



Vibrational Levels and Resonances on a new Potential Energy Surface for the Ground Electronic State of Ozone

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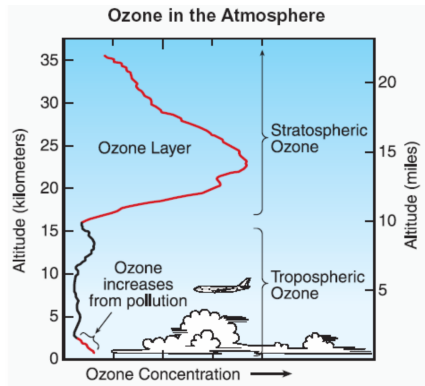
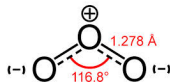
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About the ozone molecule...

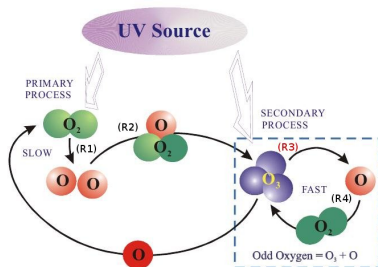
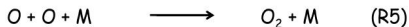
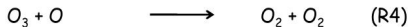
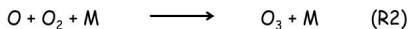
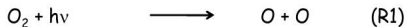
- Ozone, though of little abundance, is the principal filter against harmful UV solar radiation.
- Due to the absorption of VIS-IR-UV radiation, it has an impact on the **atmospheric energetic budget**
- It is also a **precursor of numerous chemical processes** involving atomic oxygen

Oxygen has 3 stable isotopes:

- ¹⁶O abundant at **99.76%**
- ¹⁷O abundant at **0.039%**
- ¹⁸O abundant at **0.201%**



Ozone is formed and destroyed in the atmosphere according to the Chapman's cycle¹



Besides those reactions, other catalytic reactions with ClO_x, NO_x, HO_x contribute to the ozone depletion

¹S. Chapman, Mem. R. Meteorol. Soc. 3, 103 (1930)

- ✘ Until recently, the best available Potential Energy Surfaces included a spurious reef feature along the Minimum Energy Path for formation causing a large discrepancy between observed and calculated rates of exchange and formation. Still no experimental rovibrational spectra of ozone and its isotopologues exist for energies beyond 8000 cm^{-1} above the ZPE.
- ☞ The highest lying bound states and resonances are thought to be an important part of the still unexplained anomalous fractionation of heavier isotopologues. We expect that our new accurate Potential Energy Surface without a reef feature will help explain the spectroscopy, kinetics and dynamics.

- ✕ For the past three decades, the **ozone isotopic anomaly** has been a major research interest for various groups around the world.
- 👉 Its description requires, amongst other things, an adequate account of the vibrational states just below (bound) and above (resonances) the dissociation threshold.
- 📎 In particular, the **thermal rate constants** needed for the ozone **exchange** and **recombination** rates can be expressed using the resonances positions and widths from the formula²:

$$Q_r(\alpha)k_{rec}(T|\alpha) = \sum_J(2J+1)\sum_n \frac{\Gamma_n^\alpha(J)\omega}{\omega + \Gamma_n(J)} e^{-E_n(J)/k_B T} \quad (1)$$

²T.C. Germann and W.H. Miller, J. Chem. Phys. 101, 6358 (1997)

- 1 Ozone Ground State PES
- 2 Vibrational Bound states of $^{16}\text{O}_3$
- 3 Resonances of $^{16}\text{O}_3$ ($J = 0$)
- 4 Conclusion – Perspectives

Ozone Ground State PES

Previous calculations:

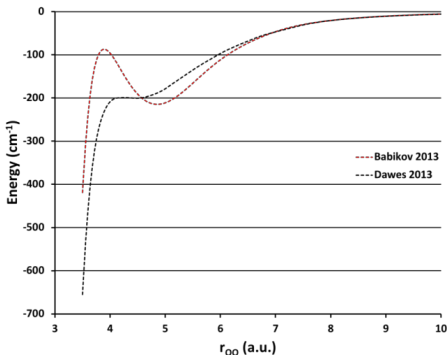
- Siebert, Schinke and Bitterova (SSB) PES in 2002 at the MRCI/VQZ from a one state CASSCF calculation using a (12e,9o) active space.
- Ayouz and Babikov PES in 2013 for a one state CASSCF calculation using (12e,9o) active space at the MRCI/CBS limit.
- Tyuterev *et al* spectroscopic PES using a one-state Davidson corrected MRCI data with full-valence (18e,12o) CASSCF reference combining data from the AV5Z with extrapolated CBS(5,6) data. A "**Dawes correction**" to remove the reef feature improved agreement with experiment for the highest lying levels.

"New Calculation" (Dawes *et al* 2011, 2013):

- Full valence **dynamically weighted state-averaged** CASSCF (DW-SA-CASSCF) (20 singlet states included)
- **MRCI-F12/VQZ-F12** (explicitly correlated method) are used to produce data without CBS extrapolation.
- The long-range (electrostatic) interaction model of Lepers *et al* used to describe the long-range part of the PES.
- Spin-orbit coupling correction added to the surface.

The "new" ozone PES, possesses 4 features that makes it suitable for dynamics calculations:

- Excellent equilibrium structural parameters:
 $r_e = 2.4031 \text{ a.u.}$, $\theta_e = 116.84^\circ$
(Expt: 2.4052 a.u. and 116.75°)
- Good agreement with experimental vibrational levels (as we will show later)
- Accurate dissociation energy
 $D_e = 9253 \text{ cm}^{-1}$ (Expt: $9219 \pm 10.0 \text{ cm}^{-1}$)
- Transition region with accurate topography (without a spurious reef)



Vibrational Bound states of $^{16}\text{O}_3$

The bound vibrational states of $^{16}\text{O}_3$ up to dissociation have been computed with the RTR3D and MCTDH codes.

RTR3D (One well and three wells calculations)

- Hamiltonian in Jacobi coordinates
- DVR calculations with **symmetry adapted rovibrational basis functions** using (400×400) Sine or PO-DVR functions for the R and r direction, and 150 Legendre or Shared-K functions for the θ direction.
- Parallel symmetry adapted Lanczos diagonalisation were carried on a basis of up to **65 million functions** in order to check convergence.

MCTDH (One well calculation)

- Hamiltonian written either in Valence or Jacobi coordinates
- DVR calculations using (256×256) Sine DVR functions for the r 's directions, and 128 Legendre or extended Legendre DVR functions for the θ direction.
- Block improved relaxation (wavepacket propagation of a block of wavefunctions in imaginary time) of 12 eigenstates on an optimized basis of about **60000 functions**.

Table: First 40 vibrational levels of $^{16}\text{O}_3$ ($J = 0$) in cm^{-1} .

N Γ	(v_1, v_2, v_3)	Lanczos	MCTDH	O-L	N Γ	(v_1, v_2, v_3)	Lanczos	MCTDH	O-L
1A	(0,0,0)	1451.49 ³	1451.49	-7.97	14A	(1,3,0)	3150.60	3150.60	23.33
2A	(0,1,0)	695.17	695.18	5.76	8B	(2,0,1)	3184.95	3184.95	1.87
1B	(0,0,1)	1048.81	1048.80	-6.72	15A	(3,0,0)	3269.04	3269.04	20.89
3A	(1,0,0)	1096.95	1096.95	6.19	16A	(0,2,2)	3393.33	3393.34	-2.41
4A	(0,2,0)	1387.64	1387.64	11.63	17A	(0,5,0)	3444.49	3444.49	33.5
2B	(0,1,1)	1727.98	1727.98	-1.24	9B	(1,2,1)	3447.91	3447.91	7.91
5A	(1,1,0)	1784.38	1784.38	11.87	18A	(2,2,0)	3544.02	3544.02	24.05
6A	(0,0,2)	2069.27	2069.27	-11.38	10B	(0,1,3)	3709.88	3709.88	-11.12
7A	(0,3,0)	2077.07	2077.07	17.92	19A	(1,1,2)	3742.80	3742.80	3.37
3B	(1,0,1)	2111.72	2111.72	-0.94	11B	(0,4,1)	3744.97	3744.97	15
8A	(2,0,0)	2188.37	2188.37	12.79	20A	(1,4,0)	3828.46	3828.46	30.5
4B	(0,2,1)	2404.06	2404.06	3.88	12B	(2,1,1)	3843.77	3843.77	6.14
9A	(1,2,0)	2468.96	2468.97	17.62	21A	(3,1,0)	3940.67	3940.67	26.02
10A	(0,1,2)	2733.35	2733.35	-7.24	22A	(0,0,4)	4020.20	4020.20	-18.89
11A	(0,4,0)	2762.92	2762.92	25.0	13B	(1,0,3)	4035.09	4035.09	13.24
5B	(1,1,1)	2781.70	2781.70	3.54	23A	(0,3,2)	4048.77	4048.77	2
12A	(2,1,0)	2867.64	2867.64	18.54	14B	(1,3,1)	4109.88	4109.88	12.19
6B	(0,0,3)	3061.11	3061.11	-15.02	24A	(0,6,0)	4122.43	4122.43	42
7B	(0,3,1)	3076.31	3076.31	9.91	25A	(2,0,2)	4149.75	4149.75	-8.33
13A	(1,0,2)	3090.44	3090.44	-6.74	26A	(2,3,0)	4217.23	4217.24	29.5

The RMSE for the first 40 states is 11.0 cm^{-1} and 21.0 cm^{-1} for the first 120 (6500 cm^{-1} above the ZPE).

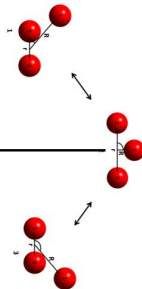
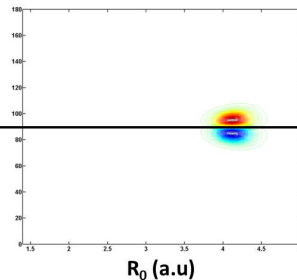
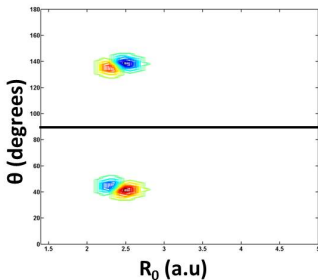
³Zero Point Energy in cm^{-1}

Ozone belongs to the $C_{3v}(M)$ symmetry group. However, in our calculations we apply C_{2v} symmetry operations to the wavefunctions.

C_{3v}	E	$2C_3(z)$	$3\sigma_v(xz)$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

This symmetry operation allows to discriminate the eigenstates of the C_{2v} symmetry which are equivalent to the A_1 , A_2 and E (doubly degenerate) representations of the $C_{3v}(M)$ group.

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1



Level	A	B
1	1451.46266	1451.46469
2	1451.46469	2146.62959
3	2146.62919	2500.25681
4	2146.62959	2500.25744
5	2500.25744	2548.40380
6	2548.40044	2839.09063
7	2548.40380	3179.42685
8	2839.09063	3179.42712
9	2839.09156	3235.82998

Diagram labels: A₁ (blue arrow), A₂ (green arrow), E (red arrow)

Table: Last 40 A₁ and 20 A₂ states^{abc}.

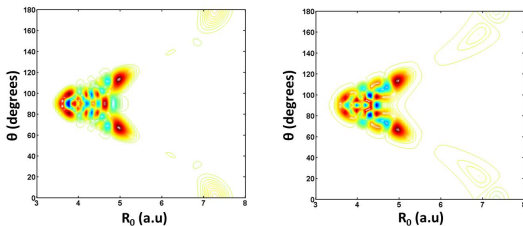
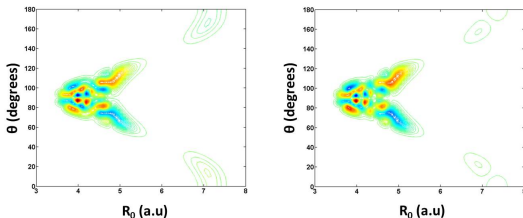
A ₁ states				A ₂ states	
N Γ	Lanczos	N Γ	Lanczos	N Γ	Lanczos
121A	8029.82	141A	8463.05	106B	8398.28
122A	8053.95	142A	8479.68	107B	8416.10
123B	8066.16	143A	8494.16	108B	8478.49
124A	8116.71	144A	8515.02	109B	8488.62
125A	8138.68	145A	8518.40	110B	8516.00
126A	8141.18	146A	8533.91	111B	8522.48
127A	8149.74	147A	8540.11	112B	8530.97
128A	8179.33	148A	8543.56	113B	8536.33
129A	8189.67	149A	8560.71	114B	8539.32
130A	8225.43	150A	8565.73	115B	8541.19
131A	8232.70	151A	8573.61	116B	8551.37
132A	8257.23	152A	8576.86	117B	8559.42
133A	8309.86	153A	8584.42	118B	8567.87
134A	8317.19	154A	8589.17	119B	8575.78
135A	8357.42	155A	8593.93	120B	8583.92
136A	8369.55	156A	8595.40	121B	8588.79
137A	8379.62	157A	8601.99	122B	8593.34
138A	8428.14	158A	8608.39	123B	8598.75
139A	8439.06	159A	8608.56	124B	8603.77
140A	8446.92	160A	8613.65	125B	8613.23

- $D_0 = 8615 \text{ cm}^{-1}$.
- 160 and 125 states of A₁ and A₂ symmetry respectively.
- Near numerical degeneracy of A and E states close to the bottom of the well, lifted with increasing energy due to the tunneling.
- No Van der Waal states as observed in the previous works
- Close to dissociation we identify about 1 vibrational state every 3 cm^{-1} . We converged several more bound states than were found on the 2002 SSB PES.

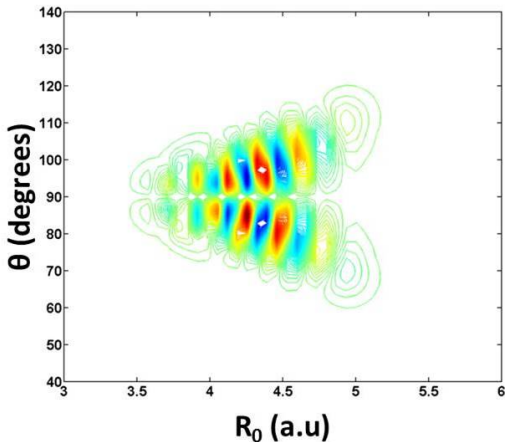
^aGrebenschchikov et al., J. Chem. Phys., 119, 6512 (2003).

^bLee and Light, J. Chem. Phys., 120, 5859 (2004)

^cBabikov et al., J. Chem. Phys., 119, 2577 (2003)

Figure: Two highest A_1 statesFigure: Two highest A_2 states

(0,11,1)
8319.57 cm^{-1}



Resonances of $^{16}\text{O}_3$ ($J = 0$)

There are 3 common methods to determine resonances positions and widths in quantum systems:

- The **complex coordinate rotation** method and its variants ($r \rightarrow re^{i\theta}$)
- The **stabilization** method (box size R_{max} varied)
- The **complex absorbing potential** (CAP) method (complex potential added to the Hamiltonian): $\hat{H} = \hat{H}_0 - i\lambda W(R)$.

We combined the **stabilization** and the **CAP methods** with the MCTDH package to obtain our resonances.

The calculation proceeds in two steps:

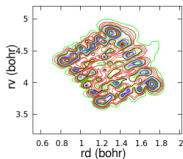
- ➔ First a Block Improved Relaxation with a **blocking potential** is done on a set (12 states) and converged states are identified. The blocking potential simulate a change of the box size when his strength (slope is varied).
- ➔ The second step consists in performing Improved relaxation calculation with a CAP, starting from the selected **stable** and **converged** wavefunctions from the Block Improved Relaxation. The wavefunctions shall then converge (or at least oscillate) around the correct values.

(v_1, v_2, v_3)	Position	Width	Lifetime
(5,5,0)	8653.5	0.588	56.7
(?, ?, ?)	8685.4	0.041	813.0
(7,2,0)	8760.3	0.076	438.6
(?, ?, ?)	8791.9	0.072	463.0
(?, ?, ?)	8795.3	0.416	80.1
(?, ?, ?)	8805.6	0.246	135.5
(0,13,0)	8810.8	0.809	41.2
(0,0,10)	8835.3	1.227	27.2
(?, ?, ?)	8909.6	0.282	118.2
(?, ?, ?)	8947.7	1.246	26.8
(0,12,1)	8960.3	1.765	18.9
(?, ?, ?)	9158.1	0.017	1960.8
(?, ?, ?)	9560.2	0.021	1587.3
(?, ?, ?)	9562.4	29.282	1.1

Table: Resonances and widths of $^{16}\text{O}_3$ ($J = 0$)
 in cm^{-1} , lifetime in ps. $D_0 = 8615 \text{ cm}^{-1}$.

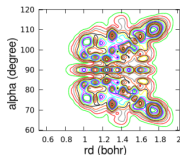
$$E = 8653 \text{ cm}^{-1}$$

$$\Gamma = 0.588 \text{ cm}^{-1}$$



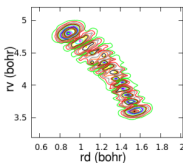
$$E = 8795 \text{ cm}^{-1}$$

$$\Gamma = 0.416 \text{ cm}^{-1}$$



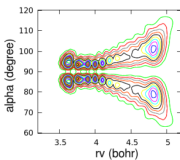
$$E = 8810 \text{ cm}^{-1}$$

$$\Gamma = 0.809 \text{ cm}^{-1}$$



$$E = 8960 \text{ cm}^{-1}$$

$$\Gamma = 1.765 \text{ cm}^{-1}$$



Conclusion and Perspectives

- We computed all the bound vibrational states of $^{16}\text{O}_3$ for $J = 0$ and $J = 1$ (RTR3D and MCTDH) in the one well and three wells cases.
- We are able to discriminate up to the dissociation A_1 and A_2 states.
- A method/process is built to compute resonances of O_3 (and maybe other polyatomic molecules) with MCTDH which proceeds by a **stabilization** and **CAP** calculation.
- Results suggest that ozone possesses numerous resonances with lifetimes ranging from the picosecond to the nanosecond.

Further works:

- ✎ Calculation of resonances for higher J (work in progress) and other isotopologues in order to characterize the **isotopic exchange and recombination rates** of ozone.
- ✎ The MCTDH approach is a powerful method for higher dimensionality systems; the technique presented for the calculation of resonances may be conveniently applied for such systems.

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- Prof Dr Hans-Dieter Meyer @Universität Heidelberg and Dr Fabien Gatti @Université de Montpellier 2 (MCTDH)
- Dr Richard Dawes @Missouri S&T (RTR3D calculations and Project Leader)

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