Dissociation cross sections for $N_2 + N \rightarrow 3N$ and $O_2 + O \rightarrow 3O$ using the QCT method

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Cross sections for the homo-nuclear atom-diatom collision induced dissociations (CIDs): $N_2 + N$ and $O_2 + O$ are calculated using Quasi-Classical Trajectory (QCT) method on *ab initio* Potential Energy Surfaces (PESs). A number of studies for these reactions carried out in the past focused on the CID cross section values generated using London-Eyring-Polanyi-Sato PES and seldom listed the CID cross section data. A highly accurate CASSCF-CASPT2 N_3 and a new O_3 global PES are used for the present QCT analysis and the CID cross section data up to 30 eV relative energy are also published. In addition, an interpolating scheme based on spectroscopic data is introduced that fits the CID cross section for the entire ro-vibrational spectrum using QCT data generated at chosen ro-vibrational levels. The rate coefficients calculated using the generated CID cross section compare satisfactorily with the existing experimental and theoretical results. The CID cross section data generated will find an application in the development of a more precise chemical reaction model for Direct Simulation Monte Carlo code simulating hypersonic re-entry flows. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983813>]

I. INTRODUCTION

A re-entry vehicle encounters extreme atmospheric conditions during its descent.¹ The air in the vicinity of the vehicle can reach high temperatures² and begin to react. The possible reactions occurring during the re-entry can be classified into four categories:

- dissociation of N_2 or O_2 or NO colliding with another molecule,
- dissociation of N_2 or O_2 or NO colliding with another atom (N or O),
- recombination of two atoms to form a molecule,
- exchange (Zeldovich) reactions: $N_2 + O \rightleftharpoons NO + N$ and $O_2 + N \rightleftharpoons NO + O$.

In addition to the above reactions, if the temperatures exceed 9000 K, ionization can occur. Modeling chemical reactions in the air flow accurately and efficiently is vital in predicting the overall flowfield around the re-entry vehicle, in turn designing the Thermal Protection System (TPS).

One of the numerical techniques used to simulate the hypersonic flow past a re-entry vehicle in rarefied ambient atmosphere is the Direct Simulation Monte Carlo (DSMC) method. DSMC^{3,4} is a particle method capable of simulating non-equilibrium rarefied gas flows. Various collision models have been developed for DSMC that give an accurate collision rate. However, the cross sections for chemical reactions are calculated using models that are either phenomenological in nature or a function of macroscopic parameters, for example, the Total Collision Energy (TCE)⁵ and Quantum Kinetic (QK)⁶ models. Alternatively, modelling the reaction cross section based on *ab initio* methods offers higher theoretical supremacy over such phenomenological models. One of

the approaches to determine reaction cross sections uses the Quasi-classical Trajectory (QCT) method.

QCT calculations have been used extensively in calculating thermal rate coefficients for various reactions. Karplus⁷ *et al.* introduced the procedure to simulate the exchange reaction ($H_2 + H \rightarrow H + H_2$). This was followed by various groups studying different reactions.^{8–13}

Collision Induced Dissociation (CID) of nitrogen and oxygen molecules is a key step in the initiation of air chemistry. The CID process is initiated due to collisions between molecules and then continues with collisions with atoms and molecules. Collision induced dissociation of N_2 and O_2 with other molecules as collision partners has a higher effect on heat flux in the DSMC re-entry simulation compared to collision with nitrogen and oxygen atoms. However, constructing the PESs and calculating the CID cross section for the latter are simpler. Although the two systems (N_3 and O_3) are different, they are both simple and homonuclear. Hence the focus of the present work is to calculate the CID cross section for the dissociation of a N_2 molecule interacting with a N atom [Eq. (1)] and an O_2 molecule interacting with an O atom [Eq. (2)], while the interaction of N_2 and O_2 with molecules as well as DSMC simulations will be considered in the future.

Towards this end, the present work reports a global *ab initio* PES for the O_3 ground state generated using a combination of Restricted Active Space Self-Consistent Field (RASSCF) and Complete Active Space Second Order Perturbation Theory (CASPT2) methods. Constructing an accurate PES and running trajectories are time and memory intensive procedures. In addition to the new global PES, a new

method is proposed that calculates the CID cross section for the entire spectrum of ro-vibrational levels using spectroscopy data-dependent weights and CID cross section at selected ro-vibrational levels. This reduces the computational effort significantly and provides the prospect of increasing the number of trajectories, which in turn decreases the statistical scatter. The maximum energy of collision while simulating the hypersonic flow around a re-entry vehicle² is known to be in excess of 24 eV. Hence, the CID cross section data are calculated for an extended range of relative translation energies (up to 30 eV). Such high energies will introduce non-adiabatic effects and at present we restrict the calculations of the cross sections only for the ground state and will address the excited states in the future. To the best of our knowledge, this is the first instance of publishing CID cross section data for such high energy collisions. Additionally, the complete data of the CID cross section are published in the [supplementary material](#). The reported cross section data may also find utility in reaction models in Computational Fluid Dynamics (CFD). The reason for choosing the reactions represented by Eqs. (1) and (2) is the availability of resources¹⁴ that serve as a good validation for the QCT code. Once the veracity of the proposed model is established, CID cross sections for other air chemistry reactions will be calculated and reported.

Section II describes the generation and validation of global N₃ and O₃ PESs. Section III outlines the QCT method and discusses the CID cross section data for selected ro-vibrational numbers generated using the QCT method. Furthermore, a fitting technique to get the CID cross section for other ro-vibrational numbers is proposed and explained in Sec. IV. The CID cross section data are consolidated to obtain the dissociation rate coefficients for nitrogen and oxygen dissociation in Sec. V.

II. GLOBAL POTENTIAL ENERGY SURFACE (PES)

A. O₃ system

The quantal studies for the dissociation of an O₂ molecule require the inclusion of non-adiabatic effects.¹⁵ This is due to the closely spaced multiple electronic states for the O₃ system. In total, 27 electronic states need to be considered in the absence of the spin-orbit interaction. Also the conical intersection between the two lowest PESs increases complications. The complexities of the O₃ system are discussed at length by Tashiro and Schinke¹⁶ and Andrienko and Boyd.¹⁵ The inclusion of such complexities is presently beyond the scope of this work. At present, the trajectories are performed on a single ground state with adiabatic assumption. Previous studies¹⁷ suggest multiplication with a degeneracy factor 16/3 to account for the multiple surface problem in calculating the dissociation rate coefficients.

An analytically derived PES by Varandas¹⁸ in the Double Many Body Expansion (DMBE) form has been used extensively^{15,19–22} to study the O₃ system. This PES has a simple analytical form, formulated using experimental data on scattering and dissociation rate coefficients.

Several authors have presented a global PES or a part of it using *ab initio* methods.^{23–26} Müller *et al.*²⁵ conducted

a comparative study of characterization of open and ring minima using singles and doubles coupled-cluster (CCSD) method and a variety of basis sets. They concluded that the results calculated using Couple-Cluster Singles and Doubles with perturbation-correction of Triples [CCSD(T)] and MR-AQCC (Multi-reference interaction with Averaged Quadratic Coupled Cluster) with a quadruple-zeta correlation consistent basis set were within 3% of the experimental findings.²⁷ However, using methods such as the single and double excitation perturbation method for studying systems with strong electron correlation such as bond breaking and bond formation cannot be justified with full confidence.²⁸ A superior procedure of generating PES for a few atom systems is by implementing a multi-configurational method to account for static electron correlation followed by a dynamic correlation step.

Recently developed PESs^{29–34} have incorporated the complete active space self-consistent field (CASSCF) method followed by multi-reference methods. The PES created is further used to study the kinetics of ozone formation $O_2 + O \rightarrow O_3$ and determining isotope exchange rates. Deviation from the isotope exchange rates with experimental findings, especially at low temperatures, and limited understanding of the anomalous mass independent fractionation effect has been widely perceived as a direct consequence of unavailability of a satisfactory global PES. Seibert *et al.*²⁹ reported a global PES (SSB PES) using the multireference configuration interaction (MRCI) calculation and cc-PVQZ basis set. The SSB PES accurately described the open minima (C_{2v}), ring minima (D_{3h}), and dissociation threshold. Ozone dissociates to $O_2 + O$ when an end atom in the C_{2v} structure is removed. The SSB PES has a small barrier (45 cm⁻¹) above the dissociation limit and a van der Waals minimum in the exit channel of the minimum energy path. Babikov *et al.*³⁰ have concluded that this barrier is an artifact.

Dawes *et al.*^{33,34} have reported PES constructed with the MRCI-F12 method and VQZ-F12 basis set. A spin-orbit correction was added and it was observed that their PES showed accurate parameters of equilibrium structures (C_{2v} , D_{3h}) and a transition region without the reef structure. In addition to this, the vibrational levels calculated using their PES showed a satisfactory match with experiments. Moreover, substantial work^{24,35} has been carried out focussing on higher electronic states of ozone.

We have constructed a new PES that employs the RASSCF method to account for the static correlation followed by the CASPT2.³⁶ The calculations are performed using the MolCAS^{37–39} *ab initio* platform. The advantage of CASPT2 is its ability to handle complex systems with practicable computational cost. However, CASPT2 cannot be used as a black box method and needs careful consideration while choosing the appropriate active electrons and active space.²⁸ Different combinations of active electron (e) and active orbitals (o) (12e/9°, 12e/7°, 12e/12°, 18e/15°, and 18e/12°) for a small portion of the PES near the transition region were tested, and it was found that the PES with 12 active electrons consisting of only 2p orbitals of all O atoms and nine active orbitals was reasonably accurate and computationally inexpensive. It has been noted

that the proposition of placing only 2p orbitals for such systems as active orbitals is acceptable. Previous PESs also use the same active space. An augmented correlation-consistent polarized valence triple zeta (aug-cc-PVTZ) basis set is employed.

Different points on the O₃ PES are expressed in a coordinate system comprising of the distance between a pair of atoms forming the molecule (R1), distance between the third atom and one of the atoms of the molecule (R2), and the included angle (θ). Let R3 be the length of the third side of the triangle. The distances R1 and R2 are varied from 0.7 Å to 9.0 Å with more points clustered around the equilibrium bond distance of O₂ (1.208 Å). θ is distributed evenly between 0 and π in incremental steps of 12°. The various combinations of R1-R2- θ add up to a total of 15 376 points. All calculations were performed parallel on an Intel Xeon Phi processor and the total computation cost was 1152 CPU hours.

Ab initio calculations have shown that the O₃ system has a characteristic open minima (C_{2v}) and ring minima (D_{3h}). The existence of the ring minima is yet to be substantiated using experiments. The value of energy separation between the two minima and the dissociation barrier of ozone (C_{2v}) form to O₂ + O and the atomic configuration of the open and ring minima are presented and compared with other computational and available experimental references in Table I. The generated O₃ PES is within reasonable limits of the experimental values and existing computed values. Different two-dimensional contour plots by fixing one of the three variables give us a visual insight on the topography of the PES, as depicted in Fig. 1. Figures 1(a) and 1(b) show the contour plots with bond lengths (R1 and R2) as axes and fixing the included angle at 60° and 116.8°, respectively. The adjacent contour lines have a difference of 5 kcal/mol. Figures 1(a) and 1(b) show the ring minima and open minima, respectively. Contour plots in Figs. 1(c) and 1(d) show the structure of PES with a fixed R1 distance and varying included angle. The stationary point at 37° and 117° corresponds to two of the three open minima and the point at 60° in Fig. 1(d) corresponds to the ring minima. The transition state between C_{2v} and D_{3h} lies at around 75°.

TABLE I. Comparison of parameters with existing PES for O₃ system.

Geometry	C_{2v}		D_{3h}
	R(Å)	θ	R(Å)
Minima type			
Müller ²⁵	1.27	117.2	1.438
Experiment ²⁷	1.272	116.8	
Dawes ³⁴	1.271	116.8	1.436
Present	1.282	114.8	1.449
Energy differences (kcal/mol)			
	$E(C_{2v}) - E(D_{3h})$		$E(C_{2v}) - E(O_2) - E(O)$
Müller ²⁵	-29.5		-24.5
Experiment ²⁷			-26.1
Dawes ³⁴	-30.75		-26.7
Present	-34.4		-23.4

The variation of energy with included angle (θ) for C_{2v} configurations with a relaxed bond length is shown in Fig. 2. In addition to the characteristic minima C_{2v} and D_{3h} points, the transition point (R1 = R2 = 1.4 Å, θ = 75°), local minima M1 (R1 = R2 = 3.2 Å, θ = 24°), and local maxima (R1 = R2 = 1.8 Å, θ = 44°) are demonstrated in the energy profile.

The present PES is constructed with the purpose of studying oxygen dissociation. However, the surface involved in analyzing ozone dissociation is a subspace of the present global PES. Hence, all appropriate features involved in a Minimum Energy Path (MEP) of ozone dissociation should have a reasonable match with previous works. As mentioned earlier, many authors have found that the minimum energy path for the dissociation of ozone has an unusual reef structure as a result of an avoided intersection with a higher electronic state. As seen in Fig. 3, the submerged reef and van der Waals minima are observed along the minimum energy path. The submerged reef is located at R1 = 1.26 Å, R2 = 2.32 Å, and at a depth of 1.194 kcal/mol below the dissociation threshold. The van der Waals minimum is located at R1 = 1.248 Å, R2 = 3.19 Å, and at a depth of 1.954 kcal/mol below the dissociation threshold. Tyuterev *et al.*³¹ and Dawes *et al.*^{33,34} have reported PESs with and without the reef structures in their MEP. The PESs without the reef structure employ spin orbit correction which has not been included in the present work.

In addition to these features, the present PES estimates accurately the dissociation energy for an oxygen molecule at 119.2 kcal/mol (experimental value 119.14 kcal/mol). The lowest vibrational frequencies for the symmetric, bending, and antisymmetric stretch modes are 1109.36 cm⁻¹, 699.99 cm⁻¹, and 1048.68 cm⁻¹, respectively. The corresponding experimental results⁴⁰ for the modes are 1103.14 cm⁻¹, 700.93 cm⁻¹, and 1043.9 cm⁻¹, respectively, and as it can be observed the values are in a good match.

B. N₃ system

Several studies have reported the classical trajectory analysis of N₂-N collision⁴¹⁻⁴⁴ using N₃ PES. Laganà *et al.*⁴⁵ proposed the London-Eyring-Polanyi-Sato (LEPS) PES with a linear transition structure and a barrier height of 36 kcal/mol. Computational results⁴⁶ have suggested that the transition structure has a double barrier contrary to the LEPS structure.

Wang⁴⁷ reported a global PES using open-shell Couple-Cluster Singles and Doubles with perturbation-correction of Triples (CCSD(T)) technique and augmented correlation consistent basis set (aug-cc-pVQZ) using 3326 points. They reported a double barrier at a height of 47.2 kcal/mol above the reactant energy separated by a shallow well at a depth of 3.5 kcal/mol relative to the barrier. The transition state as calculated due to Wang was a non-linear bent shaped structure. At the double barrier, the bond lengths between the adjacent N atoms were 1.18 Å and 1.48 Å with an included angle 119°. At the shallow well, having the C_{2v} symmetry, the bond lengths were both 1.27 Å with 120° included angle. The PES was used to study the N₂ + N exchange reac-

FIG. 1. Detailed O₃ topology by constraining one of the three parameters (R₁, R₂, θ). Sub-figures (a) and (b) show the structure at a fixed included angle of 60° and 116.8°, respectively. Sub-figures (c) and (d) show the 2D topology at fixed R₁ = 1.164 196 Å and 1.449 9532 Å, respectively. Reference energy for the PES E(O₂ + O) = 119.2 kcal/mol.

tion using quantum dynamics wave packet calculations. The reported PES showed significant differences with the Laganà LEPS.

A series of PESs (L0-L4) were reported by Garcia *et al.*⁴⁴ based on the CCSD(T)/aug-cc-pVTZ system. PESs were based on *ab initio* calculations on a smaller data set of geometric configurations or points. The points were clustered around the

FIG. 2. Optimized energy profile in the C_{2v} symmetry for the O₃ system. Different points corresponding to D_{3h}, C_{2v}, TS, and local minima and maxima (M1 and M2) are demonstrated on the energy profile. Reference energy for the PES E(O₂ + O) = 119.2 kcal/mol.

FIG. 3. Variation of energy (with respect to dissociation threshold) along the minimum energy path (ρ) for ozone dissociation O₃ → O₂ + O. Reference energy for the PES E(O₂ + O) = 0 kcal/mol.

transition state region and minimum energy path. The calculated values of bond lengths and included angle for transition states and the well geometry agreed well with the work of Wang *et al.* Paukku *et al.*⁴⁸ have constructed a highly accurate global PES for the N_4 system, wherein they calculated energies for a total of 16 380 configurations points for various molecular arrangements of N_4 . They have chosen $12e/12^\circ$ (12 electron, 12 orbital) active space for the CASSCF method and Dunning style augmented correlation-consistent polarized (maug-cc-pVTZ) as the basis set. Different molecular arrangements for N_4 systems were considered in constructing the PES. The PES for the current N_3 system is drawn as a subset of this N_4 global PES.

A six-dimensional global least squares fit for the N_4 system is available.⁴⁸ Using a six dimensional surface fit for the present nitrogen dissociation is computationally expensive. Instead, we have obtained points corresponding to different N_3 configurations from the N_4 global fit and constructed a three dimensional least square fit. An N_3 data point can be visualized as an N_4 configuration with one of the four atoms at a far away distance from the other three atoms so that it has no influence on the potential of the N_3 system. The energy for each configuration is calculated using the global least squares fit.⁴⁸ The analytical local and global fits for the N_4 system are available at the POTLIB library.⁴⁹ Various configurations of N_3 system are chosen in the same manner as the ones for the O_3 system. The only point of difference between the two sets of configurations is that points for N_3 are more clustered near the equilibrium distance of N_2 ($=1.098$ Å).

Quasi-classical trajectories using the six-dimensional N_4 analytical fit need six times more computational time than that required for trajectories using the three dimensional N_3 analytical fit (initialized at same conditions). The computational gain of using the three-dimensional analytical fit over the six dimensional fit is obvious.

The N_3 PES constructed is a $^4A''$ state. The value of the dissociation energy is 228.7 kcal/mol and is in good agreement with the experiments (228.47 kcal/mol). Table II shows the

TABLE II. Comparison of parameters with existing PES for the N_3 system.

	$r_A(\text{\AA})$	$r_B(\text{\AA})$	$\theta(^{\circ})$	$\Delta E(\text{kcal/mol})$ w.r.t. $N_2 + N$
Transition state				
Present	1.18	1.48	119	47.12
Wang ⁴⁷	1.184	1.491	117	47.2
Garcia ⁴⁴	1.174	1.505	116	47.0
Galvão ⁵⁰	1.18	1.46	119	45.9
Well				
Present	1.262	1.262	120	44.66
Wang ⁴⁷	1.27	1.27	117	43.7
Garcia ⁴⁴	1.268	1.268	119	44.5
Galvão ⁵⁰	1.25	1.25	119	42.6

comparison of the position and the energy (relative to the well) of the double barrier transition state between the present and previous PESs. Figure 4 shows the two-dimensional contour plot with a fixed included angle ($\theta = 120^\circ$) and variables R_1 and R_2 . The symmetrical transition points and the shallow well are all visible in the contour plot. The shallow well is located at $R_1 = R_2 = 1.262$ Å and $\theta = 120^\circ$. The double barrier transition state geometry was symmetrical about the $R_1 = R_2$ line and located at $R_1 = 1.18$ Å, $R_2 = 1.48$ Å, and ($\theta = 119^\circ$) at a height of 47.12 kcal/mol. The difference between the shallow well and the transition states was 2.45 kcal/mol. The accuracy of characteristic points of the N_3 PES is within reasonable limits^{44,47,50} and this goes to show the robustness of the global N_4 PES.

Similar to the O_3 system analysis, the variation of energy with an included angle (θ) for C_{2v} configurations with relaxed bond length for the N_3 system is shown in Fig. 5. In addition to the characteristic minima C_{2v} and D_{3h} points, the transition point ($R_1 = R_2 = 1.4$ Å, $\theta = 75^\circ$), local minima M1 ($R_1 = R_2 = 3.2$ Å, $\theta = 24^\circ$), and local maxima ($R_1 = R_2 = 1.8$ Å, $\theta = 44^\circ$) are demonstrated in the energy profile.

FIG. 4. 2D contour plot of N_3 PES with fixed included angle at 119° and varying R_1 - R_2 depicting the transition state and the well structure. Reference energy for the PES $E(N_2 + N) = 228.7$ kcal/mol.

FIG. 5. Optimized energy profile in the C_{2v} symmetry for the N_3 system. Different points corresponding to D_{3h} , C_{2v} , TS, and local minima and maxima (M1 and M2) are demonstrated on the energy profile. Reference energy for the PES $E(N_2 + N) = 228.7$ kcal/mol.

III. QUASI-CLASSICAL TRAJECTORY METHOD

The QCT method employed for the present work is principally similar to the works of Karplus *et al.*⁷ and Truhlar.⁵¹ Trajectory studies of reactions require gradients at different points on the PES. Since a detailed calculation at each and every point is not practical for the present study, the energies are calculated for a few discrete points on the PES and the data at these selected points are used to create an analytical representation of the entire PES using interpolation or data fitting methods. As compared to interpolation schemes, a permutationally invariant data fitting method such as global and local least squares fitting^{48,52} has yielded more favorable results for PES. In addition to these methods, a functional form proposed by Aguado and Paniagua⁵³ is also widely used to fit three atom systems. Although PES fitting using both the global and the local least squares fit was calculated, the former was used in the QCT method to reduce the computational time. Also, as the systems are simple, the permutationally invariant global fit was found to be sufficiently accurate (Table III). The interpolated fit and the actual energy as a function of R_2 , for different R_1 and $\theta = 0^\circ$, for the two systems under consideration are shown in Figs. 6 and 7. The tabulated values (Table III) of the relative maximum and the root mean square errors show the quality of the fits.

The impact parameter (b) is randomly sampled using the relation $b = \xi^{1/2} b_{max}$, where b_{max} is the maximum impact parameter and ξ is a random number between 0 and 1. Second order accurate Verlet integrator⁵⁴ is implemented for the time integration in the present study. The values of the turning radii for the ro-vibrational number are determined by

TABLE III. Error analysis detailing the quality of the fit.

	N_3	O_3
Equilibrium distance (r_e)	1.098 Å	1.208 Å
Non-linear parameter (a_e)	0.9 Å	0.8 Å
M (highest index of the polynomial function)	9	9
Relative max. error (%)	0.105	0.785
RMS error	0.071	0.119

FIG. 6. Comparison of global fit with actual data at $\theta = 0^\circ$ for O_3 PES.

solving the vibrational Schrödinger equation using the semi-classical Wentzel-Brillouin-Kramers (WKB)^{55,56} method or using the numerical Numerov's method. The value of internal energy (e_{vj}) of many ro-vibrational states is greater than the dissociation enthalpy and such states trapped by the centrifugal barrier are regraded as quasibound states. The remaining ro-vibrational states are bound states. At higher temperature, the quasibound states have a significant contribution in the kinetics.^{57,58} Trajectories with quasibound states are treated just as trajectories with bound states.⁵⁹

The number of vibrational levels calculated for the $j = 0$ rotational level is 55 for the nitrogen molecule. The number of bound states and quasibound states are 6998 and 2021, respectively, adding up to a total of 9019 states. In contrast, the maximum vibrational levels for the $j = 0$ rotational level, the number of bound states, and the number of quasibound states are 37, 4221, and 1872, respectively, for the oxygen molecule. There is slight variation with existing values^{43,56} of the number of bound and quasibound states for the nitrogen system. It has been argued previously that the variation can be due to the accuracy of the numerical methods employed and the quality of the curve fit. However, as the internal energy increases, the states are more closely spaced and often regarded as band instead of distinct lines. It is safe to assume that the effect of the difference in closely spaced higher ro-vibrational levels would

FIG. 7. Comparison of 3-body N_3 global fit with data calculated using the N_4 global fit by Paukku *et al.* ($\theta = 0^\circ$).

not be menacing on the CID cross section obtained using the QCT method and the DSMC chemical model.

Batches of 25 000 trajectories each were run for 21 different relative velocities each ranging from 0 to 30 eV which are spaced more densely below the dissociation enthalpy (9.9 eV for N_2 and 5.2 eV for O_2). This process is repeated for all vibrational levels at the zero rotational level. As each trajectory is independent, generating a large sample is an embarrassingly parallel problem. The total run time for the N_3 system is 8750 CPU hours on an Intel Xeon E5 processor workstation using the Intel MPI compilers. For O_3 systems, the total vibrational levels are fewer compared to N_3 and hence it takes lesser computational time (6100 CPU hours). Additional details about the QCT code are reported in the [supplementary material](#).

The CID cross section is an effective area used to indicate the measure of the probability for a collision to result in a successful chemical reaction. A large sample of trajectories are run for a molecule at the $\{v, j\}$ ro-vibrational level colliding with a third participating atom approaching with relative velocity V_R and maximum impact parameter b_{max} . The cross section for an ensemble of trajectories is

$$\sigma(V_R, v, j) = (\pi b_{max})^2 \frac{N_R(V_R, j, v)}{N(V_R, j, v)}, \quad (3)$$

where N is the total number of trajectories progressed and N_R is the number of trajectories that result in a successful dissociation.

Table IV shows a sample comparison between the trajectory results tabulated by Wysong *et al.* and the results calculated using the present QCT code. Wysong *et al.*¹⁴ have provided the cross section data by Esposito *et al.*^{42,43} for nitrogen dissociation using LEPS PES. The results compared correspond to an N_3 system with the molecule at the 20th vibrational level. The CID cross section data in the present simulations and the reference values are not free of statistical scatter. The variation with relative translational energy and the order of the CID cross section calculated are in reasonable agreement with the reference values. Additionally, the CID cross section calculated for other ro-vibrational states also compared well with the published data. A comparison between the CID cross sections calculated by the QCT code using the LEPS PES and the present CASPT2 PES is also tabulated in Table IV. It is apparent that the value of the CID cross section obtained from the QCT sample using LEPS is consistently larger as compared to the CID cross section obtained using

TABLE IV. Comparison of the CID cross section (m^2) for the N_3 system at $v = 20$, $j = 0$.

Translational energy (eV)	Benchmark ^{14,42,43} (m^2)	Present code	
		LEPS (m^2)	CASPT2 (m^2)
6.06	5.49×10^{-22}	6.11×10^{-22}	1.02×10^{-22}
6.73	1.91×10^{-21}	1.08×10^{-21}	7.79×10^{-22}
7.40	3.81×10^{-21}	3.81×10^{-21}	2.14×10^{-21}
8.06	5.15×10^{-21}	6.47×10^{-21}	4.23×10^{-21}
8.73	9.22×10^{-21}	9.56×10^{-21}	8.86×10^{-21}
9.40	1.48×10^{-20}	1.40×10^{-20}	1.09×10^{-21}

FIG. 8. Comparison of the CID cross section (σ) of dissociation at various vibrational levels for the N_3 system at $j = 0$ along with error bars ($\Delta\sigma$) calculated using Eq. (4). (The dotted lines are just a guide to the eye.)

CASPT2 PES. Dissociation rate coefficients obtained using the CID cross section tabulated in Refs. 14, 42, and 43 have a slightly larger deviation from the experimental⁶⁰ results compared to the rate coefficients calculated using the CID cross section obtained using the present CASPT2 PES. The comparison of CID reaction rate coefficients with experimental data is shown in Sec. V (Figs. 12 and 13).

Figures 8 and 9 show the variation of the CID cross section for the dissociation of nitrogen and oxygen with relative translational energy for different vibrational numbers at the zero rotational number. The scatter ($\Delta\sigma$) in the cross section (σ) is calculated using the following expression:

$$\Delta\sigma = \sigma \times \left(\frac{N - N_R}{NN_R} \right), \quad (4)$$

where N_R is the number of trajectories resulting in a successful dissociation and N is the total number of trajectories. As anticipated, the CID cross section increases as the vibrational level and relative translational energy increase. At a higher vibrational level, the overall energy of the system given by the sum of internal energy and relative translational energy increases. In such a case, the chance of a dissociation at a

FIG. 9. Comparison of the CID cross section (σ) of dissociation at various vibrational levels for the O_3 system at $j = 0$ along with error bars ($\Delta\sigma$) calculated using Eq. (4). (The dotted lines are just a guide to the eye.)

lower translational energy increases and the threshold energy value shifts towards a lower value. It is also evident that the threshold energy for nitrogen dissociation is higher compared to oxygen dissociation. No observations are counter-intuitive and this substantiates as a sanity test.

IV. CID CROSS SECTION FITTING METHOD

The QCT method is a Monte Carlo scheme that needs a large sample to gain confidence about the accuracy of the results. As mentioned earlier, there are more than 9000 ro-vibrational levels for the N_3 system and 6000 levels for the O_3 system. Monte Carlo simulation for each and every ro-vibrational level is impossible in practice.

In the present work, a new fitting technique is suggested that aims to drastically reduce the numerical load. At the core of the technique is the conjecture that at a given vibrational level, the variation of the CID cross section (σ) with the relative translational energy (E_{tr}) at different rotational levels has a similar form. As the rotational number increases, it is observed that the difference between the CID cross section ($\sigma(j+1) - \sigma(j)$) for a fixed relative translational energy increases. The difference in the energy between two successive rotational levels also varies in a similar pattern. The proposed technique utilizes this observation and uses spectroscopic data for data fitting. The algorithm for this technique is explained in the following paragraph.

In addition to the results at the zeroth rotational number, another batch of trajectories is run at half the maximum possible rotational number ($j = j(v)_{max}/2$). The procedure remains the same with an added complexity due to a non-zero rotational quantum number. The CID cross section for the remaining rotational numbers is either interpolated or extrapolated using the cross section data at $j = 0$ and $j = j(v)_{max}/2$. The general formula for interpolation is of the form

$$\sigma(V_R, v, j) = \left((w_1 \sigma(V_R, v, 0)^{0.5} + w_2 \sigma(V_R, v, j(v)_{max}/2)^{0.5}) / (w_1 + w_2) \right)^2, \quad (5)$$

where w_1 and w_2 are the weights

$$w_1 = \tilde{v}(v, j(v)_{max}/2) - \tilde{v}(v, j) \quad (6)$$

$$w_2 = \tilde{v}(v, j) - \tilde{v}(v, 0) \quad (7)$$

and $\tilde{v}(v, j)$ is the internal energy,

$$\tilde{v}(v, j) = \omega_e(v + 0.5) - \omega_e x_e(v + 0.5)^2 + \omega_e y_e(v + 0.5)^3 + (B_e - \alpha_e(v + 0.5))j(j + 1) - D_e j^2(j + 1)^2. \quad (8)$$

FIG. 10. Comparison of trajectories' results at $j = 30$ with interpolated values using the data at $j = 0$ and $j = \max(j)/2$ for the nitrogen system. The vibrational number for all the line plots corresponds to 20.

The vibrational and rotational constants in Eq. (8) obtained from data fitting energy levels calculated using the WKB method and Numerov's method and corresponding experimental values⁶¹ are tabulated and compared in Table V. Spectroscopic constants generated from the WKB data are used in the present work in calculating CID cross sections and dissociation rate coefficients. Again the comparison shows a reasonable match.⁶¹

An extra set of trajectories was calculated with a different rotational energy level between 0 and maximum rotational number for a N_3 system at a vibrational level of 20. The comparison of the generated data with the interpolated data for the rotational number $j = 30$ is shown in Fig. 10. The close agreement is a testament of the validity of the method. The average relative difference between interpolated values and values obtained using the QCT method for different rotational numbers and different relative translational energies was less compared to the average relative difference for simple interpolation without any weights (i.e., $w_1 = w_2 = 1$). This highlights that the CID cross section for different rotational levels at a given vibrational level does not follow a linear fitting scheme and a weighted scheme is more reasonable.

Figure 11 shows the comparison between the CID cross section generated using trajectories at different rotational levels at a constant relative translational energy ($E_{trans} = 9.4$ eV) and the CID cross section generated using the fit described by Eqs. (5)–(8) for all rotational levels for different vibrational numbers ($v = 20, 30, 40$). It is evident that the CID cross section calculated using the fit is in good agreement with the CID cross section calculated using trajectories.

TABLE V. Spectroscopy constants (cm^{-1}).

	N_2^{61}	N_2 (WKB)	N_2 (Numerov)	O_2^{61}	O_2 (WKB)	O_2 (Numerov)
ω	2358.57	2382.23	2315.24	1580.39	1620.93	1606.69
$\omega_e x_e$	14.324	14.57	14.01	12.112	12.74	11.79
$\omega_e y_e$	-0.002 26	-0.002 28	-0.002 62	0.0754	0.028 12	0.091
B_e	1.998 24	2.006	1.999	1.4451	1.4147	1.3291
α_e	0.017 318	0.017 75	0.017 81	0.015 23	0.015 04	0.016 12
D_e	5.76×10^{-6}	6.459×10^{-6}	5.971×10^{-6}	4.839×10^{-6}	3.734×10^{-6}	4.07×10^{-6}

FIG. 11. Comparison of trajectory results (represented by scatter plot) with fitted values (line plot) using the data at $j = 0$ and $j = \max(j)/2$ for the N_3 system at $E_{trans} = 9.4$ eV and for different rotational and vibrational numbers.

The benefits of the proposed technique are apparent. A larger sample of trajectories can be calculated for a limited number of ro-vibrational numbers. The CID cross section for all rotational levels at a particular vibrational level can be interpolated using the CID cross section data generated at just two levels: $j = 0$ and $j = \max(v(j)/2)$. The overall computational effort reduces significantly and overall reliance on the calculated data can increase. The final application of the CID cross section is aimed at modeling chemical reactions in DSMC. The same fitting technique can also be incorporated in DSMC. An *ab initio* based chemical reaction model in DSMC will calculate the CID cross section from the database generated using the QCT method instead of using the TCE or QK models. The fitting procedure introduced here will improve the overall efficiency in developing a more computationally efficient *ab initio* based chemical reaction model in DSMC. Thus, the advantage of the fitting model is twofold: a reduction in memory usage by storing lesser CID cross section data and a decrease in the computational time when calculating the CID cross section as a function of translational and internal energies.

The results and comparisons suggest that the fitting method is promising. However, an extrapolation of this idea to other complex molecular systems might be more involved and a systematic theory needs to be evolved. In the present case, the cross section essentially depends on the total energy of the system. This may not be the case for other reactions. The effect of increase in rotational energy might be contrary in other systems. The excellent match seen in Figs. 10 and 11 indicates a possibility that a more sound theory is involved.

V. DISSOCIATION RATE COEFFICIENTS FROM THE CID CROSS SECTION DATA

CID cross section results obtained through the PES-QCT method will be used to develop a true non-equilibrium chemistry model. However, the data should at the least match the Arrhenius equation at equilibrium conditions. Integrating the cross section over the equilibrium distribution function of

FIG. 12. Dissociation rate coefficients calculated using data from the present work (—) for the dissociation $O_2 + O \rightarrow O + O + O$ compared with theoretical studies by Park¹ (---), shock tube experimental results by Shatalov⁶² (●), and computational result by Andrienko¹⁵ (○).

E_T (or V_R), v , and j will give the required dissociation rate coefficients.

The dissociation rate coefficients have the following final form:

$$k(T) = Q_{v,j}^{-1} \left[\sum_{v,j} g_j (2j+1) \exp\left(-\frac{E(v,j)}{2kT}\right) \times N_A \frac{2^{1/2}}{\pi} \frac{\mu^{3/2}}{kT} \times \int_0^\infty \sigma(v,j, V_R) \exp\left(-\frac{\mu V_R^2}{2kT}\right) V_R^3 dV_R \right], \quad (9)$$

where $Q_{v,j}$ is the partition function, g_j is the nuclear degeneracy, and N_A is the Avogadro number. The above procedure is applied to obtain dissociation rate coefficients for oxygen (Fig. 12) and nitrogen (Fig. 13) systems. A constant factor of $16/3$ ¹⁷ that accounts for degeneracy due to multiple electronic states is considered for calculating the dissociation rate coefficients for oxygen. The dissociation rate coefficients are compared with both experimental^{1,62} and computational results.¹⁵ Overall match between the present data and the experimental rates is good.

FIG. 13. Dissociation rate coefficients calculated using data from the present work (—) for the dissociation $N_2 + N \rightarrow N + N + N$ compared with theoretical studies by Park¹ (---) and shock tube experimental results by Appleton⁶⁰ (●), and computational result using N_3 LEPS by Esposito⁴¹ (○).

VI. SUMMARY

A new O₃ PES using the RASSCF-CASPT2 method is presented. The arrangement of the O atoms and the energy barriers for the ring minima and the open minima is in good agreement with the corresponding values from experiments and previously generated PESs. The new O₃ PES along with N₃ PES derived from the CASSCF-CASPT2 global N₄ PES is used to calculate the CID cross section for the two atom-diatom dissociations using the QCT method. Trajectories are carried out for only a selected number of ro-vibrational levels. A new fitting technique for determining the CID cross section for the remaining ro-vibrational spectrum is presented and tested. The fitting procedure uses the spectroscopic data as weights. The CID cross section data generated are suitable for the high energy collisions encountered in the shock region in front of a vehicle entering the atmosphere at hypersonic speed. However, the CID cross section data for the oxygen dissociation are limited to the ground state and an accurate model for dissociation at higher enthalpy will require CID cross section data for higher electronic states also. This will require generation of global PESs for the higher electronic states for the O₃ system and a QCT code capable of handling non-adiabatic effects. The future work will focus on the generation of a more robust database in order to deal with this shortcoming. The CID cross section data generated will be used in developing an *ab initio* based chemical reaction model to be implemented in DSMC. The CID cross section fitting procedure is tailor-made for developing an efficient DSMC chemical reaction model particularly in non-equilibrium situations.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the CID cross section data (with estimated error), reaction rate coefficients, python code for O₃ and N₃ PES, and additional details on QCT code.

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