules [7]. Sulfur lamps contain $S_2$ molecules as an important ingredient [8]. Although electron collision with $S_2$ molecules is an important elementary process in these plasmas, there has been little work on this subject. As far as we are aware, no experimental measurement nor theoretical calculation of electron-$S_2$ elastic cross section have been performed. Garrett et al. [9] calculated integral cross section for electron impact excitation of the $S_2$ $B^3\Sigma_u^-, 2^3\Sigma_u^-$ and $B''^3\Pi_u$ states using the semiclassical

Email address: tashiro@fukui.kyoto-u.ac.jp (Motomichi Tashiro).

$^1$ FAX: +81 75 781 4757

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impact-parameter (IP) method extended to include nuclear motion. Since the IP method is designed to treat optically allowed transitions, electron impact excitation to the other electronic state was not investigated. Le Coat et al. [10] performed experimental measurement on dissociative electron attachment of S\textsubscript{2} molecules and identified two resonances, however, they did not present absolute value of the cross section.

Recently, we have performed the R-matrix calculations on the spin-exchange effect in electron collision with homo-nuclear open-shell diatomic molecules including S\textsubscript{2} [11]. We have also calculated the integral cross section of elastic electron collision with S\textsubscript{2} molecules for the first time. Here, we extend our previous study to the electron impact excitations of S\textsubscript{2} molecules. Since S\textsubscript{2} molecule has a valence electron structure similar to O\textsubscript{2}, comparison of the cross sections will be interesting. Also, the cross section of electron impact excitation of the S\textsubscript{2} B\textsuperscript{3}\Sigma\textsubscript{u} would be important in analyzing sulfur plasma. As in our previous works on electron impact excitation of O\textsubscript{2} and N\textsubscript{2} [12,13,14], we employ the fixed-nuclei R-matrix method using state-averaged complete active space SCF molecular orbitals. The size of basis set for the scattering electron is slightly extended in this work compared to our previous calculation on the spin-exchange effect [11].

2 Theoretical methods

The details of the R-matrix method has been described in the literature [15,16,17], thus we do not repeat general explanation of the method here. We used a modified version of the polyatomic programs in the UK molecular R-matrix codes [15] in this work. These programs utilize the Gaussian type orbitals (GTO) to represent target electronic states as well as a scattering electron. In the present R-matrix calculations, we have included 13 target states; \textit{X}\textsuperscript{3}\Sigma\textsubscript{g}\textsuperscript{−}, \textit{a}\textsuperscript{1}\Delta\textsubscript{g}, \textit{b}\textsuperscript{1}\Sigma\textsubscript{g}\textsuperscript{+}, \textit{c}\textsuperscript{1}\Sigma\textsubscript{u}\textsuperscript{−}, \textit{A}\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}, \textit{B}\textsuperscript{3}\Delta\textsubscript{g}, \textit{B}\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{−}, \textit{1}\textsuperscript{1}\Pi\textsubscript{g}, \textit{1}\textsuperscript{1}\Delta\textsubscript{u}, \textit{B}\textsuperscript{3}\Pi\textsubscript{u}, \textit{B}′\textsuperscript{3}\Pi\textsubscript{u}, \textit{B}′′\textsuperscript{3}\Pi\textsubscript{u}, and \textit{1}\textsuperscript{1}\Pi\textsubscript{u}. These target states were represented by valence configuration interaction wave functions constructed by state averaged complete active space SCF (SA-CASSCF) orbitals. In this study, the SA-CASSCF orbitals were obtained by calculations with MOLPRO suites of programs [18]. The target orbitals were constructed from the cc-pVTZ basis set [19]. Fixed-nuclei approximation was employed with inter-nuclear distance of 3.7 \textit{a} \textsubscript{o}. The radius of the R-matrix sphere was chosen to be 13 \textit{a} \textsubscript{o} in our calculations. In order to represent the scattering electron, we included diffuse Gaussian functions up to \textit{l} = 5, with 13 functions for \textit{l} = 0, 11 functions for \textit{l} = 1, 10 functions for \textit{l} = 2, 8 functions for \textit{l} = 3, 6 functions for \textit{l} = 4 and 5 functions for \textit{l} = 5. Exponents of these diffuse Gaussians were taken from Faure et al. [20]. In addition to these continuum orbitals, we included 8 extra virtual orbitals, one for each symmetry. The construction of the configuration state functions (CSFs) for
the electron-molecule system is the same as in our previous paper\cite{11}. Note
that The R-matrix calculations were performed for all 8 irreducible represen-
tations of the $D_{2h}$ symmetry, $A_g, B_{2u}, B_{3u}, B_{1g}, B_{1u}, B_{3g}, B_{2g}$ and $A_u$, in
doublet and quartet spin multiplicities of the whole system.

One of the transitions studied in this work, the excitation of the $B^3\Sigma_u^-$ state
from the ground state, is optically allowed. Thus, we have to consider the
effect of transition dipole moment between these two states. A lot of $l$ partial-
waves has to be included in the R-matrix calculation to obtain converged
cross sections because of the long-range interaction of the dipole, although it
is difficult to include partial waves with $l \geq 7$ in the usual ab initio R-matrix
calculation. In this work, the R-matrix calculations are performed with partial
waves up to $l = 5$. The effects of the higher $l$ partial waves are included by
the Born closure approximation as in the previous works \cite{21,22}. Following
Gibson et al.\cite{22}, we evaluate the differential cross sections (DCSs) with the
Born correction, $d\sigma^{BC}/d\Omega$, by the expression,

$$
d\sigma^{BC}/d\Omega = d\sigma^{FBA}/d\Omega + \left[d\sigma^{R-\text{matrix}}/d\Omega - d\sigma^{FBA}_{FE}/d\Omega\right]. \quad (1)
$$

Here, $d\sigma^{FBA}/d\Omega$ is the DCS obtained by the first Born approximation, $d\sigma^{R-\text{matrix}}/d\Omega$
is the cross section obtained by the R-matrix calculation and $d\sigma^{FBA}_{FE}/d\Omega$ is the
DCS from the first Born approximation including the same number of partial
waves as in the R-matrix calculation. $d\sigma^{FBA}_{FE}/d\Omega$ is evaluated by the angular
momentum representation of the T-matrix elements for the first Born approx-
imation. These T-matrix elements as well as $d\sigma^{FBA}/d\Omega$ are available in close
form\cite{23}. The total cross sections are obtained by the integration of eq.(1).

3 Results and Discussion

In table\cite{11} excitation energies of $S_2$ molecule obtained from the CASSCF cal-
culation in this work are compared with MRD CI vertical excitation energies
of Hess et al.\cite{24}, MRCI adiabatic excitation energies of Kiljunen et al.\cite{25}
and experimental values quoted in Hess et al. Our results agree well with the
previous calculations and experimental results for the lowest two excitations.
For excitations to the higher electronic states, deviations in excitation energies
become larger partly because of difference of adiabatic and vertical excitation
energy.

In figure\cite{1} the integral cross sections (ICSs) are shown for electron $S_2$ elastic
collision and excitations of the $a^1\Delta_g$, $b^1\Sigma_g^+$ and $c^1\Sigma_u^-$ states. The magnitude
of the elastic ICS is about $20 \times 10^{-16}$ cm$^2$ in low energy region below 3 eV,
then it increases to be $30 \times 10^{-16}\text{cm}^2$ at energies above 5 eV. The ICS of the excitation to the $a^1\Delta_g$ state increases gradually from threshold to 8.5 eV, where it takes a maximum value of $0.35 \times 10^{-16}\text{cm}^2$, then it decreases again. The ICSs of the excitation to the $b^1\Sigma_g^+$ and $c^1\Sigma_u^-$ states also increase gradually from threshold. In both cases, the maximum value of the ICS is about 0.1 $\times 10^{-16}\text{cm}^2$. Around 2.7 eV, a sharp resonance peak with width 0.08 eV exists in the ICSs of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ excitations. Also, a kink structure is observed in the elastic ICS at the same energy. All of these structures belong to the $^2\Pi_u$ symmetry partial cross sections. We analyzed the CSFs and found that the kink and peaks at 2.7 eV are likely related to a resonance with configuration (core)$^{20}(4\sigma_g)(4\sigma_u)(5\sigma_g)^2(2\pi_u)^3(2\pi_g)^4$, which is obtained from an attachment of the scattering electron to the excited $c^1\Sigma_u^-$, $A^3\Delta_u$ and $A^3\Sigma_g^+$ states of $S_2$ with configuration (core)$^{20}(4\sigma_g)(4\sigma_u)(5\sigma_g)^2(2\pi_u)^3(2\pi_g)^3$. The width of this resonance is about 0.08 eV at $R = 3.7\text{a}_0$. We checked the behaviour of this resonance as a function of bond-length, and found that it approaches the atomic limit $S^2(3P) + S^-(2P)$. Since the location of this resonance is higher than the atomic limit, dissociative electron attachment may occur through this resonance.

In figure 2, the ICSs for electron $S_2$ collisions are shown for excitations to the $A^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Pi_g$ and $B^3\Sigma_u^-$ states. The ICS of Garrett et al. [9] obtained by the impact-parameter method is also compared with our excitation ICS to the $B^3\Sigma_u^-$ state. In general, the slopes of these ICSs near threshold are steeper than those in fig.1. The maximum values of the ICSs below 15 eV are about 0.3, 0.1, 0.6 and 3.0 for the excitation to the $A^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Pi_g$ and $B^3\Sigma_u^-$ states, respectively. For the optically allowed $B^3\Sigma_u^-$ state excitation, the effect of the high $l$ partial waves is included by the Born approximation formula given in eq.(1). The magnitude of the Born correction is small below 10 eV, however, it increases as the scattering energy increases. The fraction of the correction to the R-matrix cross section becomes about 20% at 15 eV. Our ICS with the Born correction and the previous result of Garrett et al. [9] agree reasonably well above 8 eV. We used the CASSCF value for the $B^3\Sigma_u^-$ excitation energy in this work, whereas Garrett et al. [9] employed the experimental value for the excitation energy. In contrast to the fixed-nuclei approximation in our calculation, Garrett et al. [9] included the effect of $S_2$ vibration in their calculation. Because of these differences, the results of Garrett et al. [9] and our ICS do not agree well near the excitation threshold. A small peak is seen at 14.2 eV in the ICSs of the $A^3\Delta_u$ and $A^3\Sigma_u^+$ state excitations, which is originated from the $^4\Pi_g$ symmetry partial cross sections. Since the location of this peak is higher than the highest energy $S_2$ electronic state included in the present R-matrix calculation, we cannot determine whether this peak belongs to the real resonance or pseudo-resonance.

In figure 3, the differential cross sections (DCSs) are shown for elastic electron $S_2$ collisions as well as excitations to the $a^1\Delta_g$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$ states. The
elastic DCSs are enhanced in forward direction and tend to be more forward-enhanced as the scattering energy increases. In contrast to the elastic DCSs, the excitation DCS to the $a^1 \Delta_g$ state has backward-enhanced character in general. However, the magnitude of forward scattering cross section increases as the scattering energy increases from 7 to 13 eV. Our excitation DCSs to the $b^1 \Sigma_g^+$ state approach zero near 0 and 180 degrees, because of a selection rule associated with $\Sigma^+ - \Sigma^-$ transition \[26,27\]. Around 90 degrees, the magnitude of the DCS is about 0.06~0.08 × $10^{-17}$ cm$^2$sr$^{-1}$ and does not depend much on the scattering energy. The $B^3 \Sigma_u^-$ state excitation DCSs are shown in fig. 3 panel (d). In addition to the R-matrix results, the DCSs with the Born correction obtained by eq.(1) are also shown for scattering angles below 25 degrees. For larger angles, the magnitude of the correction is expected to be small and not shown here. The contribution of the Born correction to the DCS is small for 7 eV, however, it dominates the total DCS near zero degree at 10 and 13 eV. Although the magnitude of the R-matrix DCS at forward direction decreases as the scattering energy increases from 7 to 13 eV, the DCS with the Born correction at forward direction increases as energy increases.

The elastic and excitation cross sections of the $a^1 \Delta_g$ and $b^1 \Sigma_g^+$ states in electron S$_2$ collisions are about two times larger than corresponding cross sections in electron O$_2$ collisions studied in our previous paper \[12\]. Although the $^2 \Pi_u$ resonance peaks can be observed in the $a^1 \Delta_g$ and $b^1 \Sigma_g^+$ excitation cross sections in both e-O$_2$ and e-S$_2$ collisions, the width of the peak is much broader in e-O$_2$ case. In e-O$_2$ elastic collision, a narrow $^2 \Pi_g$ resonance peak is seen below 1 eV. In e-S$_2$ elastic case, the energy of the S$_2^- \ ^2 \Pi_g$ state is stabilized below the energy of the S$_2$ ground state and cannot be observed in the cross section. Other than these resonance features, the profiles of the cross sections are similar in e-O$_2$ and e-S$_2$ collisions.

In this work, we employed the fix-bond approximation for the R-matrix calculation. In our previous studies on electron impact excitations of O$_2$ and N$_2$ molecules \[12,13,14\], we also used the same fix-bond approximation and got good agreement with available experimental results, even if the positions of the potential curve minimum are different between the ground state and the excited state. Thus, the results of this study is also expected to be accurate enough. For more precise comparison of the excitation cross section of the $B^3 \Sigma_u^-$ state with the previous results of Garrett et al. \[9\], inclusion of the vibrational effect may be necessary. Such kind of calculation is possible by the non-adiabatic R-matrix method or the adiabatic averaging of the T-matrix elements, and will be performed in future.

We have carried out the R-matrix calculations with the maximum $l$ quantum number 4, 5 and 6 to check convergence. Except for the $B^3 \Sigma_u^-$ state excitation, the ICSs and DCSs are converged at $l=5$. For the $B^3 \Sigma_u^-$ excitation, the ICS with the Born correction is also converged at $l=5$. For the $B^3 \Sigma_u^-$ excitation
DCSs with the Born correction, however, the convergence is achieved only below 25 degrees. Note that the similar situation was observed in Gibson et al.\cite{22}. Although the $B^3\Sigma_u^-$ excitation DCS is not converged above 30 degrees, the effect of the higher $l$ partial waves is expected to be small because the magnitude of the Born DCS itself is small at larger scattering angles. In principle, this convergence problem can be solved \cite{28,29} by applying the Born correction to T-matrix elements, where we applied the correction at the R-matrix DCS in this work. We will calculate this kind of Born correction at T-matrix level when more accurate excitation DCS is required in future.

4 Summary

In this work, we have studied the low-energy electron impact excitations of $S_2$ molecules using the fixed-bond R-matrix method based on state-averaged CASSCF molecular orbitals. Thirteen target electronic states of $S_2$ are included in the model within a valence configuration interaction representations of the target states. Integral cross sections are calculated for elastic electron collision as well as impact excitation of the 7 lowest electronic states. Also, differential cross sections are shown for elastic collision and excitation of the $a^1\Delta_g$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$ states. For the excitations of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states, a narrow $^2\Pi_u$ resonance peak is observed in the ICSs at 2.7 eV. For the elastic and the excitation collisions of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states, the shapes of the cross sections are similar to those in electron $O_2$ collisions, however, the magnitudes of the cross sections are two time larger in electron $S_2$ collisions. Our ICS of the $B^3\Sigma_u^-$ state excitation agrees reasonably well with the previous result of Garrett et al. \cite{9}. However, the ICS near threshold does not agree well, because of difference in excitation energy employed in calculation as well as the treatment of the vibrational effect.
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Table 1
The vertical excitation energies of the first 8 excited states for $S_2$ molecule, with the previous MRD CI results of Hess et al.\cite{24}, MRCI results of Kiljunen et al.\cite{25} and experimental values quoted in Hess et al.\cite{24}. The unit of energy is eV.

| State       | This work | Previous MRD CI | Previous MRCI | Expt.  |
|-------------|-----------|-----------------|---------------|--------|
| $X^3\Sigma_g^-$ | 0.00      | 0.00            | 0.00          | 0.00   |
| $a^1\Delta_g$  | 0.60      | 0.68            | 0.55          | 0.71   |
| $b^1\Sigma_g^+$ | 0.92      | 1.04            | 0.99          | 0.99   |
| $c^1\Sigma_u^-$ | 2.77      |                 | 2.45          |        |
| $A^3\Delta_u$  | 2.93      |                 | 2.59          |        |
| $A^3\Sigma_u^+$ | 3.03      |                 | 2.58          |        |
| $B^3\Pi_g$     | 4.84      | 4.63            | 4.36          | 4.38   |
| $B^3\Sigma_u^-$ | 5.03      |                 | 3.89          |        |
Fig. 1. Integral elastic (panel a) and excitation cross sections of the $a^1\Delta_g$ (panel b), $b^1\Sigma_g^+$ (panel c) and $c^1\Sigma_u^-$ (panel d) states.
Fig. 2. Integral excitation cross sections of the $A^3\Delta_u$ (panel a), $A^3\Sigma^+_u$ (panel b), $B^3\Pi_g$ (panel c) and $B^3\Sigma^-_u$ (panel d) states. The R-matrix cross section with Born correction and the previous results of Garrett et al. [9] are also included in panel d.
Fig. 3. Differential cross sections of elastic collision (panel a) and excitation of the $a^1\Delta_g$ (panel b), $b^1\Sigma_g^+$ (panel c) and $B^3\Sigma_u^-$ (panel d) states. The R-matrix cross sections with Born correction are also included in panel d.