



Quantum origin of an anomalous isotope effect in ozone formation

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Received 2 January 2003; in final form 14 February 2003

Abstract

Accurate quantum mechanical calculations of the ($J = 0$) energies and lifetimes of the metastable states of ozone on a new, accurate potential energy surface are reported. These are very relevant to a famous anomalous isotope effect in the reaction that forms ozone because of their role in the energy transfer mechanism, in which metastable ro-vibrational states of ozone are formed and then stabilized by collisions with a third body. The resulting spectrum of metastable states is very dense below the delta zero-point energy threshold and sparse above it. This gives a clear qualitative explanation of why the effect occurs.

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1. Introduction

The origin of the anomalously large enrichments of stratospheric ozone in the heavy isotopes of oxygen has been a mystery for 20 years [1,2]. Oxygen has three stable isotopes: ^{16}O , ^{17}O and ^{18}O . The isotope ^{16}O is dominant in the atmosphere, so that most oxygen molecules, O_2 , only include ^{16}O atoms. However, stratospheric ozone, O_3 , is surprisingly observed to be heavily ($\sim 10\%$) enriched in ^{17}O and ^{18}O relative to the background O_2 present. Further, the enrichment is about equal in ^{17}O and ^{18}O , which led to its being called [2] ‘mass

independent’. Because of its importance for atmospheric chemistry, planetary science, and fundamental reaction dynamics, this phenomenon has been intensively studied (for recent short reviews, see Thiemens [3] and Mauersberger et al. [4]).

For several years, it was not at all clear as to which step in the atmospheric ozone cycle was isotopically selective, but careful experimental work [5] traced it clearly to the recombination reaction that forms ozone,



Here the third body M is any atom or molecule that can carry away the excess energy. The product O_3 may include any combination of ^{16}O , ^{17}O and ^{18}O isotopes. Mauersberger and co-workers [6–9] have measured the rate coefficients for reaction (R1) for almost all of the possible isotopic combinations of reactants O and O_2 . The rates *do*

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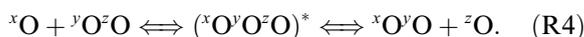
depend on the masses of the oxygen atoms involved, and, for different isotopic compositions the rates differ by more than 50%, which is a remarkably large isotope effect!

The observed isotope effect in reaction (R1) is essentially independent [10,11] of the identity of the third body M, and occurs with M being as simple as Ar or He. For this simple M, the reaction mechanism is expected to be dominated by the *energy transfer* mechanism:



Here O_3^* is a ro-vibrational metastable state (i.e., scattering resonance) which lives long enough to be stabilized by the collision with M. Again, any combination of O isotopes can be involved.

Early attempts to explain the isotope effects using simple symmetry arguments or classical mechanics had little success. However, recent progress has been rapid. Hathorn and Marcus [12] have formulated the problem using a statistical RRKM-based theory. In addition to the usual symmetry number ratio of 2, they introduced *two* other factors that could produce isotope effects. The *first* of these is an empirical *non-statistical* factor (η parameter) to describe a difference in density of dynamically active O_3^* states in symmetric and non-symmetric ozone molecules. They demonstrated that this η effect is dominant in determining the anomalous mass-independent isotope enrichments in stratospheric conditions. They [12] also mentioned a *second* factor to explain the mass-dependence observed in the recombination rates. That is a ‘partitioning factor’ that depends on the ‘differences in zero-point energies of the two transition states’ in reaction (R2) that connect with isotopically different O_2 molecules. In a paper published just a few weeks later, the Mauersberger group [7,8] noted that there is a correlation between the ozone formation rate coefficients and the *zero-point energy change* (ΔZPE) of the O_2 molecules in the atom exchange reaction,



Here, the metastable state $({}^x\text{O}^y\text{O}^z\text{O})^*$, can be formed from and decay to either the right- or left-

hand side of this reaction, and reaction (R2) is part of this reaction. When different isotopes of oxygen (x , y and z) are involved, the zero-point energies of the O_2 molecules on the right- and left-hand sides may be different, and reaction (R4) can thus be slightly exothermic or endothermic and exhibit slightly different rates. The Mauersberger group [7,8] speculated that ‘the endothermic exchange process may lead to a longer-lived collisional complex which then has a higher probability to become stabilized to ozone’.

In their next paper Hathorn and Marcus [13] further discussed the two factors. They showed that their nonstatistical empirical factor η needed to have a value of about 1.15 but could not identify its origin. They also noted that the partitioning factors are related to, and the relative rates of reaction (R1) correlate with, differences in ratios of reduced masses and rotational constants as well as the ΔZPE of the oxygen molecules involved (see also [14]). They also saw that at low energies one exit channel in reaction (R4) ‘is energetically excluded and so the excited molecule has a longer lifetime’ and a ‘greater chance to be deactivated’ by collisions. Then, a nearly simultaneous pair of papers [15,16] clearly identified the ΔZPE in reaction (R4) as the dominant factor in controlling the lifetimes of the O_3^* and producing the large differences in the relative rates of reaction (R1). The paper by Gao and Marcus [15] was submitted first, but the paper by the Mauersberger group [16] was published first.

We pause to remark that Gao and Marcus noted in this paper [15] that their η factor might arise from collisional effects in reaction (R3). We believe that to be correct and we shall discuss the idea a little farther in the discussion section. However, all the calculations in Letter deal with the ΔZPE effect in reaction (R2). Although the parameters in the semiempirical theory [15,17] have allowed the experimental data for both ozone isotope effects to be fit quite well, neither that theory [15,17] nor the experiments to date have been able to actually give the spectrum of metastable states of ozone, and neither group has been able to prove *why* such a small thing as the ΔZPE should have such a large effect. Both groups have noted that accurate quantum mechanical calculations of positions and lifetimes of the O_3^* states are required.

Charlo and Clary [18] have done approximate quantum calculations of the metastable states and recombination rate and found isotopic effects of the right order of magnitude but often in the wrong direction. It is clear that, to accurately describe the O_3^* states for a molecule as complex as ozone, one must perform state-of-the-art calculations. In this Letter we report rigorous quantum mechanical calculations of the energies and lifetimes of the O_3^* metastable states for total angular momentum $J = 0$ on a new, accurate potential energy surface. The results show the *reason* for the remarkable effect of the ΔZPE .

2. Calculations, results, and discussion

A very sophisticated potential energy surface (PES) for ozone was used for this work. It is based on an accurate ab initio PES [19,20] calculated by one of us. However, it also includes a correction in the barrier region to make it agree with even more accurate ab initio calculations which we have performed along the minimum energy path [21,22]. The resulting PES is the most accurate one currently available for the ground electronic state of ozone. It has the full symmetry of the system and goes smoothly to all the correct dissociation limits. It exhibits a small barrier along the dissociation path, but the top of that barrier is *below* the dissociation limit! This behavior is essential; the resonant states are very sensitive to this detail of the PES, and those calculated with the unmodified PES are not correct [19,20].

Full quantum reactive scattering calculations including all dimensions of this problem were performed using this new PES; no approximations were made. A coupled channel (CC) approach using APH hyperspherical coordinates [23] was employed using a parallel computer code [24]. The calculations were performed on the massively parallel supercomputer 'Seaborg' (IBM RS/6000 SP at NERSC center in Berkeley National Lab). The CC equations were propagated from 3.25 to 14.31 a.u., and convergence studies showed that as many as 190 channels were necessary. The present calculations were performed for total angular momentum $J = 0$; calculations for $J > 0$ are on-

going and will be reported elsewhere. The lifetimes of the metastable states [25] were obtained as a trace of Smith's Q -matrix.

In this Letter calculations on two isotopic compositions of ozone are reported: $^{16}O^{18}O^{18}O$ and $^{16}O^{16}O^{18}O$. The *first* of these is formed in the following recombination reactions:



Experimentally, reactions (R5) and (R6) exhibit very different rates: 1.50 and 0.92, respectively [16], relative to the reaction with all atoms being ^{16}O . (The metastable states of the symmetric isotopomer $^{18}O^{16}O^{18}O$ are also obtained in these calculations and will be discussed elsewhere.) For the *second* isotopic combination, $^{16}O^{16}O^{18}O$, there are also two entrance channels, $^{16}O + ^{16}O^{18}O$ and $^{16}O^{16}O + ^{18}O$, exhibiting relative recombination rates similar to those above: 1.45 and 0.92, respectively [16].

The low energy ($E < 110$ K) calculated lifetime spectra for the two isotopic combinations are shown as the two halves of Fig. 1. The sharp spikes (scattering resonances) correspond to formation of metastable states of O_3^* . In both cases, the spectra exhibit *very* non-statistical features: the lower parts of the spectra ($E < 29$ K for $^{16}O^{18}O^{18}O$ and $E < 36$ K for $^{16}O^{16}O^{18}O$) contain *many metastable states* with lifetimes in the optimum (picosecond) range to contribute to the recombination but the higher energy region of the spectra is *very sparse* and contains only a few such resonances.

Fig. 2 shows a schematic of $^{16}O^{18}O^{18}O$ ozone formation. There are two entrance channels: $^{16}O + ^{18}O^{18}O$ (reaction R5) is on the left-hand side of the figure and $^{16}O^{18}O + ^{18}O$ (reaction R6) is on the right. The energy difference between the two entrance channels is the ΔZPE for reaction (R4). Energies below zero (the yellow part of the figure) correspond to stable $^{16}O^{18}O^{18}O$ ozone molecules, while metastable states ($^{16}O^{18}O^{18}O$)* can be formed above zero energy. Stabilization of O_3^* to O_3 , reaction (R3), is shown schematically by descending arrows. This figure illustrates that metastable states at energies *above* the ΔZPE can be formed from both entrance channels. When metastable states formed at these energies are stabilized, they con-

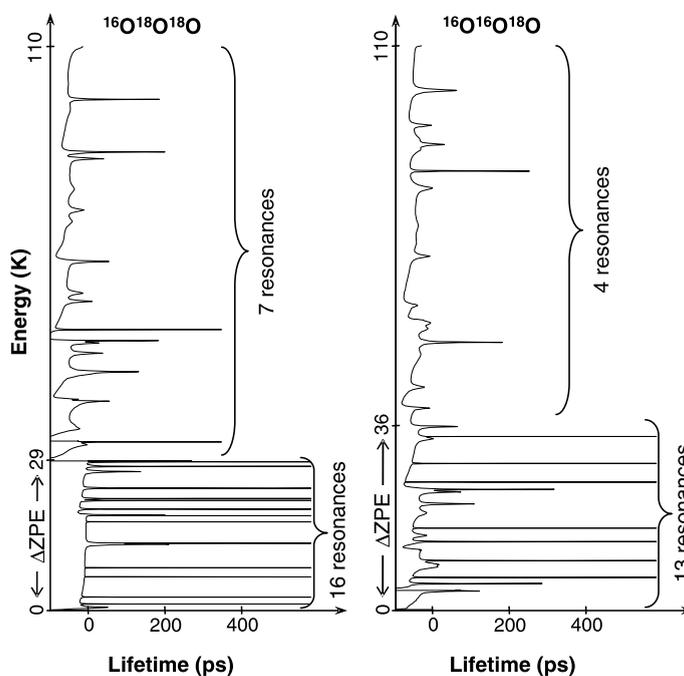


Fig. 1. Lifetime spectra for two isotopic combinations of ozone: $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ (left panel) and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ (right panel). Sharp spikes of lifetime correspond to metastable states. Both isotopic combinations exhibit a pronounced non-statistical feature: the parts of the spectra below ΔZPE contain an anomalously large number of metastable states, while the upper parts of the spectra contain only a few metastable states.

tribute equally to both reactions (R5) and (R6). We call this part of the spectrum a ‘background’, because it will not produce any anomalous difference in the rates for reactions (R5) and (R6). However, the metastable states at energies *below* the ΔZPE can be formed *only* from the lower entrance channel; namely, $^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$, i.e., from the left-hand side of Fig. 2. When stabilized, they contribute exclusively to reaction (R5). Thus, the metastable states formed in the energy range between zero and ΔZPE are responsible for the anomalous difference in rates for reactions (R5) and (R6), because they are associated with only the first of them, and not with the second.

Now, let us consider Fig. 1 again. We note that it is exactly this region below ΔZPE that has the *dense* spectrum of metastable states for *both* isotopic combinations considered ($\Delta ZPE = 29$ K for $^{16}\text{O}^{18}\text{O}^{18}\text{O}$ and $\Delta ZPE = 36$ K for $^{16}\text{O}^{16}\text{O}^{18}\text{O}$), while the upper spectra corresponding to the ‘background’ energy range, are *sparse* for both

combinations. The part of the spectrum below ΔZPE is rather narrow energetically, but it has most of the metastable states, and they lie closest to the energy of stable O_3 (see Fig. 2), so that they are more easily stabilized in collisions with the third body than are the higher lying metastable states. Not only are their *lifetimes* increased as had been expected in Refs. [7,12,14,15], but the *number* of metastable states below ΔZPE relative to those above it is drastically larger than one would expect from statistics. This dominance of low-energy metastable states not only explains *why* the anomalous isotope effect in the partitioning factor occurs, but it also provides an explanation of why the low temperature experimental [26] recombination rate coefficient has such a strong negative temperature dependence. The numbers, locations, and stabilization of the metastable states all contribute to the observed effects.

A scheme very similar to that in Fig. 2 can be drawn for formation of $^{16}\text{O}^{16}\text{O}^{18}\text{O}$, but now the

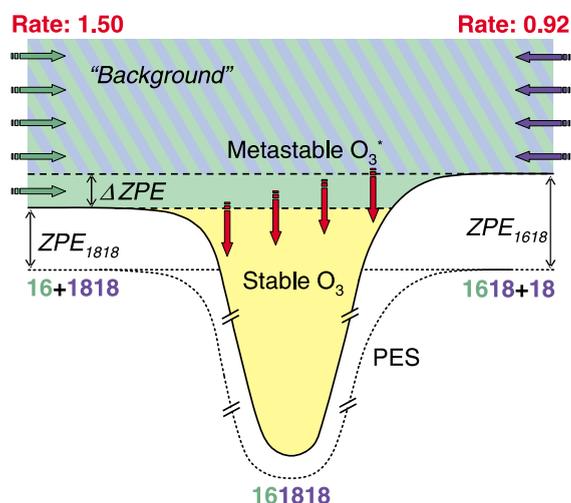


Fig. 2. Schematic for recombination processes forming ozone $^{16}\text{O}^{18}\text{O}^{18}\text{O}$. Stable ozone molecules are formed in the potential well (yellow part) as a result of collisional stabilization of metastable states formed above the well (in the green and striped blue/green part). The stabilization process is shown schematically as red descending arrows. Metastable states in the striped part of the spectrum can be formed from both entrance channels: $^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$ on the left (green arrows) and $^{16}\text{O}^{18}\text{O} + ^{18}\text{O}$ on the right (blue arrows). Metastable states in the ΔZPE part of spectrum (green) are formed exclusively from the $^{16}\text{O} + ^{18}\text{O}^{18}\text{O}$ entrance channel. The PES (dotted line) and the ZPE for both channels are shown (not to scale). Experimental relative rates of ozone formation for the two channels are given at the top.

lower entrance channel is $^{16}\text{O} + ^{16}\text{O}^{18}\text{O}$ and the upper channel is $^{18}\text{O} + ^{16}\text{O}^{16}\text{O}$. The metastable states in the ΔZPE region can be populated only from the first of them and they contribute exclusively to the corresponding reaction rate.

Another thing that is now clear is that the effect is a quantum effect, and one can now see why classical trajectories, which have no ZPE and follow along the lowest dotted curve in Fig. 2, which is the same on both sides of the reaction, could not give the effect. One also sees, as suggested by Gao and Marcus [15], that this isotope effect is a *general* quantum effect that should be seen in any A_3 type triatomic molecule for which there is no barrier to dissociation and for which the ΔZPE between the different isotopic A_2 molecules is not negligible.

Calculations of the resonance spectra of symmetric species, $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ and $^{18}\text{O}^{18}\text{O}^{18}\text{O}$, for which ΔZPE is zero, have been also performed and

will be reported elsewhere. At low energies they display only a *sparse* spectrum similar to the upper parts of Fig. 1.

We are continuing to do calculations aimed at giving a complete *quantitative* explanation of all aspects of the anomalous isotope effects in ozone, and these will be reported elsewhere. The wavefunctions of the metastable states that we have calculated are being plotted and analyzed to identify the metastable states. Also, we have calculated the lifetime spectra for the two present isotopic combinations up to an energy of 600 K. Above the range shown in Fig. 1 there is a dense spectrum of extremely narrow resonances in both $(^{16}\text{O}^{18}\text{O}^{18}\text{O})^*$ and $(^{16}\text{O}^{16}\text{O}^{18}\text{O})^*$. However, not only is their contribution slowed by the larger energy transfer in their (R3) step, but also most of them have lifetimes in the microsecond range, and, as we have shown elsewhere [27], metastable states with such long lifetimes *form* so slowly that they never build up a significant concentration and thus cannot contribute much to the recombination rate. Calculations of the resonance spectra for $J > 0$ are also underway; for low J , their spectra are similar to those shown in Fig. 1, and they contribute to the isotope effect; as J increases, the low-lying resonances are expected to disappear as the larger J shut off the reaction.

We are also doing calculations related to the other isotope effect, the η effect. It favors stabilization of asymmetric ozone metastable states (such as $(^{16}\text{O}^{18}\text{O}^{18}\text{O})^*$ or $(^{16}\text{O}^{16}\text{O}^{18}\text{O})^*$) over symmetric ones (such as $(^{18}\text{O}^{16}\text{O}^{18}\text{O})^*$ or $(^{16}\text{O}^{18}\text{O}^{16}\text{O})^*$). This is not simply because the symmetric ozone molecules contain only even rotational states while the asymmetric ozone molecules contain both even and odd rotational states. The numbers of available *states* have already been accounted for in the experimental rates reported. However, in addition to *numbers of states*, the asymmetric combinations have additional stabilization *pathways* (transitions between even and odd rotational states) that can make step (R3) have a smaller energy transfer and thus be faster. This process requires careful theoretical attention. Unfortunately, classical mechanics cannot describe this quantum symmetry effect, and exact quantum mechanical calculations are extremely

expensive for reaction (R3), because it contains four heavy atoms. We recognized this problem some time ago and have developed a symmetry-preserving semiclassical method [28] able to treat this effect and give quantum mechanical symmetry selection rules. Calculations along this line on (R3) will be pursued in the future.

3. Conclusion

While earlier work had shown that the partitioning factor or ΔZPE effect must occur to produce the observed anomalous isotope effect in the formation of ozone, the present results give the first clear, simple picture of *why* this effect occurs: In step (R4) involving unlike isotopes, the presence of closed channels causes a large *number* of metastable states to occur at energies below the ΔZPE threshold, while only a *sparse* spectrum of them occurs above the threshold. Not only are there a large number of these low-lying metastable states, but they also have the advantage of being stabilized rapidly by smaller energy transfers in the second step (R3) of the reaction. Both of these effects favor the reaction that can enter below the zero-point energy threshold.

Acknowledgements

This work was performed under the auspices of the US Department of Energy (under Contract W-7405-ENG-36). We thank Prof. Mauersberger and his group in Heidelberg for helpful discussions. Dmitri Babikov acknowledges the Laboratory Directed Research and Development program at Los Alamos for a Postdoctoral Fellowship and the NERSC center at Lawrence Berkeley National Laboratory for computing support.

References

- [1] K. Mauersberger, Geophys. Res. Lett. 8 (1981) 935.
- [2] M.H. Thiemens, J.E. Heidenreich III, Science 219 (1983) 1073.
- [3] M.H. Thiemens, Science 283 (1999) 341.
- [4] K. Mauersberger, B. Erbacher, D. Krankowsky, J. Gunther, R. Nickel, Science 283 (1999) 370.
- [5] J. Morton, J. Barnes, B. Schueler, K. Mauersberger, J. Geophys. Res. 95 (D1) (1990) 901.
- [6] S.M. Anderson, D. Hulsebusch, K. Mauersberger, J. Chem. Phys. 107 (1997) 5385.
- [7] C. Janssen, J. Guenther, D. Krankowsky, K. Mauersberger, J. Chem. Phys. 111 (1999) 7179.
- [8] C. Janssen, J. Guenther, D. Krankowsky, K. Mauersberger, J. Chem. Phys. 112 (2000) 11109.
- [9] S. Wolf, M. Bitter, D. Krankowsky, K. Mauersberger, J. Chem. Phys. 113 (2000) 2684.
- [10] J.E. Heidenreich III, M.H. Thiemens, J. Chem. Phys. 84 (1986) 2124.
- [11] J. Guenther, D. Krankowsky, K. Mauersberger, Chem. Phys. Lett. 324 (2000) 31.
- [12] B.C. Hathorn, R.A. Marcus, J. Chem. Phys. 111 (1999) 4087.
- [13] B.C. Hathorn, R.A. Marcus, J. Chem. Phys. 113 (2000) 9497.
- [14] A. Miklavc, S.D. Peyerimhoff, Chem. Phys. Lett. 359 (2002) 55, have shown that it also correlates with the probability of vibrational excitation in $O_2 + O$ collisions.
- [15] Y.Q. Gao, R.A. Marcus, J. Chem. Phys. 116 (2002) 137, and 5913.
- [16] C. Janssen, J. Guenther, K. Mauersberger, D. Krankowsky, Phys. Chem. Chem. Phys. 3 (2001) 4718.
- [17] Y.Q. Gao, W.-C. Chen, R.A. Marcus, J. Chem. Phys. 117 (2002) 1536.
- [18] D. Charlo, D.C. Clary, J. Chem. Phys. 117 (2002) 1660.
- [19] R. Siebert, R. Schinke, M. Bittererova, Phys. Chem. Chem. Phys. 3 (2001) 1795.
- [20] R. Siebert, P. Fleurat-Lessard, M. Bittererova, S.C. Farantos, R. Schinke, J. Chem. Phys. 116 (2002) 9749.
- [21] R. Hernandez-Lamonedada, M.R. Salazar, R.T. Pack, Chem. Phys. Lett. 355 (2002) 478.
- [22] P. Fleurat-Lessard, S.Yu. Grebenshchikov, R. Siebert, R. Schinke, N. Halberstadt, J. Chem. Phys. 118 (2003) 610.
- [23] B.K. Kendrick, R.T. Pack, R.B. Walker, J. Chem. Phys. 110 (1999) 6673, and references therein.
- [24] B.K. Kendrick, J. Chem. Phys. 114 (2001) 8796.
- [25] B. Kendrick, R.T. Pack, J. Chem. Phys. 106 (1997) 3519.
- [26] H. Hippler, R. Rahn, J. Troe, J. Chem. Phys. 93 (1990) 6560.
- [27] R.T. Pack, R.B. Walker, B.K. Kendrick, J. Chem. Phys. 109 (1998) 6714.
- [28] D. Babikov, R.B. Walker, R.T. Pack, J. Chem. Phys. 117 (2002) 8613.