

STRATOSPHERIC HEAVY OZONE: THE SYMMETRIC ISOMER

W. Lowell Morgan

Kinema Research
18720 Autumn Way, Monument, CO 80132 USA

and

David R. Bates

Department of Applied Mathematics and Theoretical Physics
Queen's University, Belfast BT7 1NN UK

(Camera-ready copy received 16 October 1992)

Abstract – Flips in which one of the end atoms of an energized complex like $^{16}\text{O}^{16}\text{O}^{18}\text{O}^*$ ceases to be effectively bound to the central atom and becomes effectively bound to the other end atom (so that ^{18}O is transformed into the central atom) are considered. Using the Monte Carlo method to follow the motion of three oxygen atoms on the ground state potential energy surface of ozone it is shown that the flips do indeed occur; and it is shown that their frequency relative to the dissociation frequency is consistent with the results of measurements by Anderson, *et al.* (*Chem. Phys. Lett.* 156, 175, 1989).

INTRODUCTION

In situ mass spectrometer measurements by Mauersberger (1981) led to the discovery that heavy (50 amu) ozone is enriched in the stratosphere. From measurements made in the course of later balloon flights Mauersberger (1987) showed that the isotopic enrichment is mass independent. Abbas, *et al.* (1987) verified the discovery from an analysis of balloon based high resolution thermal emission spectra in the far infrared. Moreover they showed that both $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ are enriched. Supporting evidence was provided by Carli and Park (1988) who also studied the far infrared emission spectrum and by Goldman, *et al.* (1989) who analysed solar absorption spectra in the $10\ \mu\text{m}$ region that they obtained using a balloon borne Michelson Fourier transform spectrometer. During the day an ozone molecule in the stratospheric region concerned has a lifetime of less than 2×10^3 s (cf. Brasseur and Solomon 1984) so it is patent that the enrichment must be inherent in the generation process, that is, in the termolecular association of atomic and molecular oxygen.

Thiemens and Heidenreich (1983) were the first to demonstrate in the laboratory that the termolecular association of atomic and molecular oxygen leads to mass independent isotopic enrichment of heavy ozone. Their work was confirmed by the further

laboratory research of Heidenreich and Thiemens (1986), Thiemens and Jackson (1987), and Yang and Epstein (1987). An important investigation was carried out by Morton, *et al.* (1989) on the relative abundances of ozone molecules in the mass range 48 to 54 amu formed in an electric discharge through isotopically enriched molecular oxygen. Their results showed that the enhancement is closely related to symmetry as Heidenreich and Thiemens (1986) had proposed. Another important investigation on the heavy ozone has been carried out by Anderson, *et al.* (1989). Writing X to denote a heavy oxygen atom, in order to avoid the clumsiness of distinguishing the isotopes by 18, 17, and 16 as pre-suffixes, they differentiated between OOX and OXO by using tunable infrared diode laser absorption spectroscopy. They reported finding that OOX carries about twice the enrichment on a per molecule basis so that OXO makes up about one fifth the total heavy ozone enrichment. Expressed in the form

$$\frac{[\text{OOX}]_{\text{obs}}}{[\text{OOX}]_{\text{stat}}} = 1 + a, \quad \frac{[\text{OXO}]_{\text{obs}}}{[\text{OXO}]_{\text{stat}}} = 1 + s \quad (1)$$

where the subscripts *obs* and *stat* indicate that the number density is the observed or the statistical, their results are in fact that

$$a = 0.198 \pm 0.012, \quad s = 0.054 \pm 0.014 \quad (2)$$

which correspond to OXO making up about one tenth the total heavy ozone enhancement.

Symmetry is certainly involved but, as has been proved by Bates (1990a), it cannot by itself cause isotopic fractionation. According to Bates (1988) the additional feature is the finiteness of the randomization frequencies $\nu(R)$ defined as the reciprocal of the time needed for the association energy of ozone to become randomized amongst the vibrational modes. In its original form the theory only accounts for OOX enrichment. Direct enrichment of OXO is impossible just as there clearly cannot be direct mass independent isotopic enrichment of a molecule without symmetry.

Either OOX or its energized complex OOX* must be implicated in the OXO enrichment that the research of Anderson, *et al.* (1989) has shown, though small, is undoubtedly real. Having dismissed the possibility that OOX is implicated Bates (1990b) concluded that OOX* must be responsible for the OXO enrichment. He proposed a process called a flip. In this the two end atoms of the energized complex swing together so that, in effect, a new bond is formed between them and the bond between one of them and the pristine central atom is broken. Flips lead to the following transformations:



the last of which is a null transformation. Let $\nu(F)$ be the frequency with which an energized complex makes a flip and let $\nu(D)$ be the dissociation frequency. Write

$$\nu(F) = \lambda\nu(D). \quad (6)$$

By considering the [OXO*] steady state it may be shown that

$$s/a = \lambda/(\lambda+1) \quad (7)$$

(cf. Bates 1990b). Use of result (2) hence yields that

$$\lambda = 0.40 \pm 0.17 \quad (8)$$

We shall investigate the motion of three oxygen atoms with the appropriate total energy of the potential surface of the 1A_1 ground state of ozone. There is experimental

evidence (Kleindienst, *et al.* 1980; Locker, *et al.* 1987) that some of the ozone formed by termolecular association is in the 3B_2 metastable state. However a 3B_2 potential energy surface accurate enough for a similar investigation is not available.

MOTION ON 1A_1 POTENTIAL SURFACE

The single-valued potential energy surface that Varandas and Pais (1988) obtained for the ground electronic state of ozone by the double many-body expansion method was adopted. The parameters appearing were determined by Varandas and Pais from a multiproperty analysis using *ab initio* energies and data from spectroscopic, incomplete total scattering cross section, and kinetic thermal rate measurements. Contour plots of the potential surface are shown in Figs. 1 and 2. The deep, -6.24 eV [(A) in Fig. 1], well in the ozone configuration is apparent. There are more shallow troughs of -5.11 eV [(B)] and -5.24 eV [(C)] along the direction normal to the O-O axis.

Our classical Monte Carlo trajectory simulations were performed using standard techniques (Bunker, 1971; Truhlar and Muckerman, 1979) whereby the initial conditions are chosen statistically and the classical equations of motion are numerically integrated using a fourth-order adaptive stepsize Runge-Kutta algorithm (Press, *et al.*, 1986). All trajectories were integrated until the final fate of the O_3^* was determined. Energy was typically conserved to better than several parts in 10^4 over the course of a trajectory.

Fig. 3 shows a histogram of the distribution of times the trajectories spend in the interaction region. Their average is 2.1×10^{-12} s. This is also the average for the minority

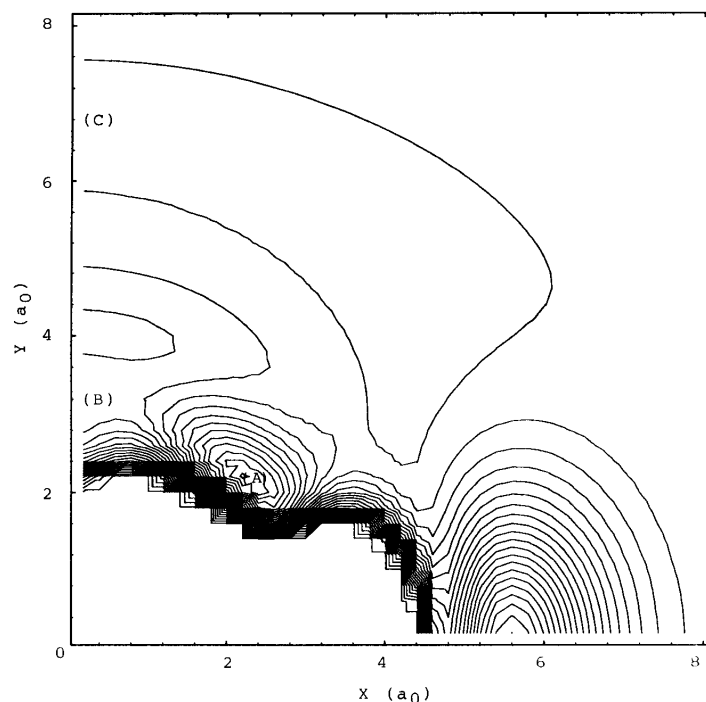


FIGURE 1: POTENTIAL ENERGY CONTOURS AT 0.1 eV INTERVALS FOR AN OXYGEN ATOM MOVING AROUND AN OXYGEN MOLECULE.

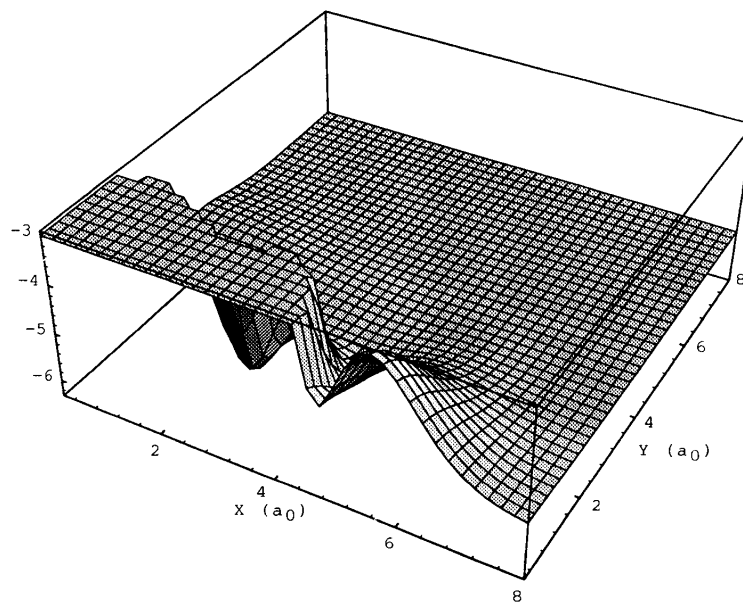


FIGURE 2: THREE-DIMENSIONAL DEPICTION OF THE POTENTIAL SURFACE

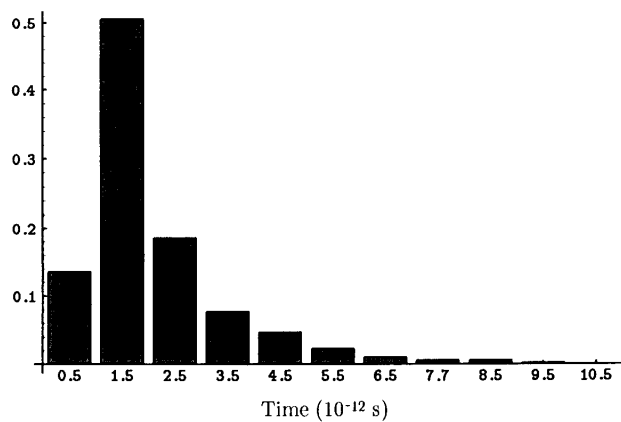


FIGURE 3: DISTRIBUTION OF TRAJECTORY LIFETIMES

group that end as $X + O_2$ whereas the average for the minority group that end as $O + OX$ is 3.4×10^{-12} s (over 50 per cent greater). Typically the trajectories involve a complicated motion of one of the oxygen atoms in the complex that takes it around one or more of the

various minima in the potential surface with a passage time between minima of tenths of picoseconds. The residence time of the loosely bound atom in the shallow trough regions normal to the O–O axis is typically less than or about equal to a ps. Atoms that get trapped in the deep -6.24 eV well typically remain there for several picoseconds. We observed one case where a very stable equilateral triangle configuration was formed that persisted for 10 ps. These long lifetimes are consistent with earlier computer simulations (Stace and Murrell, 1978; Varandas and Pais, 1988).

A check is provided by an independent determination of $\tau(D)$ the mean lifetime towards dissociation. Let k_9 be the rate coefficient for the formation of the energized complex



and let $Z\beta_c$ be the rate coefficient for the stabilizing collision



where Z is the Lennard–Jones collision coefficient and β_c is the collision efficiency. The rate coefficient for the termolecular association process



is then given by

$$k_{11} = \tau(D) k_9 Z \beta_c \quad (12)$$

Choosing the temperature as 300K and taking k_9 to be $5.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Anderson, *et al.* 1985), Z to be $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Troe 1977), and k_{11} to be $3.85 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$ (Klais *et al.*, 1980; Lin and Leu, 1982) it may hence be seen that

$$\beta_c \tau(D) = 2.5 \times 10^{-13} \text{ s} \quad (13)$$

In order to reproduce the mean lifetime given by the trajectory analysis β_c would have to be 0.12, which might seem a rather low value but is in acceptable agreement with the 0.18 that Troe (1979) deduced by combining the measured rate coefficient for process (11) with a result that he calculated from unimolecular rate theory.

As a further check on our trajectory analysis the rate coefficient for the isotope exchange process



was computed. The value obtained, $2.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, reproduces the trajectory analysis result of Varandas and Pais (1988) and agrees closely with the experimental result of Anderson *et al.* (1985). This success is important in the present context because process (14) is intimately linked with ozone generation: thus its rate coefficient k_{14} is half k_9 the rate coefficient of the first step of termolecular association and likewise is half the binary rate coefficient for the formation of ozone in the high ambient gas density limit (*cf* Anderson *et al.* 1985).

We may now turn to the issue of the frequency of flip transitions relative to the dissociation frequency. Unfortunately there is no rigorous simple means of determining to which isomer a particular configuration refers. Indeed both isomers may be involved: for example it is evident that stabilization in an equilateral configuration would yield OXO and OOX in the 1:2 ratio. We judged it adequate to monitor the three distances between atoms and to assume that the isomer is OXO if the OO distance is greater than both XO distances and that it is OOX if this condition is not met. Out of 1000 trajectories studied, 989 formed complexes, 875 ended as $\text{X} + \text{O}_2$ (as they began), and in only 3 of these 875 were there flips. These flips were double, that is, into OXO and out again. However, in

the remaining 125 trajectories that ended as O + OX there were 79 having single flips and a further 3 having multiple flips so that these trajectories have a total of 94 flips. As already noted the rate coefficient for isotope exchange, process (14) is half the rate coefficient for the first step, process (9), of termolecular association. It is, therefore, reasonable to suppose that the number of the trajectories studied that include this first step is 250 (of which 125 end as X + O₂ and have virtually no flips). On this basis the ratio of the flip frequency to the dissociation frequency is $94/250 = 0.38$, which agrees excellently with result (8) doubtless fortuitously.

We do not yet properly understand why many of the trajectories that end as X + OO form complexes yet seemingly do not contribute to ozone formation, but the relatively short lifetimes of the complexes is probably a factor.

Acknowledgements – We thank Dr. A.J.C. Varandas for providing us with the subroutines for computing the ozone potential surface and interatomic forces and the Data Center of the Joint Institute for Laboratory Astrophysics for the use of their DEC-5000 workstation. W.L.M. wishes to thank NATO for their financial support of his visit to Belfast and he thanks the folks of Belfast who, through their warm hospitality, made his visit a most enjoyable experience. D.R.B. thanks the U.S. Air Force for support under grant number AFOSR 91-0261.

REFERENCES

- Abbas, M. M., Guo, J., Carli, B., Mencaraglia, F., Carlotti, M., and Nolt, I. G. (1987) Heavy ozone distribution in the stratosphere from far-infrared observations. *J. Geophys. Res.* **92**, 13,213–13,239.
- Anderson, S. M., Klein, F. S., and Kaufman, F. (1985) Kinetics of the isotope exchange reaction of ¹⁸O with NO and O₂ at 298K. *J. Chem. Phys.* **83**, 1648–1656.
- Anderson, S. M., Morton, J., and Mauersberger K. (1989) Laboratory measurements of ozone isotopomers by tunable diode laser absorption spectroscopy. *Chem. Phys. Lett.* **156**, 175–180.
- Bates, D. R. (1988) Suggested explanation of heavy ozone. *Geophys. Res. Lett.* **15**, 13–16.
- Bates, D. R. (1990a) Symmetry considerations and the formation of isotopically heavy ozone and carbon dioxide. *J. Chem. Phys.* **93**, 2158.
- Bates, D. R. (1990b) Isotopic fractionation in the formation of ozone and of carbon dioxide. *J. Chem. Phys.* **93**, 8739–8744.
- Brasseur, G. and Solomon, S. (1984) *Aeronomy of the Middle Atmosphere*. D. Reidel Publ. Co., Dordrecht, p. 208.
- Bunker, D. L. (1971) Classical trajectory methods. *Meth. in Comp. Phys.* **10**, 287.
- Carli, B. and Park, J. H. (1988) Simultaneous measurement of minor stratospheric constituents with emission far infra-red spectroscopy. *J. Geophys. Res.* **93**, 3851–3865.
- Goldman, A., Murcray, F. J., Murcray, D. G., Kusters, J. J., Rinsland, C. P., Flaud, J.-M., Camy-Peyret, C., and Barbe, A. (1989) Isotopic abundances of stratospheric ozone from balloon borne high resolution infrared solar spectra. *J. Geophys. Res.* **94**, 8467–8473.
- Heidenreich, J. E. and Thiemens, M. H. (1986) A non-mass-dependent oxygen isotope effect in the production of ozone from molecular oxygen: the role of molecular symmetry in isotopic chemistry. *J. Chem. Phys.* **84**, 2129–2136.
- Klais, O., Anderson, P. C., and Kurylo, M. J. (1980) A reinvestigation of the temperature dependence of the rate constant for the reaction O + O₂ + M → O₃ + M (for M = O₂, N₂, and Ar) by the flash photolysis resonance fluorescence technique. *Int. J. Chem. Kinetics* **14**, 469–490.
- Kleindienst, T., Locker, J. R., and Bair, E. J. (1980) Metastable intermediates in the formation of ozone by recombination. *J. Photochem.* **12**, 67–74.
- Lin, C. L. and Leu, M. T. (1982) Temperature and third body dependence of the rate coefficient for the reaction O + O₂ + M → O₃ + M. *Int. J. Chem. Kinetics* **14**, 417–434.
- Locker, J. R., Joens, J. A., and Bair, E. J. (1987) Metastable intermediate in the formation of ozone by recombination. *J. Photochem.* **36**, 235–245.
- Mauersberger, K. (1981) Measurement of heavy ozone in the stratosphere. *Geophys. Res. Lett.* **8**, 935–937.

- Mauersberger, K. (1987) Ozone measurements in the stratosphere. *Geophys. Res. Lett.* **14**, 80–83.
- Morton, J., Schueler, B., and Mauersberger, K. (1989) Oxygen fractionation of ozone isotopes $^{48}\text{O}_3$ through $^{54}\text{O}_3$. *Chem. Phys. Lett.* **154**, 143–145.
- Press, W. H., Flannery, B. P., Teukolsky, S. A., and Vetterline, W. T. (1986) *Numerical Recipes*. Cambridge University Press, Cambridge, p. 554–560.
- Stace, A. J. and Murrell, J. N. (1978) Dynamics of the oxygen exchange reaction. *J. Chem. Soc. Faraday II* **74**, 2182–2186.
- Thiemens, M. H. and Heidenreich, J. E. (1983) The mass-independent fractionation of oxygen: a novel isotope effect and its possible cosmochemical implications. *Science* **219**, 1073–1075.
- Thiemens, M. H. and Jackson, T. (1987) Production of isotopically heavy ozone by ultraviolet light photolysis of O_2 . *Geophys. Res. Lett.* **14**, 624–627.
- Troe, J. (1977) Theory of thermal unimolecular reactions at low pressures II Strong collision rate constants. Applications. *J. Chem. Phys.* **66**, 4758–4775.
- Troe, J. (1979) Predictive possibilities of unimolecular rate theory. *J. Phys. Chem.* **83**, 114–126.
- Truhlar, D. G. and Muckerman, J. T. (1979) Reactive scattering cross sections II: quasiclassical and semiclassical methods, in *Atom-Molecule Collision Theory* (ed. Bernstein, R. B.) Plenum Press, New York, p. 505–566.
- Varandas, A. J. C. and Pais, A. A. C. C. (1988) A realistic double many-body expansion (DMBE) potential energy surface for ground-state O_3 from a multiproperty fit to *ab initio* calculations, and to experimental spectroscopic, inelastic scattering, and kinetic isotope thermal rate data. *Molecular Physics* **65**, 843–860.
- Yang, J. and Epstein, S. (1987) The effect of pressure and excitation energy on the isotopic fractionation in the formation of ozone by discharge of O_2 . *Geochimica Cosmochimica Acta* **51**, 2019–2024.