Isotopically invariant Dunham fit for the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states of oxygen

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Project procedures and goals

- Carry out band-band fit for all data to check bad measurements and misassignments
- Fit all $^{16}O_2$ data with the Dunham model (including highly accurate MW transitions) for $X^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+$ and $B^3\Sigma_u^-$
  - Extrapolate rotational energies for unobserved vibrational levels
  - Provide predictions for unobserved bands
- Employ mass relationship to add minor isotopologue data to the fit
  - Determine Born-Oppenheimer breakdown parameters
  - Provide predictions for unobserved isotopologue bands
- Derive potentials from obtained parameters

Low-lying electronic states of O_2 below 6.1 eV

Transition	Designation	0-0(cm^{-1})
$A^3\Sigma_u^+ - X^3\Sigma_g^-$	Herzberg I	35010
* $A'^3\Delta_u - X^3\Sigma_g^-$	Herzberg III	34387
* $A'^3\Delta_u - a^1\Delta_g$	Chamberlain	26346
$c^1\Sigma_u^- - X^3\Sigma_g^-$	Herzberg II	32665
$c^1\Sigma_u^- - a^1\Delta_g$		24776
$c^1\Sigma_u^- - b^1\Sigma_g^+$		19543
* $b^1\Sigma_g^+ - X^3\Sigma_g^-$	Atmospheric	13122
* $b^1\Sigma_g^+ - a^1\Delta_g$	Noxon	5233
* $a^1\Delta_g - X^3\Sigma_g^-$	IR Atmospheric	7889

* $B^3\Sigma_u^- - X^3\Sigma_g^-$ Schumann-Runge 49356
($B^3\Sigma_u^-$ not shown in the figure)

* Systems included in our fit

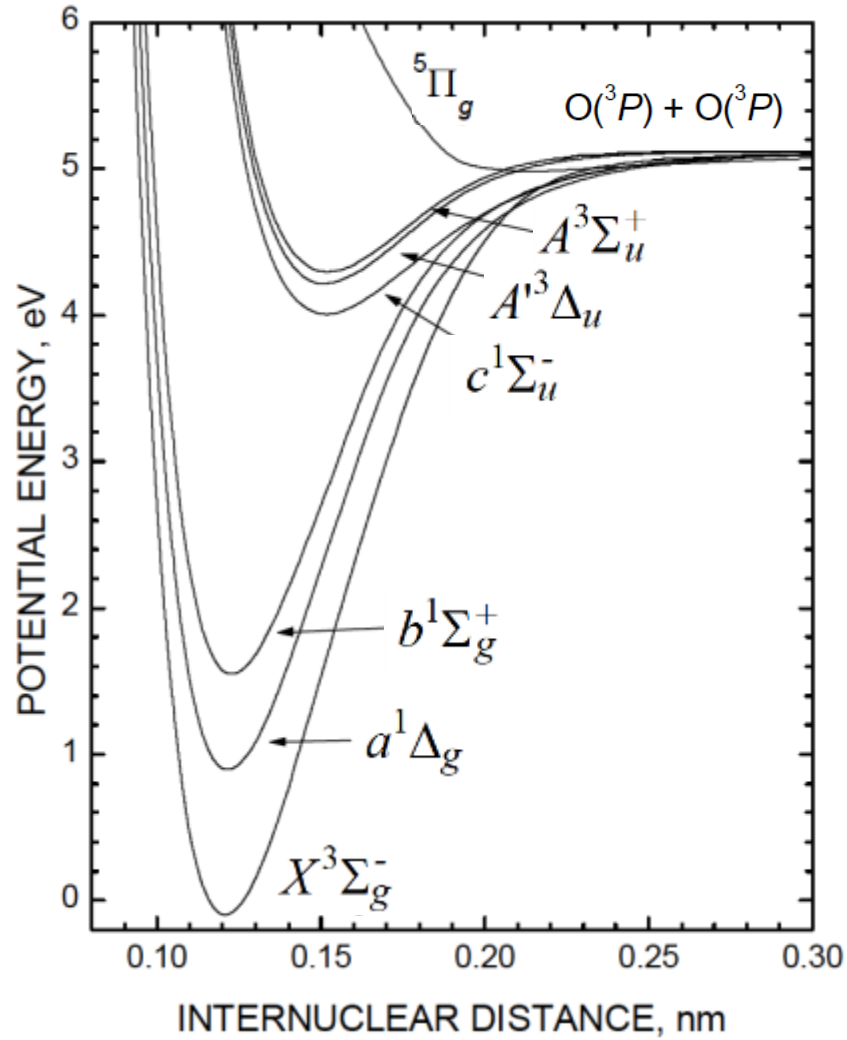
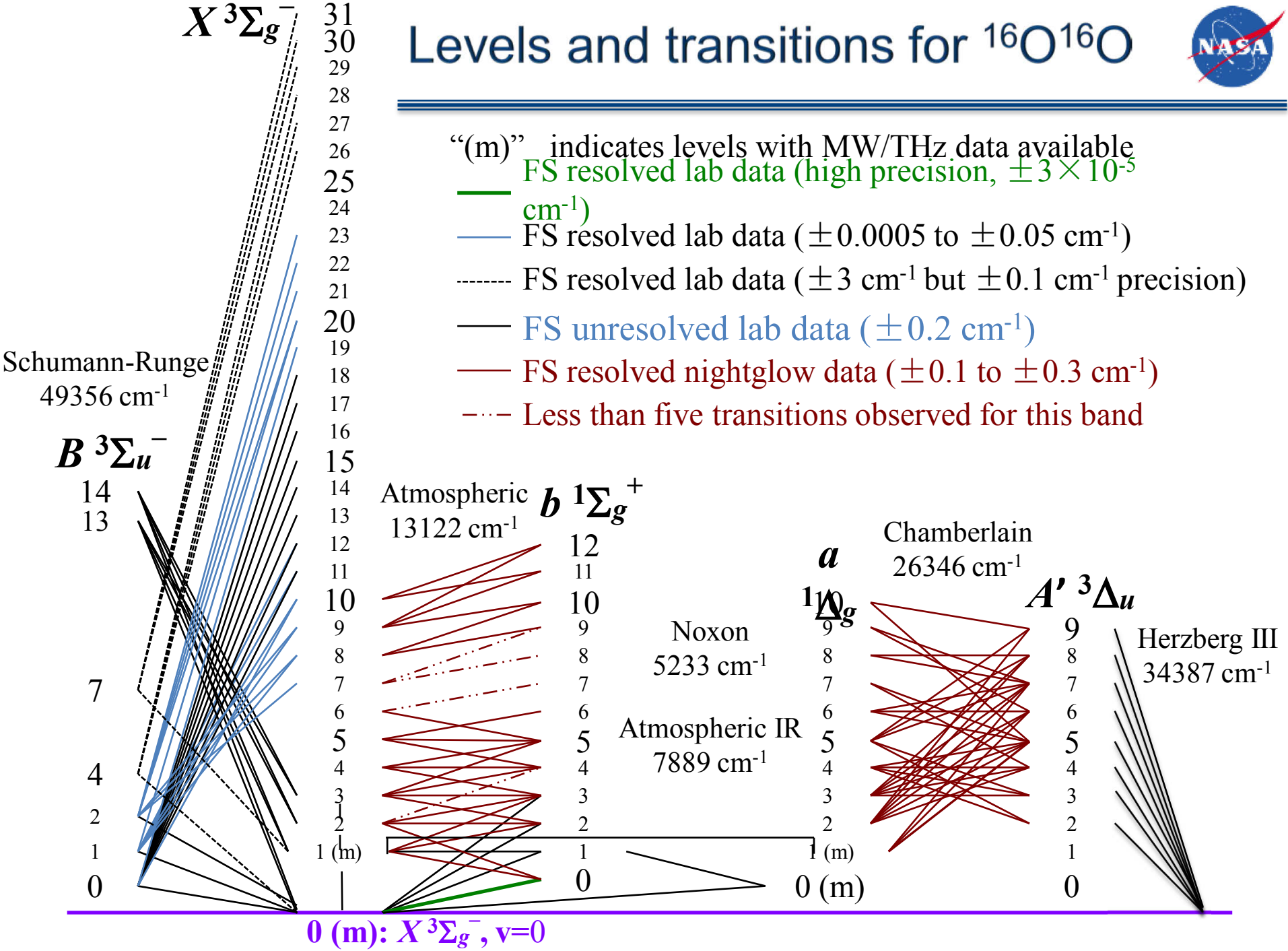
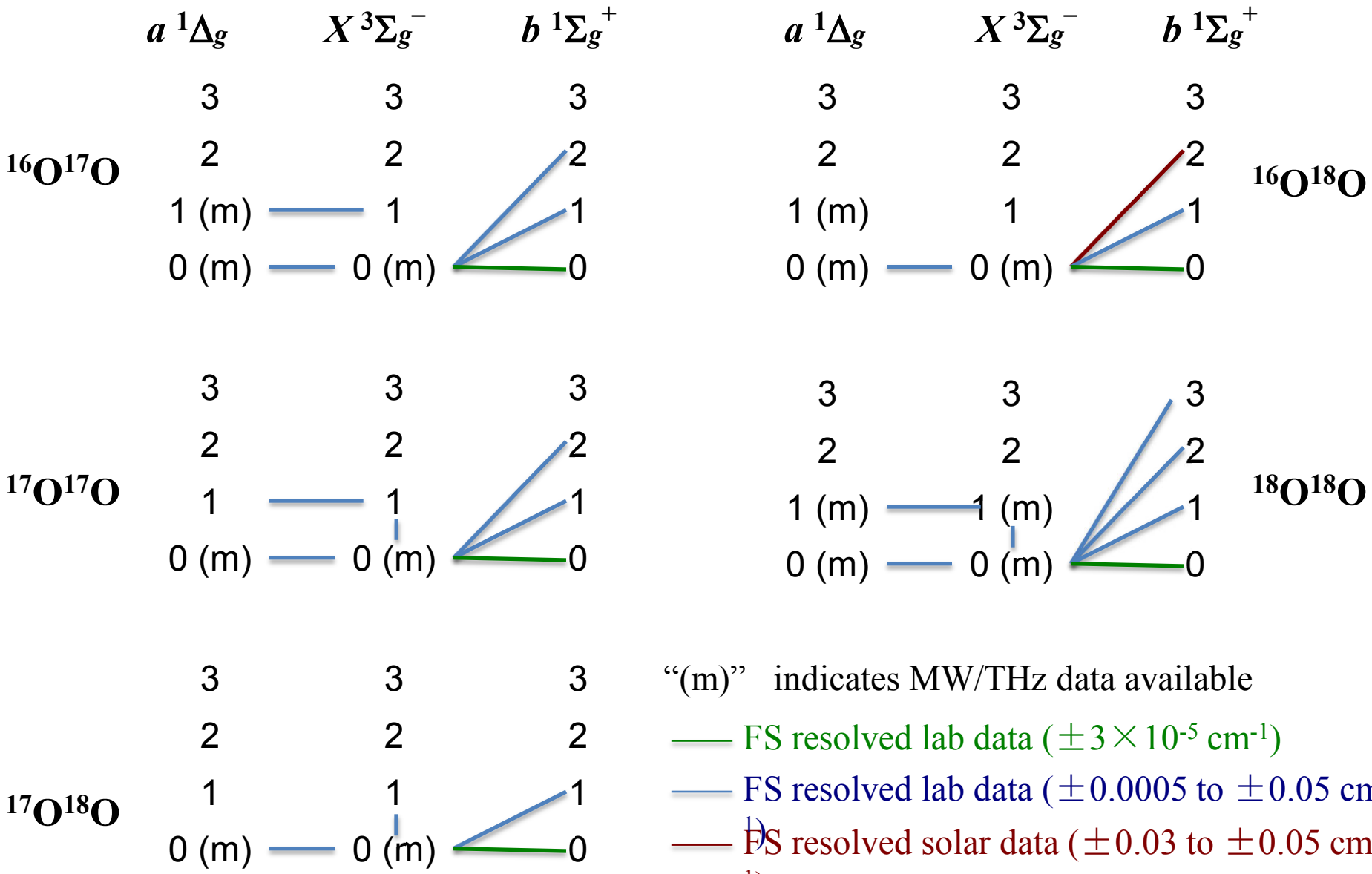


Figure and table taken from Slanger et al. Chem. Rev. 103, 4733 (2003)

Levels and transitions for $^{16}O^{16}O$



Levels and transitions for minor isotopologues



SPFIT Vibrational quantum numbers

- $^{16}O^{16}O$
  - 5 electronic states; v=0-39 for the ground state and v=0-29 for other four electronic states
  - Total 160 vibrational quanta
  - Total 7718 transitions collected for these states
- Five minor isotopologues
  - 3 electronic states; v=0-29 for each electronic state
  - Total 450 vibrational quanta
  - Total 4226 transitions collected for these states

		$^{16}O^{16}O$	$^{16}O^{17}O$	$^{16}O^{18}O$	$^{17}O^{17}O$	$^{17}O^{18}O$	$^{18}O^{18}O$
$X\,^3\Sigma_g^-$	V=0-39	0-39	300-339	400-439	500-539	600-639	700-739
$a\,^1\Delta_g$	V=0-29	40-69	340-369	440-469	540-569	640-669	740-769
$b\,^1\Sigma_g^+$	V=0-29	70-99	370-399	470-499	570-599	670-689	770-799
$B\,^3\Sigma_u^-$	V=0-29	100-129					
$A'\,^3\Delta_u$	V=0-29	130-159					

Hamiltonian

- For $X^3\Sigma_g^-$, $b^1\Sigma_g^+$ and $B^3\Sigma_u^-$

$$\mathbf{H} = T_e + G_v + B_v\mathbf{N}^2 + D_v(\mathbf{N}^2)^2 + H_v(\mathbf{N}^2)^3 + [\lambda_v + \lambda_{Dv}\mathbf{N}^2 + \lambda_{Hv}(\mathbf{N}^2)^2]\tfrac{2}{3}(3S_z^2 - \mathbf{S}^2) + [\gamma_v + \gamma_{Dv}\mathbf{N}^2 + \gamma_{Hv}(\mathbf{N}^2)^2]\mathbf{N}\cdot\mathbf{S} + b_{Fv}\mathbf{I}\cdot\mathbf{S} + c_v\left(I_zS_z - \tfrac{1}{3}\mathbf{I}\cdot\mathbf{S}\right) + eQq_v\frac{(3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + C_{Iv}\mathbf{I}\cdot\mathbf{N}$$

- For $a^1\Delta_g$ and $A'^3\Delta_u$

$$\mathbf{H} = T_e + G_v + B_v(\mathbf{N}^2 - \mathbf{L}^2) + D_v(\mathbf{N}^2 - \mathbf{L}^2)^2 + H_v(\mathbf{N}^2 - \mathbf{L}^2)^3 + a_vI_zL_z + eQq_v\frac{(3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + C_{Iv}\mathbf{I}\cdot\mathbf{N}$$

Dunham-type expansions

- Rotational parameters are expanded in ($N(N+1)$ - l^2)

$$T_e = U^{Te}\left(\frac{1}{\mu}\right)^{0} + U^{Te}\Delta^{Te,O} m_e \left(\frac{1}{\mu}\right)^{1}$$

$$Y_{l,m} = \sum_{l=1}\left(U_{l,m}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+m} + U_{l,m}\Delta^{O}_{l,m} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+m}\right)$$

$$X_{l,m} = U^{X}_{l,m}\left(\frac{1}{\mu}\right)^{\frac{l}{2}+m} + U^{X}_{l,m}\Delta^{X,O}_{l,m} m_e \left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+m}, \text{ with } X = \lambda, a, b_F, c, eQq$$

$$X_{l,m} = U^{X}_{l,m}\left(\frac{1}{\mu}\right)^{1+\frac{l}{2}+m} + U^{X}_{l,m}\Delta^{X,O}_{l,m} m_e \left(\frac{1}{\mu}\right)^{2+\frac{l}{2}+m}, \text{ with } X = \gamma, C_I$$

	Mass(u)	
^{16}O	15.994 914 619 56(16)	AME2003
^{17}O	16.999 131 756 6(9)	Phys. Rev. A 81, 064501 (2010)
^{18}O	17.999 159 613 0(13)	Phys. Rev. A 79, 012507 (2009)

Obtained $U_{l,0}$ (MHz) for $^{16}O_2$

	$X^3\Sigma_g^-$ (V_{max}=31)	$a^1\Delta_g$ (V_{max}=10)	$b^1\Sigma_g^+$ (V_{max}=12)
$U^{T_e} \times \mu^{-0.0}$		237577161(52)	395594904(149)
$U^{T_e}\Delta^{T_e,O} m_e \times \mu^{-1.0}$		9100(66)	25556(149)
$U_{1,0} \times \mu^{-0.5}/2$	23683150(166)	22624892(173)	21473929(68)
$U_{1,0}\Delta_{1,0}^{O} m_e \times \mu^{-1.5}/2$	2009(165)	1905(171)	1590(60)
$U_{2,0} \times \mu^{-1.0}/4$	-89298.8(67)	-98029.5(229)	-104798.0(75)
$U_{3,0} \times \mu^{-1.5}/8$	137.94(99)	63.28(217)	25.09(81)
$U_{4,0} \times \mu^{-2.0}/16$	-1.591(56)	-3.436(61)	-4.5355(226)
$U_{5,0} \times \mu^{-2.5}/32$	6.31(134)E-03		
$U_{6,0} \times \mu^{-3.0}/64$	-0.2165(114)E-03		

Obtained $U_{l,1}$, $U_{l,2}$, $U_{l,3}$ (MHz) for $^{16}O_2$

	$X^3\Sigma_g^-$ (V_{max}=31)	$a^1\Delta_g$ (V_{max}=10)	$b^1\Sigma_g^+$ (V_{max}=12)
$U_{0,1} \times \mu^{-1.0}$	43343.5117(110)	42766.1783(198)	41988.2188(256)
$U_{0,1}\Delta_{0,1}^{O} m_e \times \mu^{-2.0}$	-5.1592(91)	-5.6158(165)	-6.1443(213)
$U_{1,1} \times \mu^{-1.5}/2$	-238.2546(158)	-255.8725(282)	-273.320(36)
$U_{2,1} \times \mu^{-2.0}/4$	0.3600(39)	-0.1679(70)	-0.1302(105)
$U_{3,1} \times \mu^{-2.5}/8$	-0.015555(271)		-0.01875(56)
$U_{4,1} \times \mu^{-3.0}/16$	0.4723(73)E-03		
$U_{5,1} \times \mu^{-3.5}/32$	-6.602(62)E-06		
$U_{0,2} \times \mu^{-2.0}$	-0.1450753(43)	-0.1526375(167)	-0.1604358(59)
$U_{1,2} \times \mu^{-2.5}/2$	-0.0515(48)E-03	-0.3310(166)E-03	-0.5031(49)E-03
$U_{2,2} \times \mu^{-3.0}/4$	0.01241(112)E-03		
$U_{3,2} \times \mu^{-3.5}/8$	-0.5865(226)E-06		
$U_{0,3} \times \mu^{-3.0}$	-1.34E-09[a]	-0.0652E-06[a]	-0.135E-06[a]
$U_{1,3} \times \mu^{-3.5}/2$	4.52(73)E-09		

Obtained U^{λ} and U^{γ} (MHz) for $^{16}O_2$

	$X^3\Sigma_g^-$ (V_{max}=31)		$X^3\Sigma_g^-$ (V_{max}=31)
$4 \times U_{0,0}^{\lambda} \times \mu^{-0.0}$	237726.55(40)	$U_{0,0}^{\gamma} \times \mu^{-1.0}$	-252.28822(55)
$4 \times U_{0,0}^{\lambda} \Delta_{0,0}^{\lambda,O} m_e \times \mu^{-1.0}$	31.328(109)	$U_{0,0}^{\gamma} \Delta_{0,0}^{\gamma,O} m_e \times \mu^{-2.0}$	8.31(60)E-03
$4 \times U_{1,0}^{\lambda} \times \mu^{-0.5}/2$	226.24(89)	$U_{1,0}^{\gamma} \times \mu^{-1.5}/2$	-0.306488(52)
$4 \times U_{2,0}^{\lambda} \times \mu^{-1.0}/4$	23.89(46)	$U_{0,1}^{\gamma} \times \mu^{-2.0}$	.243777(283)E-03
$4 \times U_{3,0}^{\lambda} \times \mu^{-1.5}/8$	-2.661(79)	$U_{0,2}^{\gamma} \times \mu^{-3.0}$	-1.113(210)E-09
$4 \times U_{4,0}^{\lambda} \times \mu^{-2.0}/16$	0.05798(124)		
$4 \times U_{0,1}^{\lambda} \times \mu^{-1.0}$	0.21107(39)		
$4 \times U_{1,1}^{\lambda} \times \mu^{-1.5}/2$	0.02681(54)		
$4 \times U_{2,1}^{\lambda} \times \mu^{-2.0}/4$	-4.500(142)E-03		
$4 \times U_{0,2}^{\lambda} \times \mu^{-2.0}$	1.064(62)E-06		
$4 \times U_{0,3}^{\lambda} \times \mu^{-3.0}$	0.086(39)E-09		

Obtained HFS constants (MHz) for $^{16}O^{17}O$

	$X^3\Sigma_g^-$ (V_{max}=31)	$a^1\Delta_g$ (V_{max}=10)	$b^1\Sigma_g^+$(V_{max}=12)
$U_{0,0}^{a} \times \mu^{-0.0}$		-211.9276(282)	
$U_{0,0}^{b_F} \times \mu^{-0.0}$	-54.74913(209)		
$U_{0,0}^{c} \times \mu^{-0.0}$	140.0610(55)		
$1.5 \times U_{0,0}^{eQq} \times \mu^{-0.0}$	-12.317(57)	-12.398(282)	
$U_{0,0}^{C_I} \times \mu^{-1.0}$	-0.01753(93)	-0.01967(137)	

$$a_v I_z L_z$$

$$b_{Fv}\mathbf{I}\cdot\mathbf{S} + c_v\left(I_z S_z - \tfrac{1}{3}\mathbf{I}\cdot\mathbf{S}\right) + eQq_v\frac{(3I_z^2 - \mathbf{I}^2)}{4I(2I-1)} + C_{Iv}\mathbf{I}\cdot\mathbf{N}$$

Fit statistics on $^{16}O^{16}O$ *b-X* lab data

Reference	# bad lines	# good lines	*N'*	Unc. (cm^{-1})	rms(cm^{-1})	σ_{rms}	AVG (cm^{-1})
(0,0) Cheah et al (2000)[a]	61	6	0-30	NA	0.003	0.595	-0.001
(0,0) Brown et al (2000)[a]	44	0	0-22	0.0015	0.001	0.820	0.000
(0,0) O'Brien et al (2001)	36	2	22-40	0.002	0.006	1.146	0.003
(0,0) van Leeuwen (2004)	12	0	34-44	0.02	0.011	0.558	-0.008
(0,0) Robichaud et al (2008)	32	0	2-30	(1.8-9.0)E-5	0.000	0.551	0.000
(0,0) Predoi-Cross (2008)[a]	56	0	1-27	0.0001	0.000	1.089	0.000
(1,0) Cheah et al (2000)	58	1	0-30	NA	0.009	0.892	-0.001
(1,0) Domyslawska (2012)	12	0	7-25	(3.0-10.0)E-5	0.000	1.378	0.000
(2,0) Naus et al (1999)	49	0	0-26	0.01	0.009	0.904	0.001
(2,0) Cheah et al (2000)	44	1	0-24	NA	0.012	1.200	0.008
(3,0) Biennier et al (1998)	43	1	0-24	0.01	0.013	1.204	0.005
(3,0) Naus et al (1999b)	42	0	0-22	0.007	0.011	1.582	-0.009

[a] Re-calibrated based on Robichaud et al (2008)

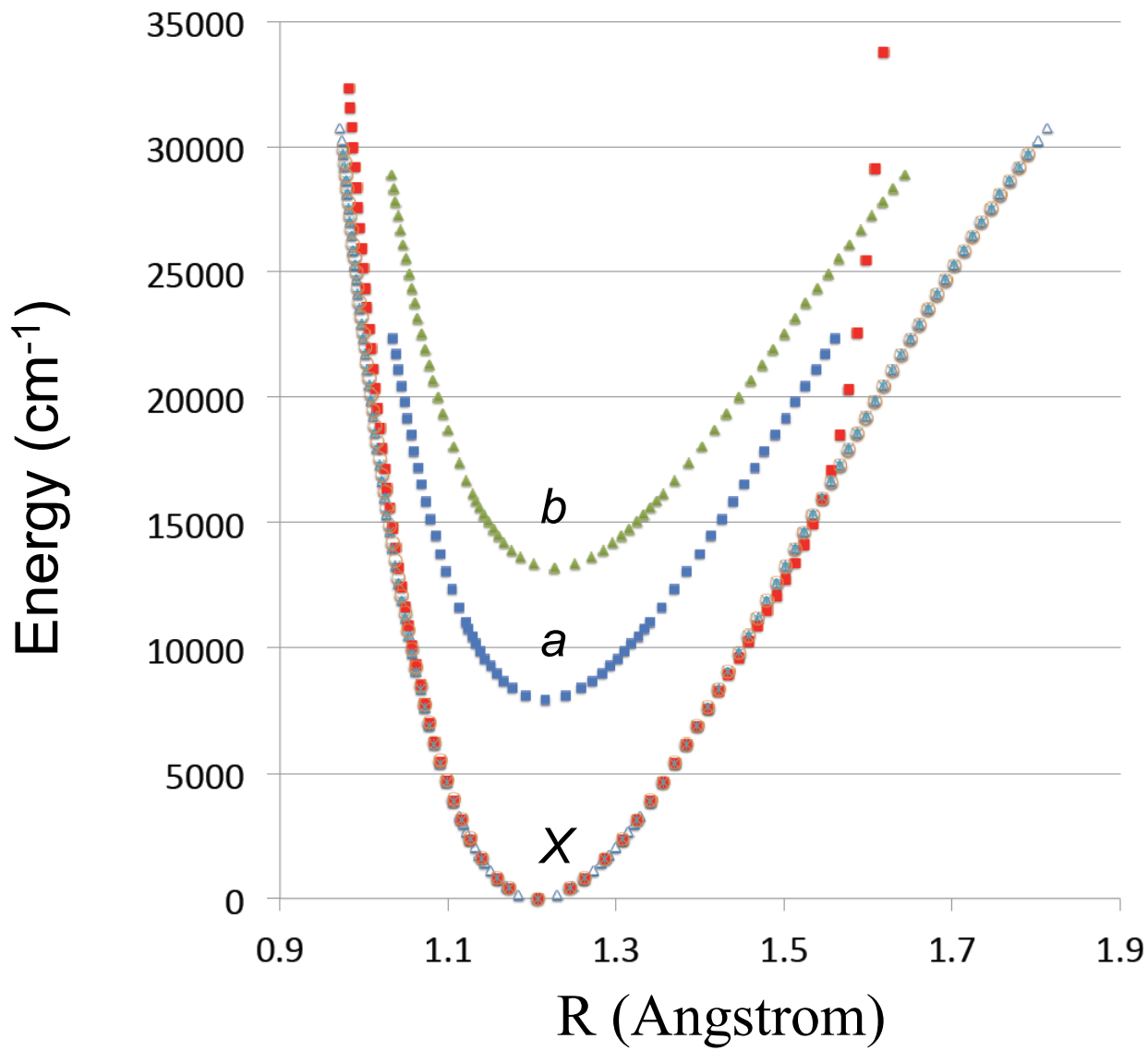
Fit statistics on Edwards et al., 1976, 1978,1981

Band	# bad lines	# good lines	N'	σ_{rms}	rms(cm^{-1})	AVG (cm^{-1})	P (Torr)	Shift (cm^{-1})
$^{16}O^{17}O$ 0-0	4	50	3-20	1.767	0.009	0.002	300	
$^{16}O^{18}O$ 0-0	4	43	3-20	2.381	0.012	-0.009	750	
$^{17}O^{17}O$ 0-0	4	53	3-21	1.788	0.009	-0.002	300	
$^{18}O^{18}O$ 0-0	2	42	3-31	1.630	0.008	0.000	750	
$^{16}O^{16}O$ 1-0	1	69	1-19	0.911	0.014	-0.010	550	
$^{17}O^{17}O$ 1-0	3	61	1-13	2.230	0.033	-0.031	550	
$^{17}O^{18}O$ 1-0	75	0	1-17	12.290	0.184	0.182	550	
$^{18}O^{18}O$ 1-0	6	70	1-19	1.027	0.015	0.006	550	

Derived BOB parameters (MHz) and r_e(Å)

	$X^3\Sigma_g^-$ (V_{max}=31)	$a^1\Delta_g$ (V_{max}=10)	$b^1\Sigma_g^+$ (V_{max}=12)
$\Delta^{Te,O}$	…	0.5584(40)	0.9418(55)
$\Delta^{O}_{1,0}$	1.24(10)	1.23(11)	1.079(41)
$\Delta^{O}_{0,1}$	-1.7353(31)	-1.9144(56)	-2.1333(74)
$\Delta^{\lambda,O}_{0,0}$	1.9212(67)		
$\Delta^{\gamma,O}_{0,0}$	-0.480(35)		
r_e^{BO} (Å)	1.20745398(15)	1.21557683(28)	1.22678627(37)
$^{16}O^{16}O$ r_e (Å)	1.20752763(17)	1.21565347(30)	1.22687500(38)
$^{16}O^{17}O$ r_e (Å)	1.20752545(17)	1.21565121(29)	1.22687238(38)
$^{16}O^{18}O$ r_e (Å)	1.20752353(17)	1.21564920(29)	1.22687006(37)
$^{17}O^{17}O$ r_e (Å)	1.20752328(17)	1.21564894(29)	1.22686976(37)
$^{17}O^{18}O$ r_e (Å)	1.20752135(16)	1.21564694(29)	1.22686744(37)
$^{18}O^{18}O$ r_e (Å)	1.20751943(16)	1.21564494(29)	1.22686512(37)

Derived potentials for $^{16}O_2$



Problem with Dunham potential

- X This work RKR
- X this work Dunham
- X Krupenie 1972 RKR
- X Bytautas 2010 ab initio
- a This work RKR
- b This work RKR

Conclusions

- 11 944 transitions collected and fitted for O_2 with a reduced RMS=1.1
- 65 independent parameters used to fit the $X^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+$ states (V_{max}=31, 10, 12 respectively, nuclear HFS included)
- $X^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+$ modeled well with Dunham model
- $A'^3\Delta_u, B^3\Sigma_u^-$ not modeled well with Dunham model; now modeled with band-by-band parameters
- High vibration excitation lab data needed to replace nightglow data for *b*-*X*
- *b*(1)-*X*(1) or a(0)-X(1) isotopologue transitions needed to clarify the existing problem fitting $^{17}O^{18}O$ *X*(1)-*X*(0) data

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Fit statistics on $^{16}O^{16}O$ ground state MW lab data

Reference	# bad lines	# good lines	N'	σ_{rms}	rms(MHz)	AVG (MHz)	P (Torr)
V=0, Endo et al., 1982	0	8	31-39	1.140	0.031	-0.031	
V=1 Endo et al., 1982	0	19	1-19	0.889	0.016	0.002	
V=0, Zink & Mizushima, 1987	1	4	5-15	2.063	0.185	0.116	
V=0 Brown et al., 1992 (CARS)	0	30	3-21	0.173	25.905	12.677	70
V=0, Park et al., 1996	1	1	9,15	0.395	0.015	0.015	
V=0, Golubiatnikov et al., 2003	0	8	3-7	1.221	0.024	-0.010	
V=0, Tretyakov et al., 2005	0	27	1-27	0.694	0.005	0.000	
V=0, Drouin et al., 2010	0	5	5-11	0.835	0.033	-0.017	

O_2 ground state $Y_{1,0}(V+1/2)$ expansion

Parameter Identifier	Parameter Value	Parameter Uncertainty	Comments
0	**23683467.0956274**	**1.00E+37**	**/$^{16}O^{16}O$ $Y_{1,0}$/2**
-1001	71050401.2868814	1.00E-37	/*3
-2002	118417335.4781370	1.00E-37	/*5
	...		
-300300	**23331072.4780496**	**1.00E-37**	**/$^{16}O^{17}O$ $Y_{1,0}$/2**
-301301	69993217.4341492	1.00E-37	/*3
	...		
-400400	**23014724.3513394**	**1.00E-37**	**/$^{16}O^{18}O$ $Y_{1,0}$/2**
-401401	69044173.0540186	1.00E-37	/*3
	...		
-500500	**22973272.9989080**	**1.00E-37**	**/$^{17}O^{17}O$ $Y_{1,0}$/2**
-501501	68919818.9967241	1.00E-37	/*3
	...		
-600600	**22651928.5332284**	**1.00E-37**	**/$^{17}O^{18}O$ $Y_{1,0}$/2**
-601601	67955785.5996850	1.00E-37	/*3
	...		
-700700	**22325959.3358630**	**1.00E-37**	**/$^{18}O^{18}O$ $Y_{1,0}$/2**
-701701	66977878.0075893	1.00E-37	/*3
	...		