

Analysis of SO₂+O Chemistry Models for Simulations of the Atmosphere of Io

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Abstract. Collisions between SO₂ and O are investigated through Molecular Dynamics/Quasi-Classical Trajectories (MD/QCT) calculations, for SO₂ internal energies and relative collision velocities that are of interests to the atmospheric dynamics study of Io. Three possible dissociation reactions are modeled, and reaction cross sections, $\sigma_{r,MD}$, and the equivalent variable hard sphere (VHS) cross sections, $\sigma_{VHS,MD}$, are obtained based on the MD/QCT results. Comparisons between $\sigma_{r,MD}$ and $\sigma_{VHS,MD}$ indicate that in high collision velocity regime the dissociation reaction is the dominant process. Reaction probabilities are further obtained by using the sum of the reaction cross section and equivalent VHS cross section as the total collision cross section. This method provides the consistent total collision cross sections and reaction probabilities that can be applied in direct simulation Monte Carlo (DSMC) for large range of total collisional energies whereas the VHS cross section and the reaction probability from the total collision energy (TCE) model can not be applied in high collision velocity regime that needs to be modeled.

Keywords: Molecular Dynamics, Quasi-Classical Trajectory, Chemistry Model, Io

INTRODUCTION

The nature of the Io's atmosphere has attracted substantial scientific interests ever since the discovery of its ionosphere by the Pioneer spacecraft in 1973 and the detection of SO₂ by the Voyager spacecraft. The relative composition of Io's atmosphere is not well known, but SO, O₂, S and O are expected to be created from SO₂ by the photon and gas phase chemistry. Collision induced SO₂ dissociation is considered as an important process leading to SO, O and S formation, and the collision model for SO₂ and O is desired as part of the atmospheric model to be implemented in the DSMC simulation that models the vertical structure and composition of Io's atmosphere. [1] However, the applicability of the VHS cross section and the TCE reaction probability that are conventionally used in DSMC is questionable in certain conditions in Io's atmosphere where the fast neutrals reach extreme high velocity up to 80 km/s.

In this work, MD/QCT method [3, 4] is employed to simulate collisions between SO₂ and O and obtain the reaction and collision cross section for applications in DSMC. MD calculations are in effect the solution of Hamiltonian equations of motion for a specified initial state and an analysis of the obtained trajectory results. To perform MD calculations, one has to know how the molecular system potential energy changes as a function of internuclear distances. The potential energy surface (PES) represents such a change, which can be obtained either using semi-empirical methods or as a fit to a series of quantum mechanical single energy point calculations. When the PES is obtained using fits to a series of quantum mechanical single energy point calculations, the MD calculations are referred to as quasi-classical trajectories calculations. The MD/QCT calculations based on reasonably accurate PES can provide a better estimate for the energy-based reaction probability.

The details of the MD/QCT calculation will be explained in the next section, followed by the description of the method to obtain the reaction and viscosity cross sections based on the MD/QCT results. The MD/QCT results will be then discussed in comparison with the VHS cross section and TCE reaction probability and conclusions will be given in the end.

DESCRIPTION OF THE MD/QCT METHOD

The MD/QCT calculations are the solutions of Hamilton's equations. Hamilton's equations of motion are

$$\dot{p}_{i,j} = -\frac{\partial V}{\partial r_{i,j}}, \quad (1)$$

$$\dot{r}_{i,j} = \frac{p_{i,j}}{m_i} \quad (2)$$

where the dotted symbol denotes a time derivative, V represents the total potential for the system of n atoms, $p_{i,j}$ and $r_{i,j}$ are the Cartesian momenta and coordinates for the i-th atom in the j-th direction, and m_i is the mass of the i-th

atom. These coupled equations can be solved for the coordinates and momenta of the n-atom system using a fourth order Runge-Kutta method. [7] The masses of atoms, their initial coordinates and momenta are needed as input. The integration is performed for a fixed length of time or until a specified condition is met, *e.g.*, the dissociation of the target molecule occurs, and the final states of each atom, *i.e.*, the coordinates and momenta, are recorded for further analysis.

A PES has been developed for the modeling of SO₂+O collisions [6] which assumes that SO₂ molecule has a potential of the central force field type. [8] For the collision pair system, the total potential is separated into

$$V(q_1, \dots, q_{12}) = V_{mol} + V_{int} \quad (3)$$

where q_1, \dots, q_{12} denote the coordinates of the atoms of SO₂ and O, V_{mol} is the molecular potential, and V_{int} is the collisional interaction potential. In this work, V_{mol} were modeled by using three Morse bond potentials as follows.

$$V_{mol} = \phi_{12}(r_{12}) + \phi_{13}(r_{13}) + \phi_{23}(r_{23}) \quad (4)$$

where $\phi_{ij}(r_{ij})$ is the pair potential between atoms *i* and *j* with a separation of r_{ij} . The Morse potential is defined as

$$\phi_{ij}(r_{ij}) = D_{ij} [1 - \exp\{-\beta_{ij}(r_{ij} - r_{ij}^e)\}]^2 \quad (5)$$

where r_{ij}^e is the equilibrium internuclear distance. The parameters for this representation are given in the Table 1. [9] The Morse parameters are chosen so that the dissociation energy, the equilibrium bond lengths, and the bond angle can be reproduced. The normal mode frequencies in Table 1 are obtained from power spectra of low energy trajectories of an isolated SO₂ molecule with harmonic pair potentials.

Furthermore, the collisional interaction is modeled by pair interactions of the form

$$V_{int} = \phi_{14}(r_{14}) + \phi_{24}(r_{24}) + \phi_{34}(r_{34}) \quad (6)$$

This has been shown to be a good approximation by Redmon *et al.* [10] The pair interactions are computed by using the standard Lennard-Jones 6-12 pair potentials as follows.

$$\phi_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (7)$$

As an approximation, all Lennard-Jones parameters for the atom-centered pair interactions are taken to be identical and they are obtained by following the combining rules

$$\sigma_{\text{SO}_2-\text{O}} = \frac{1}{2}(\sigma_{\text{SO}_2} + \sigma_{\text{O}}) = 3.668 \text{ \AA}^2 \quad (8)$$

$$\epsilon_{\text{SO}_2-\text{O}} = \sqrt{(\epsilon_{\text{SO}_2} \epsilon_{\text{O}})} = 173.68 \text{ K} \quad (9)$$

TABLE 1. Parameters for the SO₂ potential energy surface.

SO equilibrium distance in SO ₂	r_{12}^e, r_{13}^e	1.4321 \AA
O-O equilibrium distance in SO ₂	r_{23}^e	2.4742 \AA
O-S-O equilibrium bond angle	$\theta_{\text{O-S-O}}^e$	119.5°
Morse range parameters	$\beta_{12}, \beta_{13}, \beta_{23}$	2.4 \AA ⁻¹
Morse dissociation energies	$D_{12}=D_{13}=D_{\text{SO}}$	100 kcal/mole
Morse dissociation energy	D_{23}	30.5 kcal/mole
dissociation energy	$D_{\text{SO-O}}=D_{\text{SO}}+D_{\text{OO}}$	130.5 kcal/mole
vibration frequency	asymmetric stretch	1213 cm ⁻¹
vibration frequency	symmetric stretch	1187 cm ⁻¹
vibration frequency	bend	394 cm ⁻¹

In order to perform MD/QCT calculations, the initial conditions of the collision pair, *i.e.*, the collider O and each atom of the target SO₂, have to be specified. The specification of the initial conditions depends on the problem to be solved. For the future use of the MD/QCT results in DSMC simulation, this is usually done by sampling the initial conditions of the target molecule with the same internal energy while fixing the relative collision velocity for the collider.

Microcanonical sampling [3] is employed in this work to generate the initial conditions for the target molecule, in which the coordinates and momenta are determined separately. For a triatomic molecule such as SO₂, the microcanonical sampling may be summarized as follows. In order to select the Cartesian coordinates, the weighting factor for selecting a triatomic molecule with a specified set of internuclear distances r_{12}, r_{13} and angle θ is obtained as

$$W = [r_{12}r_{13}(E_{in} - V(r_{12}, r_{13}, \theta))]^2 \cdot \sin \theta \quad (10)$$

where r_{12} and r_{13} are the left and the right O-S internuclear distances, respectively, θ is the angle between them, and E_{in} is the desired value of the internal energy. To find the maximum weighting factor, Eq. 10 is evaluated for θ varying from 0 to π and internuclear distances from 0 to a maximum value, r_{max} . The latter is chosen to ensure that all possible molecule configurations with $E_{in} > V$ are included. Once the maximum weighting factor, W_{max} , is determined, r_{12} and r_{13} values are selected randomly as $R_n \cdot r_{max}$ and θ values as $R_n \cdot \pi$, where R_n is a random number between 0 and 1. The ratio W/W_{max} is evaluated using a standard acceptance-rejection technique to determine whether a specific geometric configuration should be accepted as the initial condition. The integration of the trajectory equations requires nine initial Cartesian coordinates for SO_2 . These can be determined by imposing the requirement that the molecules have an isotropic spatial distribution. First, a convenient set of Cartesian coordinates is selected, *e.g.*, a SO_2 molecule can be placed in the x-y plane with the center of mass at the origin and the central atom S on the y axis. The molecule is then rotated in a general manner using an Euler rotation matrix which is defined in terms of the three Euler angles. The Cartesian coordinates for each atom are thereby computed using the randomly chosen directional cosine angles $R_n \cdot 2\pi$ in the analytic expression for the Euler rotation matrices.

In addition to the coordinates, the initial momenta of the target molecule atoms are specified by assuming that each Cartesian momentum has the form

$$p_{i,j} = f R_{n,i,j} \sqrt{m_i} \quad (11)$$

where $R_{n,i,j}$ represents nine random numbers that are distributed according to the standard normal density function for i-th atom in j-th direction, and f is a proportionality constant that can be obtained by requiring conservation of energy through following relationships. The total energy in the laboratory coordinate reference frame (the reference frame in which the collision trajectories are integrated) has the form

$$T + V = E_{KE}^{cm} + E_{KE}^{rel} + V \quad (12)$$

where E_{KE}^{cm} and E_{KE}^{rel} represent the components of the kinetic energy of the center of mass and relative motion, respectively. Furthermore, because the microcanonical ensemble corresponds to a distribution of coordinates and momenta with a specified internal energy, E_{in} , we have

$$E_{in} = E_{KE}^{rel} + V(r) \quad (13)$$

$$E_{KE}^{cm} = \frac{1}{2M} \sum_{j=1}^3 P_{cm,j}^2 \quad (14)$$

where $V(r)$ is the potential relative to its equilibrium value, M is the mass of SO_2 , and $P_{cm,j} = \sum_{i=1}^3 p_{i,j}$.

Once the initial conditions of the target molecule is determined, the collider can be assigned with a set of coordinates and momenta that are convenient for post-processing the MD/QCT results, *e.g.*, the O atom can be placed on the y-z plane with a specified initial relative collision velocity directed along the z axis.

REACTION CROSS SECTION AND VISCOSITY CROSS SECTION

For a given target internal energy and relative collision velocity, reaction cross section and viscosity cross section are computed based on the MD/QCT results. In this work, three dissociation reactions are modeled in the MD/QCT calculation. The occurrence of a certain type of reactions is determined based on the internuclear distances of the target SO_2 . The reaction cross section, $\sigma_{r,MD}$, is then obtained by following [4]

$$\sigma_{r,MD} = \pi b_{max}^2 \frac{N_r}{N_T} \quad (15)$$

where b is the impact parameter, *i.e.*, the minimum distance between the center of mass of SO_2 and the velocity vector originated from O in the initial conditions, N_r is the number of trajectories that result in a certain type of reaction, and N_T is the total number of trajectories that are sampled. The impact parameter for each collision pair is randomly drawn from a range between 0 and b_{max} . Note that b_{max} needs to be sufficiently large so that beyond which the interaction potential of the collision pair does not affect the trajectories of the collider and the results of the reaction cross section and viscosity cross section. In our work, b_{max} is set to be 5\AA .

Because DSMC method uses the VHS model viscosity-based cross section, it is more consistent to obtain a collision cross section accordingly. The equivalent VHS collision cross section, $\sigma_{VHS,MD}$, can be obtained based on the viscosity cross section, $\sigma_{\mu,MD}$, through following procedures. [5, 4, 11] First, $\sigma_{\mu,MD}$ is calculated by the Monte Carlo evaluation of an integral based on trajectories that are not dissociated from the MD/QCT calculations as follows.

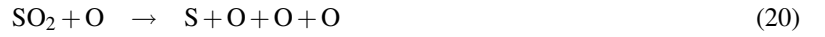
$$\sigma_{\mu,MD} = \int \left(\frac{v_{rel}^4}{4} \sin^2 \chi + \frac{1}{3} (\Delta e_{in})^2 - \frac{1}{2} (\Delta e_{in})^2 \sin^2 \chi \right) d\tau \quad (16)$$

where v_{rel} is the dimensionless relative collision velocity that is defined as $\sqrt{m_r/kT}v_{rel}$ with m_r being the reduced mass of SO_2 and O, Δe_{in} is the dimensionless internal energy that is normalized by kT , and χ is the deflection angle that is defined as the change in the direction of the relative collision velocity between the states of the collision pair in the beginning and end of the MD/QCT calculation. Then $\sigma_{VHS,MD}$ is derived by following

$$\sigma_{VHS,MD} = \frac{6\sigma_{\mu,MD}}{v_{rel}^4} \quad (17)$$

RESULTS AND DISCUSSION

Based on the conditions of interests in Io's atmosphere, MD/QCT calculations have been performed for a series of target SO_2 internal energies, E_{in} , and relative collision velocities, v_{rel} , *i.e.*, 0.5×10^{-19} , 2.0×10^{-19} , 4.0×10^{-19} , 6.0×10^{-19} J for E_{in} and 2, 4, 8, 16, 30, 45, 60 and 80 km/s for v_{rel} . Three possible dissociation reactions for SO_2 , listed below, are modeled.



The MD/QCT results show that the first reaction is the dominant process, and the reaction cross sections of the second and the third reaction are one order and two orders of magnitude smaller than those of the first reaction, respectively, for the same E_{in} and v_{rel} . Figure 1 shows the reaction cross sections, $\sigma_{r,MD}$, for the first reaction as a function of v_{rel} for different SO_2 internal energies. For each internal energy, the reaction cross section arises from zero rapidly as v_{rel} increases from 0 to 30 km/s and then reaches its maximum value asymptotically for $v_{rel} > 30$ km/s. In addition, the results demonstrate that the reaction cross section is higher for the target SO_2 with higher E_{in} at a given v_{rel} . The curve of the VHS collision cross section, σ_{VHS} , is superimposed with the reaction cross section results in Fig. 1, which is obtained by following [2]

$$\sigma_{VHS} = \sigma_{ref} \left[\left\{ \frac{2kT_{ref}}{m_r v_{rel}^2} \right\}^{\omega_{AB}-1/2} / \Gamma(5/2 - \omega_{AB}) \right] \quad (21)$$

where k is the Boltzmann constant, σ_{ref} is the reference collision cross section at the reference temperature T_{ref} , and ω_{AB} is the mean viscosity index of SO_2 and O from Ref. [2]. As shown in Fig. 1, the reaction cross sections become larger than σ_{VHS} around 10 to 16 km/s, where the VHS model starts to fail for conditions with high v_{rel} .

Based on Eq. 16, the equivalent VHS collision cross section, $\sigma_{VHS,MD}$, is related to χ and Δe_{in} from the MD/QCT results. The deflection angle distributions are shown in Fig. 2 for $E_{in} = 4.0 \times 10^{-19}$ J and three v_{rel} . The results suggest that for a specified v_{rel} more collisions where dissociation reactions do not occur have smaller χ , and that a larger portion of the sampled trajectories leads to smaller χ when v_{rel} is higher. Figure 3 offers another way to examine χ , showing it as a function of the normalized impact parameter. The fact that χ reaches to zero when b/b_{max} is close to unity indicates that the appropriate b_{max} is used in the MD calculations. As expected, collisions with smaller impact parameters result in larger χ , and instead of the head-on collision that leads to $\chi = 180^\circ$ from simpler collision models, MD/QCT calculations yields $\chi < 180^\circ$ at $b = 0$. The distributions of Δe_{in} are shown in Fig. 4 for $E_{in} = 6.0 \times 10^{-19}$ at two v_{rel} which are centered close to $\Delta e_{in} = 0$ in both cases.

$\sigma_{VHS,MD}$ is shown in Fig. 5 as a function of v_{rel} for four internal energies, in comparison with σ_{VHS} . The results indicate that the MD/QCT calculations predict greater collision cross sections than σ_{VHS} when $v_{rel} < 30$ km/s, and a trend of $\sigma_{VHS,MD}$ similar to σ_{VHS} that the collision cross section decreases as v_{rel} increases and eventually reaches zero asymptotically. The comparison between $\sigma_{r,MD}$ and $\sigma_{VHS,MD}$ shows that in high v_{rel} regime the dissociation reaction is the dominant process. This is because when the impact energy of the collider O becomes large as v_{rel} increase, only the collisions with large impact parameters do not result in dissociation of SO_2 , and χ and Δe_{in} of those collisions are small.

When the sum of $\sigma_{r,MD}$ and $\sigma_{VHS,MD}$ is used as the total collision cross section, $\sigma_{T,MD}$, the reaction probability can be obtained as $\sigma_{r,MD}/\sigma_{T,MD}$. Meanwhile, the reaction probability can be calculated using the TCE model by following [2]

$$P_r(E_c) = \frac{\pi^{1/2} \varepsilon \Lambda T_{ref}^\eta}{2\sigma_{ref}(kT_{ref})^{\eta-1+\omega_{AB}}} \frac{\Gamma(\bar{\zeta}_{in} + 5/2 - \omega_{AB})}{\Gamma(\bar{\zeta}_{in} + \eta + 3/2)} \left(\frac{m_r}{2kT_{ref}} \right)^{1/2} \frac{(E_c - E_a)^{\eta + \bar{\zeta}_{in} + 1/2}}{E_c^{\bar{\zeta}_{in} + 3/2 - \omega_{AB}}} \quad (22)$$

where E_c is the total collisional energy, $\varepsilon = 1$ is the symmetry factor, $\bar{\zeta}_{in}$ is the mean number of internal degrees of freedom, Λ is the pre-exponential factor, η is the temperature dependence, and E_a is the activation energy. The

Arrhenius parameters are listed in Table 2. [12] The vibrational degrees of freedom for SO₂ and SO are fixed to be the maximum value given by the simple harmonic oscillator model *i.e.*, $\zeta_{rot}^{SO_2} = 3$, $\zeta_{vib}^{SO_2} = 6$. Figure 6 shows the comparison of the reaction probabilities between the MD/QCT method and the TCE model as functions of E_c . For the TCE model, the reaction probability arises from zero when $E_c > E_a$ and reaches unity quickly at $E_c = 1.6 \times 10^{-18}$ J, whereas the reaction probability based on the MD/QCT method gradually increases towards unity within the large range of total collisional energies..

TABLE 2. Arrhenius parameters.*

Reaction	Λ [m ³ s ⁻¹ molecule ⁻¹]	η	E_a [J]	Temperature Range [K]	Source
SO ₂ +O → SO+O+O	2.491×10^{-14}	0	7.782×10^{-19}	2500-5200	Grillo <i>et al</i> [12]

CONCLUSIONS

The MD/QCT calculations have been performed to simulate collision between target molecule SO₂ and collider O for a series of SO₂ internal energies and relative collision velocities that are of interests to the atmospheric dynamics study of Io. Three possible dissociation reactions are modeled and the one in which SO₂ becomes SO+O is determined as the dominant reaction. Reaction cross sections, $\sigma_{r,MD}$, and the equivalent VHS cross sections, $\sigma_{VHS,MD}$, are obtained based on the MD/QCT results. Comparisons between $\sigma_{r,MD}$ and $\sigma_{VHS,MD}$ indicate that in high v_{rel} regime the dissociation reaction is the dominant process. For the future application of the MD/QCT results in DSMC, reaction probabilities as functions of SO₂ internal energy and total collisional energy are calculated by using the sum of the reaction cross section and equivalent VHS cross section as the total collision cross section. This method provides the consistent total collision cross sections and reaction probabilities that can be applied in DSMC for large range of total collisional energies. Processes other than dissociation reactions such as the heavy particle impact ionization of SO₂ may also be present at the high end of the v_{rel} range which could affect the dissociation reaction cross sections. Further investigation is needed in this aspect.

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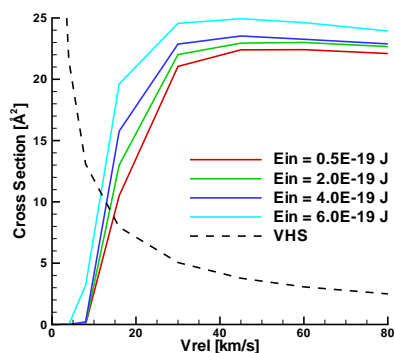


FIGURE 1. Reaction cross section [\AA^2] based on the MD/QCT calculations as functions of the relative collision velocity for different target SO_2 internal energies.

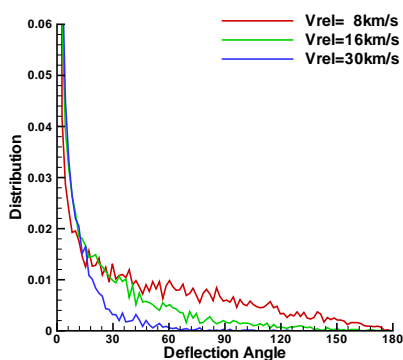


FIGURE 2. Deflection angle distribution for target SO_2 internal energy, $E_{in} = 4.0 \times 10^{-19}$ J.

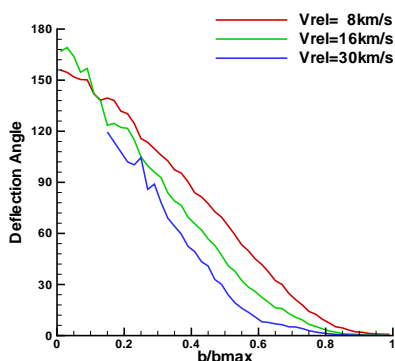


FIGURE 3. Deflection angle as a function of the normalized impact parameter ($b_{max} = 5 \text{\AA}$) for target SO_2 internal energy, $E_{in} = 4.0 \times 10^{-19}$ J.

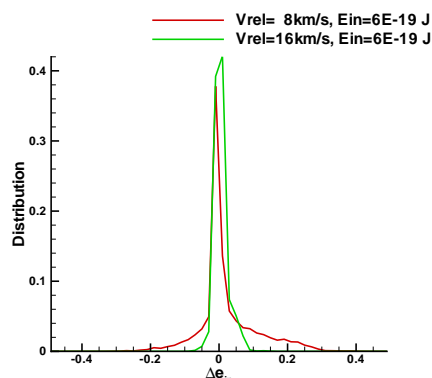


FIGURE 4. Distribution of changes in normalized internal energies of the target SO_2 that are not dissociated, Δe_{in} .

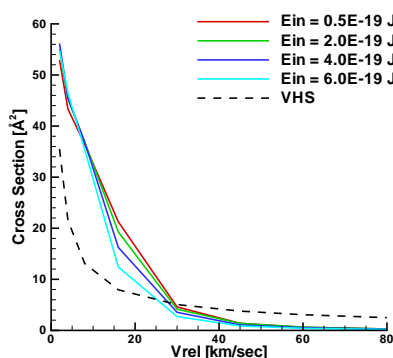


FIGURE 5. Equivalent VHS collision cross section [\AA^2] based on the MD/QCT calculations as functions of the relative collision velocity for different target SO_2 internal energies.

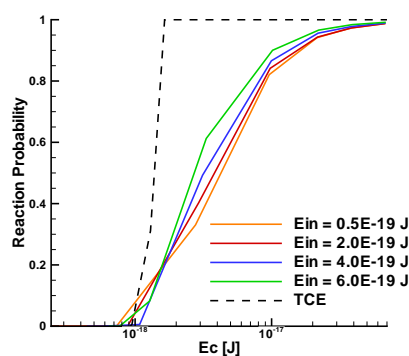


FIGURE 6. MD/QCT reaction probability as a function of the total collisional energy for different target SO_2 internal energies in comparison with the TCE reaction probability based on the Arrhenius parameters of Grillo *et al* [12].