Accurate Reproducing Kernel-Based Potential Energy Surfaces for the Triplet Ground States of N$_2$O and Dynamics for the N+NO$\leftrightarrow$O+N$_2$ and N$_2$+O$\rightarrow$2N+O Reactions

Debasish Koner,$^1$ Juan Carlos San Vicente Veliz,$^1$ Raymond J. Bemish,$^2$ and Markus Meuwly$^{1, a)}$

$^1$Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

$^2$Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, New Mexico 87117, USA

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Accurate potential energy surfaces (PESs) have been determined for the $^3A'$ and $^3A''$ states of N$_2$O using electronic structure calculations at the multireference configuration interaction level with Davidson correction (MRCI+Q) and the augmented Dunning-type correlation consistent polarize triple zeta (aug-cc-pVTZ) basis set. More than 20000 MRCI+Q/aug-cc-pVTZ energies are represented using a reproducing kernel Hilbert space (RKHS) interpolation scheme. The RKHS PESs successfully describe all reactant channels with high accuracy. The analytical PESs are characterized by computing the minima and transition states on it. Quasiclassical dynamics simulations are then used to determine thermal and vibrational relaxation rates for the N+NO and O+N$_2$ collisions. The agreement between results obtained from the simulations and from available experiments is favourable for both types of observables, which provides a test for the accuracy of the PESs. The PESs can be used to calculate more detailed state-to-state observables relevant for applications to hypersonic reentry.

$^a)m.meuwly@unibas.ch$
I. INTRODUCTION

The [NNO] reactive collision system is relevant for atmospheric and environmental chemistry, and at the hypersonic flight regime. Two particularly relevant reactions involve the N+NO $\leftrightarrow$ O+N$_2$ processes. Both the forward (N+NO $\rightarrow$ O+N$_2$) and reverse (O+N$_2$ $\rightarrow$ N+NO) reactions are major processes in modelling the hyperthermal interactions during reentry of space vehicles and thus play significant role in aerospace engineering. The forward reaction produces molecular nitrogen while the reverse reaction generates nitric oxide via the Zeldovich mechanism. The forward reaction also plays important role in the Martian and Venusian atmospheres. The ground state of the N$_2$O molecule is singlet (1$A'$) and asymptotically connects with the N(1D)+NO(X$^2\Pi$) and O(1D)+N$_2$(X$^1\Sigma_g^+$) channels. For the singlet electronic state of N$_2$O the photodissociation dynamics and reactive collisions have been studied previously using theory and experiment. On the other hand, the triplet manifold of N$_2$O connects with the N(4S)+NO(X$^2\Pi$) and O(3P)+N$_2$(X$^1\Sigma_g^+$) states, with all the atomic and diatomic fragments in their electronic ground states in both channels. The N(4S)+NO(X$^2\Pi$) $\rightarrow$ O(3P)+N$_2$(X$^1\Sigma_g^+$) is highly exothermic and plays an important role in the upper atmosphere in removing N(4S). The reaction also helps removing the NO pollutant from the atmosphere which leads to ozone depletion. The 4S state of N and 2$\Pi$ state of NO lead to 3$A'$, 3$A''$, 5$A'$ and 5$A''$ states in Cs symmetry while the O(3P)+N$_2$(1$\Sigma_g^+$) channel results 3$A'$ and 3$A''$ states. In the absence of spin orbit coupling both reactions occur adiabatically on the triplet PESs.

For the forward reaction, several experiments have reported rates using different techniques. One experiment measured the N-atom concentration via line absorption and reported a rate of $3 \pm 1 \times 10^{-11}$ cm$^3$s$^{-1}$ at 300 K. Conversely, using discharge flow-resonance fluorescence (DF-RF) and flash photolysis-resonance fluorescence and a value of $3.4 \pm 0.9 \times 10^{-11}$ cm$^3$s$^{-1}$molecule$^{-1}$ was suggested in the 196–400 K temperature range. This rate was recommended for chemical modeling of stratospheric processes, while another DF-RF experiment reported a rate of $(2.2 \pm 0.2) \times 10^{-11}$ exp$(160 \pm 50/T)$ cm$^3$s$^{-1}$molecule$^{-1}$ over the range 213–369 K. In two different shock tube studies, the rate was measured at 1850–3160 K and 1251–3152 K to be $3.32 \times 10^{-11}$ and $3.7 \times 10^{-11}$ cm$^3$s$^{-1}$molecule$^{-1}$, respectively. The low temperature rates for this reaction is measured as $(3.2 \pm 0.6) \times 10^{-11}$ cm$^3$s$^{-1}$molecule$^{-1}$.
exp(25±16/T) cm$^3$s$^{-1}$molecule$^{-1}$ in a continuous supersonic flow reactor at 48–211 K. The recommended value, suggested by Baulch et. al., for combustion modelling is 3.5 × 10$^{-11}$ cm$^3$s$^{-1}$molecule$^{-1}$ over the temperature range 210–3700 K. Most of the experiments mentioned above suggest high rates for the forward reaction at low temperatures which points towards a barrierless process.

For the reverse reaction only few experimental studies have been reported. The rate expression obtained from a shock tube experiment at 2384–3850 K by heating N$_2$/O$_2$/N$_2$O/Kr mixtures was given as $1.84 \times 10^{14}\exp(-76250/RT)$ cm$^3$s$^{-1}$mol$^{-1}$ (corresponding to $3.055 \times 10^{-10}\exp(38370/T)$ cm$^3$s$^{-1}$molecule$^{-1}$). Another, later, experiment determined the rate coefficient from O- and N-concentration measurements in shock heated N$_2$/N$_2$O/Ar mixtures at 2400–4100 K to be $3.0 \times 10^{-10}\exp(-38300/T) \pm 40\%$ cm$^3$s$^{-1}$molecule$^{-1}$. The rate of NO formation in the burned gas region of high temperature oxypropane flame has been estimated from experiment and using a mathematical modelling at 2880 K as $10^{7.93}$ cm$^3$s$^{-1}$mol$^{-1}$ (corresponding to $1.413 \times 10^{-16}$ cm$^3$s$^{-1}$molecule$^{-1}$).

Theoretical studies focused primarily on exploring the electronic structure for the system, constructing potential energy surfaces (PESs) and carrying out dynamical simulations on these PESs. *Ab initio* PESs have been determined for the $^3A^\prime$ and $^3A^\prime\prime$ states of N$_2$O using complete active space self consistent field (CASSCF)/contracted CI (CCI) calculations. For the forward reaction, a small barrier of 0.5 kcal/mol was found on the $^3A^\prime\prime$ PES whereas a considerably larger barrier of 14.4 kcal/mol was found on the $^3A^\prime$ PES. For the reverse reaction the endoergicity was calculated to be 75 kcal/mol. An analytical PES for the $^3A^\prime\prime$ state of N$_2$O was constructed from CASSCF/CCI energies using a Sorbie-Murrell functional form and quasiclassical trajectory (QCT) calculations were performed for the N+NO collisions at 300 K.

Although the triplet states of N$_2$O have immense importance in environment, atmospheric chemistry and high energy collisions in hyperthermal flow, only three PESs are available in the literature. More recent electronic structure calculations have been performed on both the triplet states of N$_2$O using CASSCF, CASPT2 methods and different basis sets. Later the CASPT2/cc-pVTZ, energies from Ref. 29 were used along with additional energies at
the same level of theory to construct analytical representations for the $^3A'$ and $^3A''$ PESs. The root mean square deviations (RMSD) of these fits were 2.28 and 1.8 kcal/mol for the $^3A'$ and $^3A''$ PESs, respectively. This work confirms that there is no barrier to form N$_2$+O when approaching from the N+NO side for the $^3A'$ state. The rates for the forward and the reverse reactions were calculated from improved canonical variational transition-state (ICVT) theory on the new PESs and also on the PESs from Ref. 25. Quantum wave packet dynamics had been carried out to study the N+NO reaction on both triplet states and rates were calculated for a wide range of temperatures using the $J$-shifting approximation. The forward reaction was studied using QCT to obtain the rates up to 5000 K and explore the energy distributions and reaction mechanisms. Also, the reverse reaction was studied again via QCT on the CASPT2/cc-pVTZ PESs to obtain the vibrational relaxation rates from $v = 1$ to $v' = 0$ states.

Analytical PESs were also constructed for the two lowest triplet states of N$_2$O based on MRCI/maug-cc-pVTZ calculations and applying the dynamically scaled external correlation method with root-mean-squared errors (RMSE) of 4.44 and 3.71 kcal/mol for the $^3A'$ and $^3A''$ PESs, respectively. Six states were included in the dynamically weighted state-averaged CASSCF calculations and permutational invariant polynomials were used to represent the many-body part of the PESs. Geometries and energetics of the stationary states were found to differ from the earlier PESs. QCT calculations for the O+N$_2$ collisions at high energies on the triplet PESs of Ref. 27

Finally, a reproducing kernel based PESs for the $^3A'$ and $^3A''$ states were calculated using MRCI+Q/cc-pVTZ energies and rates and product state distributions were calculated up to 20000 K. However, due to presence of a small barrier on the $^3A''$ PES in the N+NO channel the calculated QCT rates were smaller at low temperatures. Recently, a state-to-state cross section model for the forward reaction based on the $^3A'$ PES has been developed using neural network which predict the thermal rates and product state distributions accurately.

Reaction rates obtained from the PESs using fits to the CASPT2/cc-pVTZ data are in good agreement with the experiments. However, the vibrational relaxation rates for the reverse reaction are significantly smaller than the experimental results up to 7000 K.
The PESs in Ref. 26 were constructed using a lower level of theory (CASPT2/cc-pVTZ) and it is found that number and geometry of the stationary states differs using higher level (MRCI/maug-cc-pVTZ) of theory and more states in the CASSCF calculations. These PESs are meant for exploring the dynamics of the O+N\(_2\) collisions at high energies. Since the forward reaction is barrierless and is highly reactive at very low temperatures, a very reliable description of the N+NO channel is required in the asymptotic region, which was absent in Ref. 27 PESs. On the other hand the reproducing kernel Hilbert space (RKHS) interpolation procedure can capture the correct long range behavior for different types of interactions.\(^{36-39}\)

Another relevant quantity that balances the energy content of hot gas flow is the exchange and relaxation of vibrational energy which can also be determined from QCT simulations.\(^{40,41}\) This property has been found to be sensitive to different regions of the PES than thermal rates\(^{39}\) and provides an additional possibility to validate the quality of the PESs. Rates for vibrational relaxation serve also as input data for more coarse grained simulations, such as direct simulation Monte Carlo (DSMC)\(^{42}\). With N\(_2\) and O\(_2\) as two major components of air, N\(_2\)+O inelastic collisions may significantly affect the energy content and energy redistribution in high temperature air flow. The vibrational relaxation (VR) rates are calculated from relaxation time parameter (\(p\tau_{\text{vib}}\)) using the Bethe-Teller model.\(^{41,43}\)

Here, global PESs have been constructed for the \(^3\)A\(^{\prime}\) and \(^3\)A\(^{\prime\prime}\) electronic states for the reactive [NNO] system using RKHS interpolation from a large number (> 10000) of MRCI+Q/aug-cc-pVTZ energies for each state. The present RKHS PESs are constructed using \(\sim 3\) times more \textit{ab initio} energies than the previous PESs\(^{27}\) and thus cover all the important interaction regions. Using a RKHS allows one to impose the correct long range behavior for the dipole-induced dipole interactions (\(\sim 1/R^6\)) and also reproduce the topology of the \textit{ab initio} PESs accurately. Quasiclassical trajectories are then run on these new PESs to determine thermal and vibrational relaxation rates which allow validation of the PESs by comparing with experiments.

The present article is organised as follows. The methodological details of constructing the RKHS PESs and QCT dynamics are discussed in Section II followed by presenting the results.
FIG. 1. Schematic energy diagram for the N$_2$O system showing different reactant channels, minima (MIN$_i$) and transition states (TS$_i$). The black lines connect the configurations on the $^3$A$'$ while the blue lines connect the stationary states on $^3$A$''$ states. Two grids in Jacobi coordinates as defined for the two channels for the \textit{ab initio} energies are shown at bottom right.

and discussing them in Section III and finally concluding this work in Section IV.

II. METHODS

This section summarizes the methods for calculating the \textit{ab initio} energies for the diatomic and triatomic systems, construction of the analytical representation of the \textit{ab initio} PESs using RKHS, quasiclassical trajectory calculations on those PESs and finally calculation of reaction and vibrational relaxation rates.
A. Electronic structure calculations

*Ab initio* energy calculations for the triatomic system were performed on a grid defined in Jacobi coordinates ($r, R, \theta$) where $r$ is the diatomic separation, $R$ is the distance between the center of mass of the diatom and the free atom and $\theta$ is the angle between $\vec{r}$ and $\vec{R}$. For the present case, two separate grids were used for the (I) O+N$_2$ and (II) N+NO channels, respectively. The Jacobi coordinates for the two reactive systems are shown in Figure 1. For $R$, the grid included 30 and 28 points from 1.4 to 12.0 a$_0$ for the two channels. The diatomic separation $r$ for channels I and II are covered by 20 points from 1.55 to 4.0 a$_0$ and 21 points, from 1.50 to 4.0 a$_0$, respectively. For the angular grid Gauss-Legendre quadrature points were used between 0° to 180°. The quadrature points covered the angular domain more efficiently than the regular grid as in the RKHS scheme, the angular grid is transformed to a new coordinate according to $\frac{1-\cos\theta}{2}$ into a grid from 0 to 1 which leads to a denser grid near 0 or 1 and evenly spaced in between. In the present case, 13 quadrature points define the Jacobi angle which are 169.796°, 156.577°, 143.281°, 129.967°, 116.647°, 103.324°, 90.100°, 76.676°, 63.353°, 50.033°, 36.719°, 23.423° and 10.204°.

The $C_s$ symmetry, which is the highest symmetry for the present system to describe all geometries, was used to perform the electronic structure calculations. The multireference configuration interaction with Davidson correction (MRCI+Q)$^{44,45}$ method and augmented Dunning-type correlation consistent polarized triple zeta (aug-cc-pVTZ)$^{46}$ basis set were used to calculate the electronic structure for all configurations considered in this work. This level of theory has been found to describe the electronic structures for the C-, N-, O-containing species quite well for the entire region of the global PES.$^{27,37,39}$ State-averaged complete active space self-consistent field (CASSCF)$^{47-50}$ calculations were carried out prior to the MRCI calculations in order to obtain a smooth topology of the MRCI PESs. In the State-averaged CASSCF calculations a total of eight states were included (the two lowest states from each spin (singlet and triplet) and spatial ($A'$ and $A''$) symmetry). Including all these eight states in the CASSCF calculations provides consistency in the energies and numerically stabilizes the convergence for configurations with closely-lying states of the same symmetry. All the electronic structure calculations are performed using the Molpro-2019.1$^{51}$ software package.
For each of the electronic states, 4200 and 7644 ab initio electronic structure calculations have been carried out for the N$_2$+O and N+NO channel, respectively. Here it is worth to mention that $\sim 10\%$ of the electronic structure calculations converged to the excited states in the long range interaction regions (i.e., for large values of $R$ and/or $r$). These energies are excluded from the grid to construct the RKHS. A small number ($< 0.5\%$) of ab initio calculations did not converge at all. For both these cases the missing grid points were computed using a 2-dimensional reproducing kernel $(R, r)$ for a particular $\theta$ before inserting them into the final 3D RKHS. Thus $\sim 3$ times more reference ab initio energies have been used in this PESs than the previous PESs for this system.$^{27}$

B. Reproducing Kernel Representation of the PES

The reproducing kernel Hilbert space (RKHS) interpolation technique$^{52}$ has been used to construct the analytical representation of the PESs for both electronic states ($^3A'$ and $^3A''$). In the RKHS approach, the approximated value $\tilde{f}(x)$ of a function $f(x)$ is computed from a set of known values $f(x_i)$ as a linear combination of kernel polynomials, where $x$ are variables e.g. set of spatial coordinates. The RKHS procedure is documented in detail in Refs. 36, 52 and has also been used to construct PESs for other triatomic systems.$^{37–39}$

In order to well describe the atom+diatom dissociation channels the total potential $V(R, r, \theta)$ energy of N$_2$O is expanded as

$$V(R, r, \theta) = E(R, r, \theta) - V(r)$$  \hspace{1cm} (1)$$

where $V(r)$ is the diatomic potential for the respective channel. For this purpose, the ab initio energies for NO and N$_2$ are calculated separately and represented as a 1D RKHS using reciprocal power decay kernel $k^{2,6}(r, r')$. The values of $E(R, r, \theta)$ are then calculated from Eq. 1 and $E(R, r, \theta) \rightarrow 0$ for $R \rightarrow \infty$. As the values of the radial kernel function approach zero at large distances, $E(R, r, \theta)$ can be represented by a 3D kernel as

$$K(x, x') = k^{2,6}(R, R')k^{2,6}(r, r')k^2(z, z').$$  \hspace{1cm} (2)$$
Reciprocal power decay kernels are used for the radial dimensions ($R$ and $r$). For large separations they approach zero according to $\propto \frac{1}{x^n}$ (here $n = 6$) which gives the correct long-range behavior for neutral atom-diatom type interactions. For the angular coordinate a Taylor spline kernel $k^2(z, z')$ is used where $z = \frac{1-\cos\theta}{2}$. The definitions of the kernel functions can be found in Ref. 36, 52. The RKHS procedure exactly reproduces the values of the function at the known points for smooth functions. However, regularization parameter (a very small value, $10^{-19}$ is used in this work) is often used to reduce the noise in the data set and to numerically stabilize the algorithm.

The global PES is constructed by mixing three PESs for each channels (note there are two channels for N+NO) multiplying a smooth weight function $w_i(r)$ which is expressed as

$$w_i(r) = \frac{e^{-(r_i/d_\gamma)^2}}{\sum_{j=1}^{3} e^{-(r_j/d_\gamma)^2}},$$

where $r$ are the three internuclear distances ($r_i$ represents each diatomic bond length) and $d_\gamma$ are parameters for each channels which are optimized by least square fitting.

### C. Quasiclassical trajectory calculation

The N+NO and O+N$_2$ collisions systems are studied by running quasiclassical trajectories (QCT) on the global RKHS PESs for both $^3A'$ and $^3A''$ states of N$_2$O. The QCT method followed here is well documented in Refs. 53–55 and 56. In this approach, Hamilton’s coupled differential equations of motion are solved using the fourth-order Runge-Kutta method. The integration time step was $\Delta t = 0.05$ fs which guaranteed conservation of the total energy and angular momentum up to the sixth and eighth decimal places, respectively. Initial conditions for the trajectories are sampled using a Monte Carlo sampling method. The ro-vibrational states for the reactant and product are computed using the semiclassical theory of bound states. The ro-vibrational states for the product diatom are assigned to the nearest integer using histogram binning (HB) and Gaussian binning (GB) schemes. Since the results from both binning schemes are similar, only those obtained from HB are discussed unless otherwise mentioned.
The probability of an event $x$ (reactive, vibrational relaxation) can be computed as

$$P_x = \frac{N_x}{N_{tot}},$$

(4)

where $N_x$ is the number of trajectories corresponding to the event of interest and $N_{tot}$ is the total number of trajectories. The cross section for that event is then computed as

$$\sigma_x = \pi b_{\text{max}}^2 P_x$$

(5)

where $b_{\text{max}}$ is the maximum impact parameter for which the event can occur. The impact parameters are sampled using stratified sampling by subdividing the interval between 0 and $b_{\text{max}}$ into six strata.

The rates for an event $x$ at a particular temperature is then obtained as

$$k_{i,x}(T) = g_i(T) \sqrt{\frac{8k_B T}{\pi \mu}} \frac{\pi b_{\text{max}}^2}{P_x}.$$  

(6)

where $g_i(T)$ is the electronic degeneracy factor of an electronic state ‘$i$’, $k_B$ is the Boltzmann constant and $\mu$ is the reduced mass of the collision system.

For the $N(^4S) + NO(X^2\Pi)$ collision process, the temperature dependent degeneracies for both triplet states are

$$g_f(T) = \frac{3}{4 \cdot (2 + 2 \cdot e^{-\frac{177.1}{T}})}$$

(7)

whereas for the reverse $O(^3P) + N_2(X^1\Sigma)$ collision process the degeneracies are

$$g_r(T) = \frac{3}{1 \cdot (5 + 3 \cdot e^{-\frac{227.8}{T}} + 1 \cdot e^{-\frac{326.6}{T}})}$$

(8)

The numbers in Eqs. 7 and 8 are the degeneracies of the $J$ or spin states while the exponential parameters 177.1 K, 227.8 K and 326.6 K are the energy gaps between two $J$ states. The equilibrium constant is calculated as

$$K_{eq}(T) = \frac{k_f(T)}{k_r(T)},$$

(9)

where, $k_f(T)$ and $k_r(T)$ are the rates for the forward and the reverse reaction. In the rate calculations, for each trajectory the initial relative translational energies of the reactants are sampled from a Maxwell-Boltzmann distribution and ro-vibrational states of the reactant diatom is sampled from a Boltzmann distribution at temperature $T$.37,54
III. RESULTS AND DISCUSSION

In the following, the topology and accuracy of the PESs, the thermal rates and the rates for vibrational relaxation from QCT simulations are presented and discussed.

A. Topology and Accuracy of the Potential Energy Surfaces

The topography of the $^3A'$ and $^3A''$ PESs for the two collision systems N+NO and O+N$_2$ - is reported in Figure 2 which shows $r$-relaxed PESs. The center of mass of the diatom is placed at the origin and the position of the third free atom is described as $(x, y)$ on a 2D space. These 2D PESs are computed by determining the minimum energy for a given $(x, y)$ with \( r \in [2.0, 2.5] \ \text{a}_0 \) for N+NO and \( r \in [1.9, 2.4] \ \text{a}_0 \) for O+N$_2$. This was done because a ‘relaxed’ PES better represents all possible stationary states than a conventional 2D PES with a fixed $r$ value.$^{60}$

Both PESs have significantly different anisotropic topologies depending on the angle at which the reactants approach one another. The topology of the $^3A'$ PES is highly structured compared with that of the $^3A''$ PES for both channels. For both PESs, the global minimum is at the O+N$_2$ asymptote while the N+NO asymptote is higher in energy by 73.1 kcal/mol. For the N+NO collisions, reactants face barriers for all angular approach for the $^3A'$ PES. The barrier height $\sim 9.6$ kcal/mol (equivalent to 0.4 eV or $\sim 4800$ K) is lowest for $\sim 135^\circ$ approach. On the other hand, the N+NO collisions are barrierless on the $^3A''$ PES for $\sim 135^\circ$ which will profoundly affect the reactivity at lower temperatures. A potential well can be seen on the $^3A'$ PES along the near perpendicular approach (MIN2, see Figure 1) which is not present on the $^3A''$ PES. For both PESs, the O+N$_2$ collisions have highly repulsive landscapes and a deep potential well with a $C_{2v}$ symmetry at high energies on the $^3A'$ PES along the perpendicular approach (MIN2, see Figure 1).

The stationary states on the PESs are characterized and presented in Figure 1 and tabulated in Table I. The minima and transition states are calculated by using the BFGS and nudged elastic band methods$^{61,62}$ implemented in the Atomic Simulation Environment (ASE) package.$^{63}$ The N+NO $\rightarrow$ N$_2$+O reaction is barrierless on the $^3A''$ PES while the
FIG. 2. Contour plots of the RKHS interpolated energies shown in relaxed PES representation (see text) for different electronic states. The diatoms are on the ‘X’ axis while the origin of each plot is set to the center-of-mass of the diatoms. Spacing between the contour lines is 0.15 eV. Zero of energy is set to the atomization energy of N$_2$O i.e., the energy of N($^4S$)+N($^4S$)+O($^3P$).

N exchange N$_A$+N$_B$O → N$_A$O+N$_B$ reaction has a barrier of 38.03 kcal/mol which is $\sim$ 4.6 and $\sim$ 2.4 kcal/mol smaller than for the earlier PESs$^{26,27}$, respectively. A very shallow well ($\sim$ 0.5 kcal/mol) with a $C_{2v}$ symmetry exists as MIN1 between two TS1 structures.

There are two pathways from N+NO to N$_2$+O on the $^3A'$ PES which are similar to Ref. 27. The minimum energy path follows N+NO → TS5 → MIN1 → TS1 → N$_2$+O. TS5 is located 9.58 kcal/mol higher than the N+NO asymptote which compares with 10.50 kcal/mol and 8.35 kcal/mol for the PESs in Ref. 27 and 26, respectively. However, MIN1 and TS1 are not present on the $^3A'$ PES in Ref. 26. MIN1 is located at 35.86 kcal/mol higher than the O+N$_2$ asymptote and has a depth of 1.25 kcal/mol from TS1. The NN bond is shorter than the NO bonds in MIN1. The N exchange path for the N$_A$+N$_B$O → N$_A$O + N$_B$ reaction
has a barrier of 32.93 kcal/mol (TS4) and a potential well with a $C_{2v}$ symmetry of 12.23 kcal/mol. TS3 has $C_{2v}$ symmetry and it connects MIN3 and MIN2 ($C_{2v}$ geometry and close to an equilateral triangle with angles 61.8°, 59.1° and 59.1°). MIN2 is connected with MIN1 via TS2.

FIG. 3. Comparison between the ab initio energies (open symbols) (not part of the training grid) and the RKHS interpolated energies (solid lines) in Jacobi coordinates along the N+NO and O+N$_2$ channels for different angles. The diatomic bond distances for NO and N$_2$ are fixed at 2.19 and 2.08 a$_0$, respectively. Zero of energy is set to the atomization energy of N$_2$O i.e., energy of N($^4$S)+N($^4$S)+O($^3$P).

To verify the quality of the RKHS PESs, the correlation between the ab initio and the RKHS energies for both states for the training grid are reported in Figure S1 upper panel. The structures with energy 6.8 eV above the N+N+O asymptote 7908 and 7797 points for the training grid) have $R^2$ values of 0.99995 and 0.99996 and RMSE of 0.509 and 0.456 kcal/mol for the $^3A'$ and $^3A''$ states, respectively. Electronic structure calculations have also been performed for off-grid, randomly generated geometries for both states which serve as an additional test data set. A correlation diagram for the test grid is shown for 494 and
497 points for the $^3A'$ and $^3A''$ states, respectively, with energies $\leq 6.8$ eV (see Figure S1 lower panel). The correlation coefficients obtained for the test grids are 0.99985 and 0.99988 with RMSE 0.82 and 0.80 kcal/mol for the $^3A'$ and $^3A''$ states, slightly larger than for the reference points but still of high quality. The RMSE values for the present PESs are more than three times lower than for previous PES.\textsuperscript{26,27}

The quality of the RKHS PESs developed in this work is further examined by considering 1D cuts along $R$ for different values of $\theta$ and constant values of $r$ for the N+NO and O+N\textsubscript{2} channels, see Figure 3. Again, these are off-grid cuts (not part of the training grid) and the agreement between the ab initio and RKHS interpolated energies is excellent for all the cuts.

**B. Reaction and Dissociation Rates**

FIG. 4. Rate coefficients for the N(4S) + NO(X\textsuperscript{2}\Pi) $\rightarrow$ O(3P) + N\textsubscript{2}(X\textsuperscript{1}\Sigma) from 100 to 5000 K. The results calculated in the present work are shown as black open circles connected by solid black line. Experimental (assigned as ‘Expt.’) and Theoretical rates (assigned as ‘Theo.’) available in the literature are shown.\textsuperscript{15–20,26,28,31,32}
TABLE I. Geometries and energies for the minima (MIN\textsubscript{i}) and transition states (TS\textsubscript{i}) on the 3\textit{A}\textsuperscript{'} and 3\textit{A}\textsuperscript{''} PESs of N\textsubscript{2}O. Distances given in a\textsubscript{0}, angles in degree and energies in eV for $\Delta E_1$ and in kcal/mol for $\Delta E_2$ (in kcal/mol) with respect to the energy of N(\textit{4S})+N(\textit{4S})+O(\textit{3P}). For the energy level diagram and the connectivity, see Figure 1.

|         | $R_{NN}$ | $R_{NO}$ | $\angle$NON | $\Delta E_1$ | $\Delta E_2$ |
|---------|----------|----------|-------------|--------------|--------------|
| 3\textit{A}\textsuperscript{'} |          |          |             |              |              |
| TS1     | 2.21     | 2.72     | 27.1        | −7.837       | −180.736     |
| MIN1    | 2.30     | 2.41     | 26.7        | −7.892       | −181.990     |
| TS2     | 2.58     | 2.56     | 50.0        | −5.525       | −127.419     |
| MIN2    | 2.70     | 2.63     | 61.8        | −6.499       | −149.880     |
| TS3     | 3.86     | 2.56     | 97.5        | −5.061       | −116.703     |
| MIN3    | 4.38     | 2.46     | 125.9       | −5.381       | −124.080     |
| TS4     | 4.73     | 2.25     | 121.1       | −4.850       | −111.848     |
| TS5     | 3.72     | 2.19     | 47.5        | −5.863       | −135.193     |
| 3\textit{A}\textsuperscript{''} |          |          |             |              |              |
| MIN1    | 3.92     | 2.51     | 102.9       | −4.651       | −107.245     |
| TS1     | 3.97     | 2.36     | 102.0       | −4.629       | −106.746     |
| N+NO    | 2.19     |          |             | −6.278       | −144.774     |
| O+N\textsubscript{2} | 2.09 |          |             | −9.447       | −217.850     |

Total rate coefficients for the N(\textit{4S}) + NO(X\textit{2}Π) $\rightarrow$ O(\textit{3P}) + N\textsubscript{2}(X\textit{1}Σ) reaction and the N exchange reaction N\textsubscript{A}(\textit{4S}) + N\textsubscript{B}O(X\textit{2}Π) $\rightarrow$ N\textsubscript{B}(\textit{4S}) + N\textsubscript{A}O(X\textit{2}Π) have been calculated from 100 K to 20000 K. These rates are based on 50000 quasiclassical trajectories at each temperature. Individual contributions from each states are tabulated in Tables S1 and S2, respectively. Rate coefficients for N\textsubscript{2} formation (forward reaction) are plotted between 100 and 5000 K in Figure 4. In addition to the present computations, those from previous experiments and computations are shown. The rate is high at low temperature (100 K) and gradually decreases with increasing temperature before starting to increase again though the variation is small over the entire range. For the present work, the minimum and maximum
rates are $2.595 \times 10^{-11}$ and $5.095 \times 10^{-11}$ cm$^3$s$^{-1}$molecule$^{-1}$ between 100 K and 5000 K, which differs only by a factor of two, consistent with a barrierless reaction in the forward direction.

As can be seen in Table S1, due to presence of a barrier of 9.58 kcal/mol in the entrance channel on the $^3A'$ PES the contribution is considerably lower at low temperatures than that of the $^3A''$ state which is barrierless. Hence, at low temperatures the contribution from the $^3A''$ PES dominates. Rates for the forward reaction obtained from Ref. 26 using PESs from Ref. 25, 64 (black open squares) and from Ref. 28 (cyan open triangle down) are very small at low temperatures and increase monotonically with increasing temperature due to the presence of a small barrier on the $^3A''$ PES. In the present work, the results from QCT simulations correctly describe the trends of the experimental results at low temperature. However, the high temperature rate expression obtained from experimental data are temperature independent whereas the QCT rates increases slowly with temperature.

Rates for the the N exchange reaction $N_A(^4S) + N_BO(X^2\Pi) \rightarrow N_B(^4S) + N_AO(X^2\Pi)$ are given in Table S2. Due to presence of barriers along the reaction path on both PESs (see Figure 1), this channel only opens at $\sim 3000$ K (consistent with a barrier height of $\sim 4800$ K, see above) and reactivity increases with increasing temperature. However, the rates for the N exchange reaction are smaller over the entire temperature range considered.

Rate coefficients for the O($^3P$) + $N_2(X^1\Sigma) \rightarrow N(^4S) + NO(X^2\Pi)$ reaction have been calculated from 2800 K to 20000 K by running $5 \times 10^4 - 4 \times 10^5$ quasiclassical trajectories for each temperature. The rates are shown in Figure 5 and individual contributions for each PES are given in Table S3. This reaction is endothermic and starts at high temperature $\sim 3000$ K. The reaction rate increases with increasing temperature. The contribution from $^3A'$ PES is less than that from $^3A''$ PES in the entire range of temperature. Rates reported from previous experimental and theoretical work are also presented in Figure 5. Rate expression obtained by fitting experimental data are given in Ref. 23 and 22 which are shown in Figure 5 along with the recommended values provided by Baulch et al.$^{21}$ Results obtained in the present work agree well with the experimental data.
FIG. 5. Rate coefficients for the O(^3P) + N_2(X^1Σ) → N(^4S) + NO(X^2Π) reaction as a function of temperature. The results calculated in the present work are shown as black open circles connected by black line. Experimental and theoretical rates available from the literature are also shown.\textsuperscript{21–24,26,65} The shaded area shows the confidence limit for Thielen et. al. data.

The equilibrium constants for the N(^4S) + NO(X^2Π) ↔ O(^3P) + N_2(X^1Σ) reaction have been computed using Eq. \textsuperscript{9} between 3000 and 6000 K and compared with the values reported in the JANAF\textsuperscript{66} tables. The QCT results from this work are in good agreement with the JANAF data computed from thermodynamic quantities. This suggests that the present PESs are accurate enough to describe the forward and the reverse reaction and other electronic states play only a minor role in the dynamics of both reactions.

Both N(^4S) + NO(X^2Π) → O(^3P) + N_2(X^1Σ) and the reverse reaction are among the reactions which play an important role at hyperthermal conditions during the reentry of space vehicles into earth atmosphere. Analytical expression for the rates are useful to simulate hypersonic flow during reentry. In this work, the rates are calculated at hyperthermal temperature for both reactions and modified Arrhenius functions \( k(T) = AT^n \exp(-E_a/T) \) are fitted to those rates. The parameters \( (A, n, E_a) \) are given in Table II and the fits are also shown in Figure 7 along with available rate expressions from literature. For the reverse
FIG. 6. Equilibrium constant $K_{eq}(T)$ for the $N(^4S) + NO(X^2\Pi) \leftrightarrow O(^3P) + N_2(X^1\Sigma)$ process. Open circles represent the QCT results and the red line shows the results obtained from JANAF tables\textsuperscript{66} reaction, except for the fit from Ref. 26 all the fits agree well over the entire range.

TABLE II. Parameters obtained by fitting the rates to a modified Arrhenius equation. Rates in the 2000–15000 K range are used for the forward reaction while the rates from 3000–20000 K are used for the reverse reaction. Rate coefficients computed using these parameters have units in cm$^3$ molecule$^{-1}$ s$^{-1}$ with $[A] = $ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $[E_a] = $ K while $n$ is unitless.

| Reaction    | $A$         | $n$       | $E_a$       |
|-------------|-------------|-----------|-------------|
| Forward     | $2.17214 \times 10^{-14}$ | 0.88796   | -946.02910 |
| Reverse     | $7.73865 \times 10^{-12}$ | 0.46177   | 39123.1149  |
| Dissociation| $4.55027$   | -2.00227  | 129692.62993|

At very high temperatures collisions may lead to dissociation of the diatomic molecules. As the dissociation energy for molecular oxygen is considerably smaller than that of N$_2$, O$_2$ dissociates at relatively low temperatures and generates atomic oxygen. At hyperthermal
FIG. 7. Thermal rate coefficients for the \( \text{N}(^4\Sigma) + \text{NO}(^2\Pi) \rightarrow \text{O}(^3\Pi) + \text{N}_2(X^1\Sigma) \) (left panel) and the reverse reaction (right panel) at temperatures relevant to hypersonic flight regime. Black open squares represent the QCT rates and the lines represent the Arrhenius fit. Rates calculated from the rate expression reported in literature are also shown as dashed lines.$^{26,33,67}$

FIG. 8. Thermal rate coefficients for \( \text{N}_2 \) dissociation reaction for \( \text{O}(^3\Pi) + \text{N}_2(X^1\Sigma) \) collisions. Black open squares represent the QCT rates and the line represent the Arrhenius fit. Rates calculated from the rate expression reported in Refs.$^{33,67}$ are also shown as dashed lines.

conditions, dissociation of \( \text{N}_2 \) via \( \text{N}_2 + \text{O} \) collisions plays an important role to maintain the concentration of \( \text{N} \) atoms. Here, the dissociation process of molecular nitrogen during collisions with an oxygen atom is studied at high temperatures between 8000 K and 20000K. The
rate coefficients for the $\text{N}_2 + \text{O} \rightarrow 2\text{N} + \text{O}$ are shown in Figure 8 and also given in Table S4. Fit to modified Arrhenius relation is also plotted in Figure 8 along with the rate expression reported in Refs. 67 and 33. The parameters for the present fit are given in Table II. All the fits agree well except at high temperatures the fit from Ref. 67 gives higher dissociation rate.

C. Vibrational Relaxation

In three different experiments, $p\tau_{\text{vib}}$ values are reported between 300 K and 4500 K\textsuperscript{68–70} and rates were calculated from $p\tau_{\text{vib}}$ values and fitted to analytical expressions.\textsuperscript{71} Here, VR rates are calculated for $\text{O} + \text{N}_2(v = 1, j) \rightarrow \text{O} + \text{N}_2(v' = 0, j')$ for temperatures between 300 K and 10000 K and are reported in Figure 9, along with experimental\textsuperscript{68–71} and previous theoretical\textsuperscript{33} results. VR rates calculated on PESs from Ref. 26 underestimate the experiment for $T < 9000$ K.

QCT with histogram binning (QCT-HB) significantly overestimates the VR rates for $T > 800$ K while the Gaussian binning\textsuperscript{56–58} (QCT-GB) scheme leads to some improvement. Since only $v = 1$ to $v' = 0$ transitions are considered, determining the final quantum state is thus important and the type of binning scheme used plays a potentially important role. It is found that for a large number of trajectories vibrational energy exchange was less than one quantum which leads to a state with $v' = 0$ but with high energy. Although QCT-GB partly excludes the contributions from those trajectories and VR rates obtained from QCT-GB are in fair agreement. It is found that considering the trajectories with $\varepsilon_{0,j'} \leq \varepsilon_{v',j'} \leq \varepsilon_{0,j'} + 0.075$ eV (0.075 eV $\approx$ 0.3 quanta) to be a VR trajectory gives result which are in good agreement with experiment (shown as a green line with asterisk (Modified HB, QCT-MHB)). This finding suggests that a fraction of the trajectories either do not enter into the strong coupling region or sample it incompletely which leads to reduced energy exchange (not fully relaxed).

Yet another approach was followed in previous work\textsuperscript{33} by classifying the VR trajectories to ‘purely nonreactive’ (PNR) and ‘quasi-reactive’ (QR) and counting the contribution only from QR trajectories. This resulted in VR rates close to experiment for $T > 10000$ K.
FIG. 9. Vibrational relaxation rates for $\text{O} + \text{N}_2(\nu = 1) \rightarrow \text{O} + \text{N}_2(\nu' = 0)$. Green symbols represent the experimentally determined VR rates.$^{68-70}$ Olive dashed line is the fit to the experimental result.$^{71}$ Rates obtained in this work from QCT simulations and using HB, GB and a modified HB scheme are given along with the full QCT (magenta solid line) and quasi-reactive QCT (blue solid line) results from Ref.$^{33}$.

However, it could not improve the low temperature VR rates. Such an analysis is also explored here. Figure S2 shows the VR rates obtained here (green line) from considering only the QR trajectories which are close to the rates from Ref. 33 (blue line). This points towards the deficiencies of PESs from Ref. 26. It is found that the PESs from Ref. 26 describe the reactive events quite well (reaction rates for the forward and reverse process are in good agreement with the experiment)$^{26,31-33,67}$ Since QR trajectories are similar to reactive trajectories PESs from Ref. 26 also results QR rates similar to present work PESs. The PNR trajectories sample distinctly different regions in configuration space - primarily the long range part of the PES. As the VR rates from the present analysis agree with experiment over the entire temperature range, the present PESs are better suited to describe both, the low- and high-energy part of VR.

These findings underline the point that different observables (here thermal and vibrational...
relaxation rates) are sensitive to different parts of the PES in the dynamics.\textsuperscript{39} Reaction and dissociation rates obtained from the earlier PESs\textsuperscript{26} are comparable with results from the present PESs but the vibrational relaxation rates are different. Exploiting such a sensitivity will allow to further improve such global PESs with the aim to provide fully predictive simulations based on electronic structure calculations and their accurate representation as done in the present work.

IV. CONCLUSION

Accurate PESs have been constructed for the lowest lying \(^3\text{A}'\) and \(^3\text{A}''\) states for the \([\text{NNO}]\) system using \(> 20000\) MRCI+Q/aug-cc-pVTZ energies and RKHS interpolation. Both PESs have smaller RMSE compared with previously reported PESs in the literature. The present PESs accurately describe all the important interaction regions and their validity is assessed by calculating thermal reaction rates for the \(\text{N}(^4\text{S}) + \text{NO}(^2\Pi) \rightarrow \text{O}(^3\text{P}) + \text{N}_2(^1\Sigma)\) and the reverse reaction and comparing with the available experimental results. The vibrational relaxation rates for the \(\text{O} + \text{N}_2\) collisions are also computed. Good agreement between the experiment and theory confirms the high quality of the present PESs and provides useful generalized Arrhenius expressions for thermal rates. These PESs can be used to calculate state-to-state cross sections for more coarse grained simulations such as DSMC.

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Supporting Information:

Accurate Reproducing Kernel-Based Potential Energy Surfaces for the Triplet Ground States of \( \text{N}_2\text{O} \) and Dynamics for the \( \text{N}+\text{NO}\leftrightarrow\text{O}+\text{N}_2 \) and \( \text{N}_2\text{O}+\text{O}\rightarrow2\text{N}+\text{O} \) Reactions

Juan Carlos San Vicente Veliz,\(^1\) Debasish Koner,\(^1\) Raymond J. Bemish,\(^2\) and Markus Meuwly\(^1\)

\(^1\)Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

\(^2\)Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, New Mexico 87117, USA
FIG. S1. Correlation between the \textit{ab initio} and RKHS interpolated energies for the training grid (upper panel) and for the test grid (which are not part of the training grid) (lower panel) for $^3A'$ and $^3A''$ different electronic states of N$_2$O. Zero of energy is set to the atomization energy of N$_2$O i.e., energy of N($^4$S)+N($^4$S)+O($^3$P). The values of $R^2$ in upper panels for the grid energies upto 6.80 eV are 0.99995 and 0.99996 for $^3A'$ and $^3A''$, respectively where as in lower panel for the test grid values of $R^2$ are 0.99985 and 0.99988 for $^3A'$ and $^3A''$, respectively.
TABLE S1. Rate coefficients for the N(4S) + NO(X2Π) → O(3P) + N2(X1Σ) from 100 to 20000 K calculated using QCT on the 3A' and 3A'' PESs. Units are in cm^3 sec^{-1} molecule^{-1}

| T (K) | $k_1^f(3A')$ | $k_1^f(3A'')$ | $k_1^f(3A') + k_1^f(3A'')$ |
|-------|--------------|----------------|-----------------------------|
| 100   | 0.000        | 4.879×10^{-11} | 4.879×10^{-11}              |
| 200   | 0.000        | 3.928×10^{-11} | 3.928×10^{-11}              |
| 300   | 0.000        | 3.333×10^{-11} | 3.333×10^{-11}              |
| 500   | 9.743×10^{-16}| 2.837×10^{-11} | 2.837×10^{-11}              |
| 800   | 2.424×10^{-14}| 2.592×10^{-11} | 2.595×10^{-11}              |
| 1000  | 7.984×10^{-14}| 2.590×10^{-11} | 2.598×10^{-11}              |
| 2000  | 1.257×10^{-12}| 2.871×10^{-11} | 3.000×10^{-11}              |
| 3000  | 3.759×10^{-12}| 3.234×10^{-11} | 3.610×10^{-11}              |
| 3500  | 5.268×10^{-12}| 3.458×10^{-11} | 3.985×10^{-11}              |
| 4000  | 7.117×10^{-12}| 3.609×10^{-11} | 4.321×10^{-11}              |
| 4500  | 8.495×10^{-12}| 3.816×10^{-11} | 4.666×10^{-11}              |
| 5000  | 1.077×10^{-11}| 4.018×10^{-11} | 5.095×10^{-11}              |
| 5500  | 1.273×10^{-11}| 4.100×10^{-11} | 5.373×10^{-11}              |
| 6000  | 1.465×10^{-11}| 4.290×10^{-11} | 5.755×10^{-11}              |
| 7500  | 2.121×10^{-11}| 4.776×10^{-11} | 6.897×10^{-11}              |
| 10000 | 3.157×10^{-11}| 5.516×10^{-11} | 8.674×10^{-11}              |
| 12500 | 4.014×10^{-11}| 6.095×10^{-11} | 1.011×10^{-10}              |
| 15000 | 4.884×10^{-11}| 6.793×10^{-11} | 1.168×10^{-10}              |
| 17500 | 5.508×10^{-11}| 7.087×10^{-11} | 1.259×10^{-10}              |
| 20000 | 6.025×10^{-11}| 7.524×10^{-11} | 1.355×10^{-10}              |
TABLE S2. Rate coefficients for the $N'(4S) + NO(X^2\Pi) \rightarrow N(4S) + N'O(X^2\Pi)$ from 100 to 20000 K calculated using QCT on the $^3A'$ and $^3A''$ PESs. Units are in cm$^3$sec$^{-1}$molecule$^{-1}$

| T (K) | $k_2^{f}(^3A')$ | $k_2^{f}(^3A'')$ | $k_2^{f}(^3A') + k_2^{f}(^3A'')$ |
|-------|----------------|----------------|----------------------------------|
| 100   | 0.000          | 0.000          | 0.000                            |
| 200   | 0.000          | 0.000          | 0.000                            |
| 300   | 0.000          | 0.000          | 0.000                            |
| 500   | 0.000          | 0.000          | 0.000                            |
| 800   | 0.000          | 0.000          | 0.000                            |
| 1000  | 0.000          | 0.000          | 0.000                            |
| 2000  | $1.881 \times 10^{-16}$ | 0.000          | $1.8812 \times 10^{-16}$         |
| 3000  | $2.591 \times 10^{-14}$ | $3.029 \times 10^{-14}$ | $5.6202 \times 10^{-14}$         |
| 3500  | $6.513 \times 10^{-14}$ | $9.275 \times 10^{-14}$ | $1.5792 \times 10^{-13}$         |
| 4000  | $1.469 \times 10^{-13}$ | $1.718 \times 10^{-13}$ | $3.1872 \times 10^{-13}$         |
| 4500  | $2.848 \times 10^{-13}$ | $3.062 \times 10^{-13}$ | $5.9102 \times 10^{-13}$         |
| 5000  | $4.408 \times 10^{-13}$ | $4.768 \times 10^{-13}$ | $9.1752 \times 10^{-13}$         |
| 5500  | $7.233 \times 10^{-13}$ | $7.878 \times 10^{-13}$ | $1.5112 \times 10^{-12}$         |
| 6000  | $1.051 \times 10^{-12}$ | $1.086 \times 10^{-12}$ | $2.1372 \times 10^{-12}$         |
| 7500  | $2.626 \times 10^{-12}$ | $2.512 \times 10^{-12}$ | $5.1392 \times 10^{-12}$         |
| 10000 | $6.338 \times 10^{-12}$ | $6.481 \times 10^{-12}$ | $1.2822 \times 10^{-11}$         |
| 12500 | $1.187 \times 10^{-11}$ | $1.117 \times 10^{-11}$ | $2.3042 \times 10^{-11}$         |
| 15000 | $1.696 \times 10^{-11}$ | $1.650 \times 10^{-11}$ | $3.3452 \times 10^{-11}$         |
| 17500 | $2.176 \times 10^{-11}$ | $2.106 \times 10^{-11}$ | $4.2812 \times 10^{-11}$         |
| 20000 | $2.618 \times 10^{-11}$ | $2.532 \times 10^{-11}$ | $5.1502 \times 10^{-11}$         |
TABLE S3. Rate coefficients for the $\text{O}(^3P) + \text{N}_2(X^1\Sigma) \rightarrow \text{N}(^4S) + \text{NO}(X^2\Pi)$ from 2800 to 20000 K calculated using QCT on the $^3A'$ and $^3A''$ PESs. Units are in cm$^3$sec$^{-1}$molecule$^{-1}$

| T (K) | $k_b(^3A')$ | $k_b(^3A'')$ | $k_b(^3A') + k_b(^3A'')$ |
|-------|-------------|--------------|--------------------------|
| 2800  | 0.000       | 0.000        | 0.000                    |
| 3000  | 0.000       | 7.348×10$^{-16}$ | 7.348×10$^{-16}$         |
| 3500  | 0.000       | 3.534×10$^{-15}$ | 3.534×10$^{-15}$         |
| 4000  | 3.330×10$^{-15}$ | 2.079×10$^{-14}$ | 2.412×10$^{-14}$         |
| 4500  | 1.305×10$^{-14}$ | 5.743×10$^{-14}$ | 7.048×10$^{-14}$         |
| 5000  | 2.368×10$^{-14}$ | 1.293×10$^{-13}$ | 1.529×10$^{-13}$         |
| 5500  | 8.772×10$^{-14}$ | 2.555×10$^{-13}$ | 3.433×10$^{-13}$         |
| 6000  | 1.575×10$^{-13}$ | 4.374×10$^{-13}$ | 5.950×10$^{-13}$         |
| 7000  | 5.105×10$^{-13}$ | 1.171×10$^{-12}$ | 1.682×10$^{-12}$         |
| 10000 | 3.974×10$^{-12}$ | 6.773×10$^{-12}$ | 1.075×10$^{-11}$         |
| 12000 | 8.785×10$^{-12}$ | 1.392×10$^{-11}$ | 2.271×10$^{-11}$         |
| 15000 | 2.082×10$^{-11}$ | 2.859×10$^{-11}$ | 4.942×10$^{-11}$         |
| 17000 | 3.096×10$^{-11}$ | 4.010×10$^{-11}$ | 7.105×10$^{-11}$         |
| 20000 | 4.575×10$^{-11}$ | 5.804×10$^{-11}$ | 1.038×10$^{-10}$         |

TABLE S4. $\text{N}_2$ dissociation rates for the $\text{O}(^3P) + \text{N}_2(X^1\Sigma)$ collisions for 7000 to 20000 K calculated using QCT simulations on the $^3A'$ and $^3A''$ PESs. Units are in cm$^3$sec$^{-1}$molecule$^{-1}$

| T (K) | $k_d(^3A') + k_d(^3A'')$ |
|-------|------------------------|
| 7000  | 0.000                  |
| 10000 | 1.061×10$^{-13}$       |
| 12000 | 5.848×10$^{-13}$       |
| 15000 | 3.915×10$^{-12}$       |
| 17000 | 6.888×10$^{-12}$       |
| 20000 | 1.720×10$^{-11}$       |
FIG. S2. Vibrational relaxation rates for $O + N_2(\nu = 1) \rightarrow O + N_2(\nu' = 0)$. QR QCT-HB rates calculated from the quasi-reactive (QR) trajectories (see text). Fit for the experimental results is shown as dashed olive line.