Publication Year	2019
Acceptance in OA	2021-04-16T15:37:59Z
Title	Rotational and Rotational-Vibrational Raman Spectroscopy of Air to Characterize Astronomical Spectrographs
Authors	Vogt, Frédéric P. A., Kerber, Florian, Mehner, Andrea, Yu, Shanshan, Pfrommer, Thomas, Lo Curto, Gaspare, Figueira, Pedro, Parraguez, Diego, Pepe, Francesco A., Mégevand, Denis, RIVA, Marco, DI MARCANTONIO, Paolo, Lovis, Christophe, Amate, Manuel, MOLARO, Paolo, Cabral, Alexandre, Osorio, Maria Rosa Zapatero
Publisher's version (DOI)	10.1103/PhysRevLett.123.061101
Handle	http://hdl.handle.net/20.500.12386/30777
Journal	PHYSICAL REVIEW LETTERS
Volume	123

Rotational and ro-vibrational Raman spectroscopy of air to characterize astronomical spectrographs

SUPPLEMENTAL MATERIAL

Frédéric P. A. Vogt,[1,*] Florian Kerber,[2] Andrea Mehner,[1] Shanshan Yu,[3] Thomas Pfrommer,[2] Gaspare Lo Curto,[1] Pedro Figueira,[1,4] Diego Parraguez,[1] Francesco A. Pepe,[5] Denis Mégevand,[5] Marco Riva,[6] Paolo Di Marcantonio,[7] Christophe Lovis,[5] Manuel Amate,[8] Paolo Molaro,[7] Alexandre Cabral,[9] and Maria Rosa Zapatero Osorio[10]

[1]*European Southern Observatory (ESO), Av. Alonso de Córdova 3107, 763 0355 Vitacura, Santiago, Chile.*
[2]*European Southern Observatory (ESO), Karl-Schwarzschild-Str. 2, 85748 Garching, Germany.*
[3]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109, USA.*
[4]*Instituto de Astrofísica e Ciências do Espaço, Universidade do Porto, CAUP, Rua das Estrelas, 4150-762 Porto, Portugal.*
[5]*Observatoire Astronomique de l'Université de Genève, 51 chemin des Maillettes, 1290 Versoix, Switzerland.*
[6]*Osservatorio Astronomico di Brera, INAF, Via Bianchi 46, 23807 Merate, Italy.*
[7]*Osservatorio Astronomico di Trieste, INAF, Via Tiepolo 11, 34143 Trieste, Italy.*
[8]*Instituto de Astrofísica de Canarias, C/. Vía Láctea, 38200 La Laguna, Tenerife, Spain.*
[9]*Faculdade de Ciências, Instituto de Astrofísica e Ciências do Espaço, Universidade de Lisboa, Campo Grande, Edifício C8, 1749-016 Lisboa, Portugal.*
[10]*Centro de Astrobiología (CSIC-INTA), Carretera de Ajalvir km 4, Torrejón de Ardoz, 28850 Madrid, Spain.*
(Dated: April 18, 2019)

Rotational and ro-vibrational Raman line wavelengths for non-rigid singlet diatomic rotators

The vibro-rotational energy of a molecule, $E_n(J)$, for given vibrational quantum number n and rotational quantum number J, can be expressed as:

$$E_n(J) = G_n + F_n(J), \tag{A.1}$$

with G_n the vibrational component, and $F_n(J)$ the rotational component. Following [1], for diatomic molecules like $^{14}N_2$ with a $^1\Sigma$ electronic ground state or $^{16}O_2$ with a non-singlet electronic state but unresolved line splitting structure:

$$G_n \cong \omega_e(n+\frac{1}{2})-\omega_e X_e(n+\frac{1}{2})^2+\omega_e Y_e(n+\frac{1}{2})^3+\omega_e Z_e(n+\frac{1}{2})^4, \tag{A.2}$$

and

$$F_n(J) \cong B_n J(J+1) - D_n J^2(J+1)^2, \tag{A.3}$$

where

$$B_n \cong B_e - \alpha_e(n+\frac{1}{2}) + \gamma_e(n+\frac{1}{2})^2 \tag{A.4}$$

$$D_n \cong D_e + \beta_e(n+\frac{1}{2}) \tag{A.5}$$

The adopted form of $F_n(J)$ assumes that molecules are non-rigid rotators, and includes the vibrational stretching of the molecular bond driven by rotation. The parameters ω_e, $\omega_e X_e$, $\omega_e Y_e$, $\omega_e Z_e$, B_e, α_e, γ_e, D_e and β_e are molecular constants typically expressed in cm^{-1} (see Table I).We adopt the values of [2] for $^{16}O_2$, [3] for $^{14}N_2$, [4] for $^{14}N^{15}N$, and [5] for $^{14}N_2^+$.

The frequency shift of pure rotational Raman lines (with respect to the exciting frequency) associated with the elastic scattering of photons by non-rigid singlet diatomic molecules in their ground vibrational state ($n = 0$), separated in the Stokes and anti-Stokes branches, can thus be expressed as:

$$\begin{aligned}\Delta\nu_0|_{\text{Stokes}}(J) &= E_0(J+2) - E_0(J) \\ &= (4B_0 - 6D_0)(J+\frac{3}{2}) - 8D_0(J+\frac{3}{2})^3\end{aligned} \tag{A.6}$$

for $J = 0, 1, \ldots$, and:

$$\begin{aligned}\Delta\nu_0|_{\text{anti-Stokes}}(J) &= E_0(J-2) - E_0(J) \\ &= (4B_0 - 6D_0)(J-\frac{1}{2}) - 8D_0(J-\frac{1}{2})^3\end{aligned} \tag{A.7}$$

for $J = 1, 2, \ldots$. The frequency shift (with respect to the exciting frequency) associated with the ro-vibrational Raman lines, separated in the Q, S and O branches, can be expressed as:

$$\begin{aligned}\Delta\nu_{1\leftarrow0}|_{\text{Q}}(J) &= E_1(J) - E_0(J) \text{ for } J = 0, 1, \ldots \\ \Delta\nu_{1\leftarrow0}|_{\text{S}}(J) &= E_1(J+2) - E_0(J) \text{ for } J = 0, 1, \ldots \\ \Delta\nu_{1\leftarrow0}|_{\text{O}}(J) &= E_1(J-2) - E_0(J) \text{ for } J = 2, 3, \ldots\end{aligned} \tag{A.8}$$

For $^{16}O_2$, only odd values of J are allowed. In our notation, the *Raman shift* of a given diatomic molecule, a notion often employed in the literature, corresponds to:

$$\begin{aligned}\Delta\nu_{1\leftarrow0}|_{\text{Q}}(J=0) &= G_1 - G_0 \\ &= \omega_e - 2\omega_e X_e + \frac{13}{4}\omega_e Y_e + 5\omega_e Z_e,\end{aligned} \tag{A.9}$$

corresponding to 2329.913 cm^{-1} for $^{14}N_2$ and 1556.398 cm^{-1} for $^{16}O_2$, given the molecular constants of Table I.

Table I. Molecular parameters adopted in our analytical model of non-rigid singlet diatomic rotators.

	ω_e [cm^{-1}]	$\omega_e X_e$ [cm^{-1}]	$\omega_e Y_e$ [10^{-2} cm^{-1}]	$\omega_e Z_e$ [10^{-3} cm^{-1}]	B_e [cm^{-1}]	α_e [10^{-2} cm^{-1}]	γ_e [10^{-5} cm^{-1}]	D_e [10^{-6} cm^{-1}]	β_e [10^{-8} cm^{-1}]
$^{16}O_2$	1580.161^a	11.95127^a	4.58489^a	-1.87265^a	1.44562^a	1.59305^a	0	4.839^b	0
$^{14}N_2$	2358.54024^c	14.30577^c	-0.50668^c	-0.1095^c	1.9982399^c	1.731281^c	-2.8520^c	5.7376^c	1.02171^c
$^{14}N^{15}N$	-	-	-	-	1.93184882^d	1.646624^d	-2.22^d	5.3477^d	1.06^d
$^{14}{N_2}^+$	-	-	-	-	1.93176^b	1.881^b	0	6.10^b	0

[a] From [2].
[b] From [5].
[c] From [3].
[d] From [4].

Pure rotational Raman line wavelengths of ^{16}O$_2$

The spectral resolution of ESPRESSO is such that the pure rotational fine-structure lines of $^{16}O_2$ are resolved in the 4LGSF up-link laser beam spectrum presented in the main article. To compute the theoretical wavelength of these lines, $^{16}O_2$ cannot be simply treated as a non-rigid singlet diatomic rotator, given the fact that this molecule has a $^3\Sigma$ electronic ground state. Due to the interaction of the electronic spin **S**= 1 and end-over-end rotational angular momentum **N**, the rotational levels of $^{16}O_2$ are split into three fine-structure components, corresponding to the three ways of combining **S** and **N** vectorially to form the total angular momentum **J**. Each of these fine-structure levels is labelled with quantum numbers N and J, with $J = N-1$, N, and $N+1$. Once again, the nuclear spin statistics of $^{16}O_2$ only allows odd values of N.

[6] published the energies for all the fine-structure levels of $^{16}O_2$. To identify the associated lines in the spectrum acquired with ESPRESSO, we computed the pure rotational Raman shifts directly from these energy levels, with the following selection rules:

$$\Delta N = 0, \pm 2 \qquad \Delta J = 0, \pm 1, \pm 2 \tag{A.10}$$

The derived Raman shifts and predicted wavelengths for the pure rotational Raman lines of $^{16}O_2$ are presented in Table II. Each rotational transition is labelled as $^{\Delta N}\Delta J(J, N)$, with the usual conventions that $Q \equiv (\Delta = 0)$, $R \equiv (\Delta = +1)$, $P \equiv (\Delta = -1)$, $S \equiv (\Delta = +2)$ and $O \equiv (\Delta = -2)$. The strongest rotational transitions occur for $\Delta N = \Delta J$, while for $\Delta N = \Delta J \pm 1$ and $\Delta N = \Delta J \pm 2$, the transitions scale as N^{-1} and N^{-3}, respectively. One should note that the derived rotational Raman shifts have an accuracy $<0.0001\,\mathrm{cm}^{-1} \equiv 4\,\mathrm{fm}$ at the 4LGSF laser wavelength, resulting from an extensive Hamiltonian model that was used to simultaneously fit the microwave, THz, infrared, visible and ultraviolet transitions of all six oxygen isotopologues [7–9]. In Table II, wavelengths are purposely rounded to two digits (equivalent to a pm level) for simplicity. Readers interested in more precise values should derive them from the associated Raman shift $\Delta\nu$ via:

$$\lambda_{\mathrm{Stokes}} = c \cdot \left(\frac{c}{\lambda_{\mathrm{laser}}} - \Delta\nu \right)^{-1}, \text{ and} \tag{A.11}$$

$$\lambda_{\mathrm{anti\text{-}Stokes}} = c \cdot \left(\frac{c}{\lambda_{\mathrm{laser}}} + \Delta\nu \right)^{-1}, \tag{A.12}$$

with c the speed of light.

In the ESPRESSO spectrum presented in the main article, the transitions in the immediate vicinity of the laser wavelength belong to the $\Delta N = 0$, $\Delta J = \pm 2$, transitions, i.e. the ^{Q}O and ^QS branches. The line at 5892.28 Å is a blend of all ^QR and ^QP transitions together with the $^QS(0,1)$ line. The line at 5895.86 Å is $^SR(1,1)$. The line at 5896.55 Å is a blend of $^SS(1,1)$, $^SS(2,1)$ and the very weak $^SQ(2,1)$. The line at 5897.23 Å is a blend of $^SS(0,1)$ and $^SR(2,1)$. For $N \geq 3$, the line structure consists of a strong center line with a weak satellite line at each end. The strong center lines are from the blend of the three $^SS(J,N)$ lines and the very weak $^SQ(N+1,N)$ line. The weak satellites are from $^SR(N,N)$ and $^SR(N+1,N)$, respectively. Their intensities relative to the center line decrease very rapidly with N: in 900 s on-source with ESPRESSO, we detected the weak satellite lines up to $N = 9$.

Table II: Theoretical O_2 pure rotational Raman shifts and associated Stokes and anti-Stokes line wavelengths, computed from the energies of the molecule's fine-structure levels derived by [6], for the main exciting wavelength of the 4LGSF lasers.

$^{\Delta N}\Delta J(J, N)$	$\Delta\nu$ [cm^{-1}]	anti-Stokes [Å]	Stokes [Å]
^QS (4, 5)	0.0239	5891.58	5891.60
^QO (8, 7)	0.0424	5891.58	5891.61
^QO (10, 9)	0.0943	5891.56	5891.62
^QS (2, 3)	0.1347	5891.54	5891.64
^QO (12,11)	0.1397	5891.54	5891.64
^QO (14,13)	0.1816	5891.53	5891.65
^QO (16,15)	0.2213	5891.51	5891.67
^QO (18,17)	0.2597	5891.50	5891.68
^QO (20,19)	0.2971	5891.49	5891.69
^QO (22,21)	0.3338	5891.48	5891.71
^QO (24,23)	0.3701	5891.46	5891.72
^QO (26,25)	0.4059	5891.45	5891.73

Table II: continued.

$^{\Delta N}\Delta J(J,N)$		$\Delta\nu$ [cm^{-1}]	anti-Stokes [Å]	Stokes [Å]
^{Q}O	(28,27)	0.4415	5891.44	5891.74
^{Q}O	(30,29)	0.4768	5891.43	5891.76
^{Q}O	(32,31)	0.5120	5891.41	5891.77
^{Q}O	(34,33)	0.5470	5891.40	5891.78
^{Q}O	(36,35)	0.5818	5891.39	5891.79
^{Q}O	(38,37)	0.6166	5891.38	5891.81
^{Q}O	(40,39)	0.6513	5891.36	5891.82
^{Q}O	(42,41)	0.6860	5891.35	5891.83
^{Q}O	(44,43)	0.7206	5891.34	5891.84
^{Q}O	(46,45)	0.7551	5891.33	5891.85
^{Q}O	(48,47)	0.7896	5891.32	5891.86
^{Q}O	(50,49)	0.8241	5891.31	5891.88
^{Q}O	(52,51)	0.8586	5891.29	5891.89
^{Q}O	(54,53)	0.8930	5891.28	5891.90
^{Q}O	(56,55)	0.9274	5891.27	5891.91
^{Q}O	(58,57)	0.9619	5891.26	5891.93
^{Q}O	(60,59)	0.9963	5891.24	5891.94
^{Q}O	(62,61)	1.0307	5891.23	5891.95
^{Q}O	(64,63)	1.0652	5891.22	5891.96
^{Q}R	(64,65)	1.4478	5891.09	5892.09
^{Q}R	(62,63)	1.4645	5891.08	5892.10
^{Q}R	(60,61)	1.4812	5891.08	5892.10
^{Q}R	(58,59)	1.4980	5891.07	5892.11
^{Q}R	(56,57)	1.5147	5891.06	5892.12
^{Q}R	(54,55)	1.5315	5891.06	5892.12
^{Q}R	(52,53)	1.5482	5891.05	5892.13
^{Q}R	(50,51)	1.5651	5891.05	5892.13
^{Q}R	(48,49)	1.5819	5891.04	5892.14
^{Q}R	(46,47)	1.5988	5891.04	5892.15
^{Q}R	(44,45)	1.6156	5891.03	5892.15
^{Q}R	(42,43)	1.6326	5891.02	5892.16
^{Q}R	(40,41)	1.6496	5891.02	5892.16
^{Q}R	(38,39)	1.6666	5891.01	5892.17
^{Q}R	(36,37)	1.6836	5891.01	5892.18
^{Q}R	(34,35)	1.7008	5891.00	5892.18
^{Q}R	(32,33)	1.7180	5890.99	5892.19
^{Q}R	(30,31)	1.7352	5890.99	5892.19
^{Q}R	(28,29)	1.7526	5890.98	5892.20
^{Q}R	(26,27)	1.7701	5890.98	5892.21
^{Q}R	(24,25)	1.7878	5890.97	5892.21
^{Q}R	(22,23)	1.8056	5890.96	5892.22
^{Q}R	(20,21)	1.8236	5890.96	5892.22
^{Q}R	(18,19)	1.8420	5890.95	5892.23
^{Q}R	(16,17)	1.8607	5890.94	5892.24
^{Q}P	(2 , 1)	1.8768	5890.94	5892.24
^{Q}R	(14,15)	1.8801	5890.94	5892.24
^{Q}R	(12,13)	1.9003	5890.93	5892.25
^{Q}R	(10,11)	1.9217	5890.92	5892.26
^{Q}R	(8 , 9)	1.9455	5890.92	5892.27
^{Q}P	(4 , 3)	1.9496	5890.91	5892.27
^{Q}R	(6 , 7)	1.9735	5890.91	5892.28
^{Q}P	(6 , 5)	1.9877	5890.90	5892.28
^{Q}R	(4 , 5)	2.0116	5890.89	5892.29
^{Q}P	(8 , 7)	2.0159	5890.89	5892.29
^{Q}P	(10, 9)	2.0398	5890.88	5892.30
^{Q}P	(12,11)	2.0614	5890.88	5892.31
^{Q}P	(14,13)	2.0818	5890.87	5892.31
^{Q}S	(0 , 1)	2.0843	5890.87	5892.31
^{Q}R	(2 , 3)	2.0843	5890.87	5892.31
^{Q}P	(16,15)	2.1014	5890.86	5892.32
^{Q}P	(18,17)	2.1204	5890.85	5892.33
^{Q}P	(20,19)	2.1391	5890.85	5892.33

Table II: continued.

$^{\Delta N}\Delta J(J,N)$		$\Delta\nu$ [cm^{-1}]	anti-Stokes [Å]	Stokes [Å]
^{Q}P	(22,21)	2.1575	5890.84	5892.34
^{Q}P	(24,23)	2.1756	5890.84	5892.35
^{Q}P	(26,25)	2.1937	5890.83	5892.35
^{Q}P	(28,27)	2.2116	5890.82	5892.36
^{Q}P	(30,29)	2.2294	5890.82	5892.36
^{Q}P	(32,31)	2.2472	5890.81	5892.37
^{Q}P	(34,33)	2.2649	5890.81	5892.38
^{Q}P	(36,35)	2.2826	5890.80	5892.38
^{Q}P	(38,37)	2.3003	5890.79	5892.39
^{Q}P	(40,39)	2.3179	5890.79	5892.40
^{Q}P	(42,41)	2.3355	5890.78	5892.40
^{Q}P	(44,43)	2.3531	5890.77	5892.41
^{Q}P	(46,45)	2.3708	5890.77	5892.41
^{Q}P	(48,47)	2.3884	5890.76	5892.42
^{Q}P	(50,49)	2.4060	5890.76	5892.43
^{Q}P	(52,51)	2.4236	5890.75	5892.43
^{Q}P	(54,53)	2.4413	5890.74	5892.44
^{Q}P	(56,55)	2.4589	5890.74	5892.44
^{Q}P	(58,57)	2.4766	5890.73	5892.45
^{Q}P	(60,59)	2.4943	5890.73	5892.46
^{Q}P	(62,61)	2.5120	5890.72	5892.46
^{Q}P	(64,63)	2.5297	5890.71	5892.47
^{Q}R	(0 , 1)	3.9611	5890.22	5892.97
^{S}R	(1 , 1)	12.2918	5887.33	5895.86
^{S}Q	(2 , 1)	14.1686	5886.68	5896.51
^{S}S	(2 , 1)	14.3033	5886.63	5896.56
^{S}S	(1 , 1)	14.3761	5886.60	5896.59
^{S}S	(0 , 1)	16.2529	5885.95	5897.24
^{S}R	(2 , 1)	16.2529	5885.95	5897.24
^{S}R	(3 , 3)	23.8629	5883.32	5899.89
^{S}Q	(4 , 3)	25.8125	5882.65	5900.56
^{S}S	(4 , 3)	25.8364	5882.64	5900.57
^{S}S	(3 , 3)	25.8745	5882.62	5900.59
^{S}S	(2 , 3)	25.9473	5882.60	5900.61
^{S}R	(4 , 3)	27.8241	5881.95	5901.27
^{S}R	(5 , 5)	35.3953	5879.33	5903.90
^{S}S	(6 , 5)	37.3406	5878.66	5904.58
^{S}S	(5 , 5)	37.3688	5878.65	5904.59
^{S}Q	(6 , 5)	37.3830	5878.64	5904.60
^{S}S	(4 , 5)	37.4069	5878.64	5904.60
^{S}R	(6 , 5)	39.3565	5877.96	5905.28
^{S}R	(7 , 7)	46.9115	5875.35	5907.92
^{S}S	(8 , 7)	48.8331	5874.69	5908.59
^{S}S	(7 , 7)	48.8570	5874.68	5908.60
^{S}S	(6 , 7)	48.8850	5874.67	5908.61
^{S}Q	(8 , 7)	48.9274	5874.66	5908.62
^{S}R	(8 , 7)	50.8729	5873.98	5909.30
^{S}R	(9 , 9)	58.4156	5871.38	5911.94
^{S}S	(10, 9)	60.3156	5870.73	5912.60
^{S}S	(9 , 9)	60.3373	5870.72	5912.61
^{S}S	(8 , 9)	60.3610	5870.71	5912.62
^{S}Q	(10, 9)	60.4553	5870.68	5912.65
^{S}R	(10, 9)	62.3771	5870.02	5913.32
^{S}R	(11,11)	69.9076	5867.43	5915.96
^{S}S	(12,11)	71.7875	5866.78	5916.61
^{S}S	(11,11)	71.8079	5866.77	5916.62
^{S}S	(10,11)	71.8294	5866.76	5916.63
^{S}Q	(12,11)	71.9690	5866.72	5916.68
^{S}R	(12,11)	73.8693	5866.06	5917.34
^{S}R	(13,13)	81.3867	5863.48	5919.98
^{S}S	(14,13)	83.2472	5862.84	5920.63
^{S}S	(13,13)	83.2668	5862.83	5920.64

Table II: continued.

${}^{\Delta N}\Delta J(J,N)$		$\Delta\nu$ [cm^{-1}]	anti-Stokes [Å]	Stokes [Å]
${}^{S}S$	(12,13)	83.2870	5862.82	5920.64
${}^{S}Q$	(14,13)	83.4685	5862.76	5920.71
${}^{S}R$	(14,13)	85.3486	5862.11	5921.37
${}^{S}R$	(15,15)	92.8515	5859.54	5924.00
${}^{S}S$	(16,15)	94.6932	5858.90	5924.64
${}^{S}S$	(15,15)	94.7123	5858.90	5924.65
${}^{S}S$	(14,15)	94.7316	5858.89	5924.66
${}^{S}Q$	(16,15)	94.9529	5858.81	5924.73
${}^{S}R$	(16,15)	96.8137	5858.18	5925.39
${}^{S}R$	(17,17)	104.3004	5855.61	5928.02
${}^{S}S$	(18,17)	106.1237	5854.98	5928.66
${}^{S}S$	(17,17)	106.1424	5854.98	5928.67
${}^{S}S$	(16,17)	106.1612	5854.97	5928.67
${}^{S}Q$	(18,17)	106.4208	5854.88	5928.76
${}^{S}R$	(18,17)	108.2628	5854.25	5929.41
${}^{S}R$	(19,19)	115.7317	5851.69	5932.04
${}^{S}S$	(20,19)	117.5370	5851.07	5932.67
${}^{S}S$	(19,19)	117.5553	5851.07	5932.68
${}^{S}S$	(18,19)	117.5737	5851.06	5932.69
${}^{S}Q$	(20,19)	117.8708	5850.96	5932.79
${}^{S}R$	(20,19)	119.6944	5850.34	5933.43
${}^{S}R$	(21,21)	127.1436	5847.79	5936.06
${}^{S}S$	(22,21)	128.9310	5847.18	5936.69
${}^{S}S$	(21,21)	128.9492	5847.17	5936.69
${}^{S}S$	(20,21)	128.9673	5847.16	5936.70
${}^{S}Q$	(22,21)	129.3011	5847.05	5936.82
${}^{S}R$	(22,21)	131.1067	5846.43	5937.45
${}^{S}R$	(23,23)	138.5344	5843.89	5940.07
${}^{S}S$	(24,23)	140.3042	5843.29	5940.70
${}^{S}S$	(23,23)	140.3222	5843.28	5940.70
${}^{S}S$	(22,23)	140.3400	5843.28	5940.71
${}^{S}Q$	(24,23)	140.7101	5843.15	5940.84
${}^{S}R$	(24,23)	142.4978	5842.54	5941.47
${}^{S}R$	(25,25)	149.9023	5840.01	5944.09
${}^{S}S$	(26,25)	151.6545	5839.42	5944.71
${}^{S}S$	(25,25)	151.6724	5839.41	5944.71
${}^{S}S$	(24,25)	151.6900	5839.40	5944.72
${}^{S}Q$	(26,25)	152.0959	5839.27	5944.86
${}^{S}R$	(26,25)	153.8661	5838.66	5945.49
${}^{S}R$	(27,27)	161.2453	5836.15	5948.10
${}^{S}S$	(28,27)	162.9801	5835.56	5948.71
${}^{S}S$	(27,27)	162.9980	5835.55	5948.72
${}^{S}S$	(26,27)	163.0155	5835.55	5948.72
${}^{S}Q$	(28,27)	163.4569	5835.40	5948.88
${}^{S}R$	(28,27)	165.2096	5834.80	5949.50
${}^{S}R$	(29,29)	172.5618	5832.30	5952.10
${}^{S}S$	(30,29)	174.2793	5831.71	5952.71
${}^{S}S$	(29,29)	174.2971	5831.71	5952.72
${}^{S}S$	(28,29)	174.3144	5831.70	5952.73
${}^{S}Q$	(30,29)	174.7913	5831.54	5952.89
${}^{S}R$	(30,29)	176.5265	5830.95	5953.51
${}^{S}R$	(31,31)	183.8498	5828.46	5956.11
${}^{S}S$	(32,31)	185.5501	5827.88	5956.71
${}^{S}S$	(31,31)	185.5678	5827.88	5956.72
${}^{S}S$	(30,31)	185.5851	5827.87	5956.72
${}^{S}Q$	(32,31)	186.0971	5827.70	5956.90
${}^{S}R$	(32,31)	187.8150	5827.11	5957.51
${}^{S}R$	(33,33)	195.1076	5824.64	5960.10
${}^{S}S$	(34,33)	196.7907	5824.07	5960.70
${}^{S}S$	(33,33)	196.8084	5824.06	5960.71
${}^{S}S$	(32,33)	196.8256	5824.05	5960.71
${}^{S}Q$	(34,33)	197.3725	5823.87	5960.91

Table II: continued.

${}^{\Delta N}\Delta J(J,N)$		$\Delta\nu$ [cm^{-1}]	anti-Stokes [Å]	Stokes [Å]
${}^{S}R$	(34,33)	199.0733	5823.29	5961.51
${}^{S}R$	(35,35)	206.3332	5820.83	5964.09
${}^{S}S$	(36,35)	207.9992	5820.27	5964.69
${}^{S}S$	(35,35)	208.0168	5820.26	5964.69
${}^{S}S$	(34,35)	208.0340	5820.26	5964.70
${}^{S}Q$	(36,35)	208.6158	5820.06	5964.90
${}^{S}R$	(36,35)	210.2995	5819.49	5965.50
${}^{S}R$	(37,37)	217.5248	5817.04	5968.08
${}^{S}S$	(38,37)	219.1738	5816.48	5968.66
${}^{S}S$	(37,37)	219.1914	5816.48	5968.67
${}^{S}S$	(36,37)	219.2085	5816.47	5968.68
${}^{S}Q$	(38,37)	219.8251	5816.26	5968.90
${}^{S}R$	(38,37)	221.4917	5815.70	5969.49
${}^{S}R$	(39,39)	228.6807	5813.27	5972.05
${}^{S}S$	(40,39)	230.3126	5812.72	5972.63
${}^{S}S$	(39,39)	230.3302	5812.71	5972.64
${}^{S}S$	(38,39)	230.3472	5812.71	5972.65
${}^{S}Q$	(40,39)	230.9986	5812.49	5972.88
${}^{S}R$	(40,39)	232.6481	5811.93	5973.47

* frederic.vogt@alumni.anu.edu.au; ESO Fellow

[1] G. Herzberg, *Molecular Spectra and Molecular Structure. Vol.1: Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand Reinhold, New York, 1950).

[2] M. Shimauchi, T. Miura, and H. Takuma, "Determination of Molecular Constnts of the X3Σg- State of O2," Japanese Journal of Applied Physics **34**, L1689 (1995).

[3] M. L. Orlov, J. F. Ogilvie, and J. W. Nibler, "High-Resolution Coherent Raman Spectra of Vibrationally Excited14N2and15N2," Journal of Molecular Spectroscopy **185**, 128–141 (1997).

[4] J. Bendtsen, "High-resolution Fourier transform Raman spectra of the fundamental bands of 14N15N and 15N2," Journal of Raman Spectroscopy **32**, 989–995 (2001).

[5] K.-P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Vol.4: Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[6] S. Yu, B. J. Drouin, and C. E. Miller, "High resolution spectral analysis of oxygen. IV. Energy levels, partition sums, band constants, RKR potentials, Franck-Condon factors involving the X3Σg-, a1Δg and b1Σg+ states," The Journal of Chemical Physics **141**, 174302 (2014).

[7] S. Yu, C. E. Miller, B. J. Drouin, and H. S. P. Müller, "High resolution spectral analysis of oxygen. I. Isotopically invariant Dunham fit for the X3Σg-, a1Δg, b1Σg+ states," The Journal of Chemical Physics **137**, 024304 (2012).

[8] B. J. Drouin, H. Gupta, S. Yu, C. E. Miller, and H. S. P. Müller, "High resolution spectral analysis of oxygen. II. Rotational spectra of a1Δg O2 isotopologues," The Journal of Chemical Physics **137**, 024305 (2012).

[9] B. J. Drouin, S. Yu, B. M. Elliott, T. J. Crawford, and C. E. Miller, "High resolution spectral analysis of oxygen. III. Laboratory investigation of the airglow bands," The Journal of Chemical Physics **139**, 144301 (2013).