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Communication: Highly accurate ozone formation potential and implications for kinetics

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Atmospheric ozone is formed by the $O + O_2$ exchange reaction followed by collisional stabilization of the O_3^* intermediate. The dynamics of the $O + O_2$ reaction and to a lesser extent the O_3 stabilization depend sensitively on the underlying potential energy surface, particularly in the asymptotic region. Highly accurate Davidson corrected multi-state multi-reference configuration interaction calculations reported here reveal that the minimal energy path for the formation of O_3 from $O + O_2$ is a monotonically decaying function of the atom-diatom distance and contains no "reef" feature found in previous *ab initio* calculations. The absence of a submerged barrier leads to an exchange rate constant with the correct temperature dependence and is in better agreement with experiment, as shown by quantum scattering calculations. © *2011 American Institute of Physics*. [doi:10.1063/1.3632055]

The ozone layer protecting Earth from harmful UV radiation is formed by reactions of molecular oxygen, $O_2(^3\Sigma_g^-)$, with atomic oxygen, $O(^3P)$, which is generated by photodissociation of O_2. In this so-called Chapman cycle, the metastable O_3^* complex is prepared by $O_2 + O$ collisions with energies above the dissociation limit. This high energy intermediate is subsequently stabilized to O_3 by energy transfer to a third body. However, the detailed kinetics and dynamics of this seemingly simple chemical reaction are still not well understood. A fascinating and surprising aspect of ozone chemistry is the discovery of selective enrichment of heavy ozone isotopomers in the atmosphere and in laboratory settings.[1,2] This so-called mass-independent fractionation (MIF) effect is at odds with the conventional mass-dependent isotope effect,[3–5] highlighting the complex mechanisms of the reaction and energy transfer in ozone formation. Recently, convincing evidence has started to emerge from both experimental and theoretical studies that the ozone MIF is likely to originate from zero-point energy (ZPE) differences between different O_2 isotopomers involved in the $O + O_2$ exchange reaction,[6–12] underscoring the quantum mechanical nature of the process. So far, however, there has not been any first-principles model that is capable of explaining the ozone MIF in a satisfactory fashion.

One of the major obstacles in our understanding of the ozone chemistry is the lack of a quantitatively accurate potential energy surface (PES).[13] While the ground electronic state of $O_3(X^1A')$ near its C_{2v} minima is well separated from low-lying excited states, the asymptotic regions of the PES involve interaction with many low-lying excited electronic states. Due to the multi-reference nature of the system in these regions, it was only recently that reasonable agreement has been achieved between the calculated and measured dissociation energies of O_3.[14–18] Even the most up-to-date O_3 global

PES (Ref. 19) based on multi-reference configuration interaction (MRCI) data[16,20] still requires empirical adjustments to match the experimental dissociation energy.

Although it is well established that the formation of O_3 from O and O_2 does not have a potential barrier, high-level *ab initio* calculations have found this process is dictated by a tight bottleneck region on the PES, where a saddle point exists along the formation pathway of O_3, but beneath the $O + O_2$ dissociation limit.[16,20] This small submerged "reef" separates the deep O_3 chemical well from a shallow van der Waals well. Since its initial discovery, this "reef" feature has been found in *all* high-level *ab initio* calculations up to the complete basis set (CBS) limit.[17,18,21,22] As a result, it has been taken as a true signature of the O_3 PES and was incorporated into the widely used hybrid O_3 PES developed by Babikov *et al.*,[19] as shown in Fig. 1.

The bottleneck regions of the ozone PES, in particular the "reef" feature, have important implications for kinetics. Here, we will focus on the rate constant of the $O + O_2$ exchange reaction, which is related to that of the ozone formation reaction in the high pressure limit. The cross section for the nominally barrierless reaction is dominated by large impact parameter collisions,[23] where the centrifugal potential transforms the submerged "reef" into a real barrier. Two important consequences are the following.[20,24] First, the calculated rate constants are about 3–5 times smaller than the measured ones due to attenuated reaction cross sections at low collision energies. Second and perhaps more importantly, these calculated rate constants have qualitatively different temperature dependence from the experimental kinetic data,[25–27] which show a negative slope with T. The theory-experiment differences cannot be attributed to non-adiabatic interactions in the $O + O_2$ asymptote, as shown by Tashiro and Schinke for $J = 0$.[28] We have also confirmed independently that non-adiabatic couplings do not significantly affect reaction probabilities for up to $J = 45$. So what could be the source of the discrepancies?

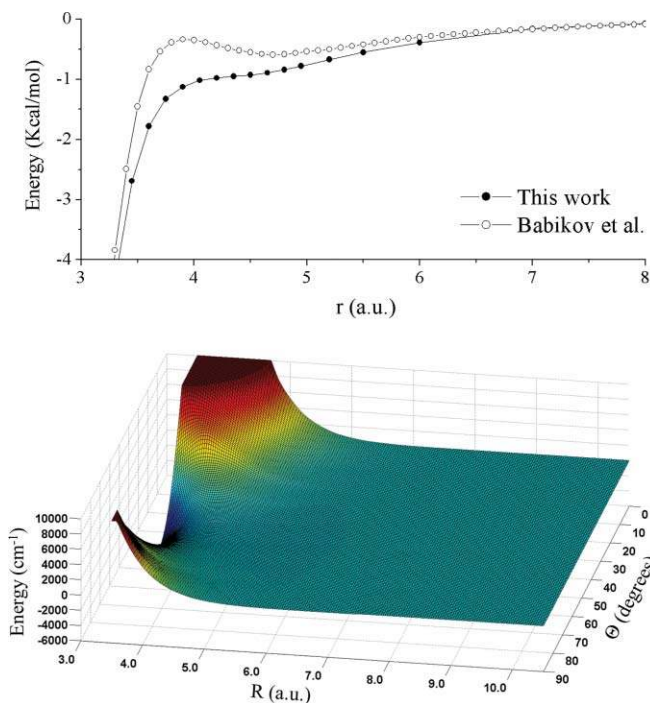a)Authors to whom correspondence should be addressed. Electronic addresses: dawesr@mst.edu and hguo@unm.edu.

FIG. 1. Upper panel: Minimal energy path for O_3 formation along an O–O bond length obtained in this work (filled circles) and its comparison with that on the hybrid PES of Babikov *et al.* (Ref. 17) (open circles). Lower panel: The corresponding two-dimensional potential energy surface in the O–O_2 Jacobi coordinates.

A hypothetic numerical "experiment" performed by Schinke *et al.* is quite revealing.[20] These authors found that the artificial removal of the "reef" structure in the O_3 PES substantially increased the reaction cross section and brought the calculated rate constants to much better agreement with the experiment. Nonetheless, this modification of the O_3 PES was dismissed for lack of support from electronic structure theory.

To resolve this puzzle, we have undertaken extensive *ab initio* calculations at the MRCI level[29,30] with the Davidson correction (+Q),[31] using MOLPRO.[32] Considering adiabatic dissociation of ozone in the C_s group,

$$O_3(^1A') \rightarrow O(^3\Sigma_g^-) + O(^3P_g),$$
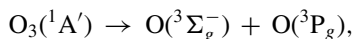
where Σ_g^- corresponds to A″ and P_g corresponds to (A′ + 2A″), combining to give (2A′ + A″). Diabatically, the ground state of ozone correlates to excited states of both the atomic and molecular oxygen products:

$$O_3(^1A') \rightarrow O_2(^1\Delta_g) + O(^1D_g),$$
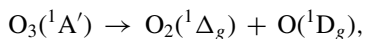
where Δ_g correlates to (A′ + A″), and D_g correlates to (3A′ + 2A″), combining to give (5A′ + 5A″), a ten-fold asymptotic degeneracy of the excited states. Thus, there are a total of 13 singlet states (7A′, 6A″) potentially relevant to the dissociation of ozone.

Some of these states interact strongly in the bottleneck and asymptotic regions. Indeed, the "reef" structure observed in some earlier calculations is due to an avoided crossing between the ground state in the molecular well (correlating di-

abatically with excited products) and the lowest lying excited $^1A'$ state correlating (diabatically) with the $O_2(^3\Sigma_g^-) + O(^3P)$ asymptote.[16]

This raises the intriguing question of how many states should be included in calculating a global PES for ozone in its ground electronic state. In multi-state complete active space self-consistent field (CASSCF) reference calculations, state averaging (SA) variationally optimizes the weighted-average energy of included states based on pre-assigned weights. If the ground state is well separated from the excited state, such as the case of ozone near its equilibrium geometry, it is sufficient to include only the ground $^1A'$ state in CASSCF. While this strategy maximizes convergence of the ground state, it can lead to root flipping and other convergence problems toward the asymptotes where multiple electronic states become quasi-degenerate. The MRCI studies of the asymptotic region by Schinke *et al.*[16] have thus included the three (2A′) + A″ asymptotically degenerate states (with equal weights) as a SA-CASSCF reference. However, the "reef" structure in the transition region is caused by an avoided crossing with a higher lying excited state, which was not included.

To explore the effect of including 13 singlet states in the CASSCF calculations, we have used the method of dynamical weighting (DW).[33,34] With an energy-dependent weighting function, the DW-SA-CASSCF method typically includes many more states (than fixed weight calculations) without compromising convergence of the state of interest. At a given geometry, the largest weight is assigned to the state of interest, while weights for other states are assigned (self-consistently) based on their energy difference to the state of interest. Consequently, far-away states receive negligible weights, while neighboring states are heavily weighted. Furthermore, a far-away state that becomes closer in energy will see its weight increased, and vice versa. This allows the electronic wavefunction to smoothly evolve across the PES and correctly preserves differing asymptotic electronic state degeneracy patterns. For a given choice of included states there are typically crossings with still higher lying excluded states. The DW scheme allows those crossings to occur seamlessly due to the negligible weights assigned to the states that are switching character.

We have carried out extensive MRCI calculations of the ozone formation PES with various basis sets and active spaces. These results are summarized in the supporting information (SI). In Fig. 1, we compare our newly calculated minimal energy path (MEP) for the formation of ozone with that on the hybrid PES of Babikov *et al.*[19] Contrary to previous studies, the MRCI + Q calculations reported here used the two lowest full-valence 13-state DW-SA-CASSCF reference wavefunctions, instead of one such reference wavefunction. The results were extrapolated with AVTZ and AVQZ; the correlation consistent aug-cc-pVQZ basis sets to the CBS limit. In addition, the rotated reference Davidson (+Q) correction was included. As shown in the SI, the Davidson correction is relatively large in the results presented here, underscoring the importance of high order excitations for this system. The MEP was obtained by relaxing the O–O distance and O–O–O angle as the atomic oxygen approaches the molecular oxygen.

It is clear from Fig. 1 that the new *ab initio* MEP is a monotonically decaying function of the dissociation coordinate. The disappearance of the "reef" structure is attributed primarily to including the ten upper states in the DW-SA-CASSCF reference, which smoothes the transition through the region of the avoided crossing. Also in the subsequent MRCI calculation, a small but significant mixing occurs between the ground state and the first excited A′ state (both are included in the MRCI calculations). Interestingly, if the ten upper states are excluded from the DW-SA-CASSCF reference and only one A′ state is included in the MRCI calculation, as shown in the SI, our results reproduce the "reef" structure observed previously.

We have constructed a two-dimensional (2D) PES at the same level of theory, using Jacobi coordinates with the O–O distance fixed at 2.2819 bohrs. The PES, which was fitted using the interpolating moving least squares method[35, 36] with 120 points, is also shown in Fig. 1. Using this PES, we have computed the thermal rate constant for the exchange reaction $^{16}O + ^{32}O_2 \rightarrow ^{32}O_2 + ^{16}O$, using a quantum statistical model (QSM).[24] While the computational details are given in the SI, we note here that all odd O_2 rotational states up to $j = 21$ were included and the partial waves were summed to $J_{max} = 80$. In Fig. 2, the calculated rate constant is compared with available experimental data and previous theoretical results. It is clear that the absence of the "reef" structure in the PES produces a substantial enhancement of the rate constant, bringing it into a much better agreement with experimental data. More importantly, the calculated rate constant has clear negative temperature dependence as observed experimentally. We note here that the QSM model is an approximation, since the exchange reaction is known to have a non-negligible non-statistical component.[23] While exact quantum dynamics calculations require a full-dimensional PES, the QSM results based on the 2D PES reported here strongly suggest that a new full-dimensional PES at the same level of theory will close the gap between theory and experiment in this respect.

While the absence of the "reef" structure in the ozone formation potential has a large effect on kinetics, it is still not clear if it will significantly affect the reaction dynamics. It is interesting to note that the MEP has essentially the same O–O
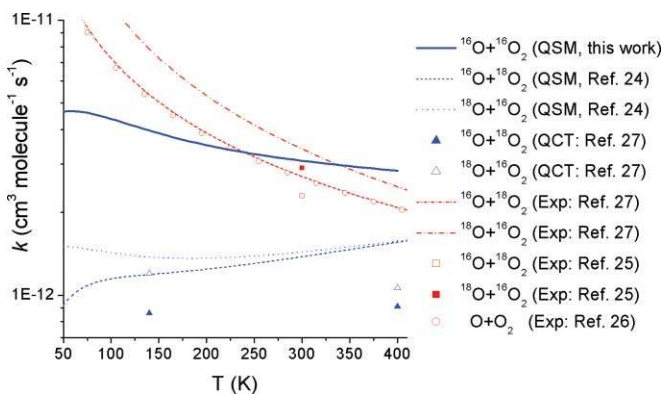
TABLE I. Calculated MRCI dissociation energies (cm^{-1}) with applied relaxed ($+Q_{rel}$) or modified ($+Q_{mod}$) Davidson corrections.

Method	CBS34	CBS45	CBS56	CBS_pow
MRCI	8889.2	8792.3	8808.9	8765.7
MRCI ($+Q_{rel}$)	9220.0	9114.5	9127.0	9079.8
MRCI ($+Q_{mod}$)	9232.9	9127.4	9139.9	9093.2
Experiment	9234.1[a]			

[a]Derived from D_0 (Ref. 38). CBS34, CBS45, and CBD56 refer to basis set extrapolations using the l^{-3} formula and the AVnZ bases with n = 3, 4 (CBS34), n = 4, 5 (CBS45), or n = 5, 6 (CBS56). CBS_pow refers to extrapolation using an optimized power-law (see the SI). All calculated values include core-valence, spin-orbit, and scalar relativistic corrections (see the SI).

distance and O–O–O angle until the system enters the deep O_3 well, as shown in the SI. It is, thus, unlikely that dynamics for both the $O + O_2$ exchange and ozone formation reactions will be greatly affected by the absence of the "reef" structure. Indeed, using the hybrid PES of Babikov *et al.*,[19] reasonably good agreement with experimental product state distributions has been obtained for the $O + O_2$ exchange reactions.[37] However, it is certainly worthwhile to revisit these issues when a full-dimensional PES using the same methods as reported here becomes available in the near future.

Another well-known discrepancy between theory and experiment has been the dissociation energy of ozone. Holka *et al.* reported recently a discrepancy of ∼200 cm^{-1} between their best calculations and experiment.[18] The best current experimental estimate of D_0 for $O_3 \rightarrow O_2 + O$ is 8563.6 ± 3.5 cm^{-1}.[38] Accounting for the ZPEs of O_3 and O_2 results in an estimated D_e of 9234.1 cm^{-1} (there is more than 3.5 cm^{-1} uncertainty in D_e due to uncertainty in the ZPE of ozone). In Table I, calculated dissociation energies are listed for various CBS extrapolation schemes (more detailed results are included in the SI).[39] Here, CBS energies are estimated using the l^{-3} formula as well as by separate extrapolation of the reference and correlation energies using a separately optimized power-law. In addition, two implementations of the Davidson correction are compared, and a core-valence correlation correction (CV) was estimated from all-electron calculations. Finally, scalar relativistic (SR) effects were computed and the effect of spin-orbit (SO) coupling was added.

Including the smaller corrections (SO, CV, and SR), D_e is certainly underestimated without Davidson corrections, even at the CBS level. With Davidson corrections and various CBS extrapolations, calculated values for D_e vary by approximately 150 cm^{-1}, with the largest calculated value coming within experimental error bounds. Near exact agreement comes from the simple l^{-3} extrapolation of the smaller triple and quadruple zeta bases, whereas CBS extrapolations of the largest bases with the l^{-3} formula or separate power-law extrapolation of the correlation energy produces values for D_e that are further from experiment. From these results, it appears that the largest remaining uncertainties lie in the CBS extrapolations and the Davidson correction. The significance of Davidson corrections also confirms the importance of higher order correlation effects.

To summarize, we have shown in this work that dynamically weighted Davidson corrected multi-state

FIG. 2. Comparison of calculated (blue) and measured (red) rate constants for the $O + O_2$ exchange reactions. The quantum statistical model and quasi-classical trajectory results in Refs. 24 and 27 were obtained using the PES of Babikov *et al.* (Ref. 19).

multi-reference configuration intersection calculations allow a much more accurate characterization of the ozone formation potential. Specifically, the calculated dissociation energy is in good agreement with experiment. Perhaps more importantly, the iconic "reef" structure in the MEP is shown to be absent, apparently due to a smoother transition through the region of avoided crossing with a higher electronic state. The absence of this submerged barrier has important implications for kinetics. As we have demonstrated with an approximate quantum scattering model, the new PES brings the calculated rate constant for the $O + O_2$ exchange reaction into much better agreement with experiment and produces a negative temperature dependence as observed experimentally. These new developments set the stage for future quantitative characterization of the $O + O_2$ exchange reaction and ozone formation in full dimensionality, including an understanding of the puzzling mass-independent fractionation phenomenon.

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