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

SUPPLEMENTAL MATERIAL

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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:

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

with G_n the vibrational component, and $F_n(J)$ the rotational component. Following [1], for diatomic molecules like $^{14}\text{N}_2$ with a $^1\Sigma$ electronic ground state or $^{16}\text{O}_2$ with a non-singlet electronic state but unresolved line splitting structure:

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

and

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

where

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

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

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 $^{16}\text{O}_2$, [3] for $^{14}\text{N}_2$, [4] for $^{14}\text{N}^{15}\text{N}$, and [5] for $^{14}\text{N}_2^+$.

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:

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

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

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

for $J = 1, 2, \dots$. 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:

$$\Delta\nu_{1\leftarrow 0}|_Q(J) = E_1(J) - E_0(J) \text{ for } J = 0, 1, \dots \quad (\text{A.8})$$

$$\Delta\nu_{1\leftarrow 0}|_S(J) = E_1(J+2) - E_0(J) \text{ for } J = 0, 1, \dots$$

$$\Delta\nu_{1\leftarrow 0}|_O(J) = E_1(J-2) - E_0(J) \text{ for } J = 2, 3, \dots$$

For $^{16}\text{O}_2$, 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:

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

corresponding to 2329.913 cm^{-1} for $^{14}\text{N}_2$ and 1556.398 cm^{-1} for $^{16}\text{O}_2$, 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 ¹⁶O₂

The spectral resolution of ESPRESSO is such that the pure rotational fine-structure lines of ¹⁶O₂ are resolved in the 4LGSF up-link laser beam spectrum presented in the main article. To compute the theoretical wavelength of these lines, ¹⁶O₂ cannot be simply treated as a non-rigid singlet diatomic rotator, given the fact that this molecule has a ³Σ 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 ¹⁶O₂ 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 ¹⁶O₂ only allows odd values of *N*.

[6] published the energies for all the fine-structure levels of ¹⁶O₂. 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:

$$\Delta N = 0, \pm 2 \quad \Delta J = 0, \pm 1, \pm 2 \quad (\text{A.10})$$

The derived Raman shifts and predicted wavelengths for the pure rotational Raman lines of ¹⁶O₂ are presented in Table II. Each rotational transition is labelled as ^{ΔN}ΔJ(*J*, *N*), with the usual conventions that *Q* ≡ (Δ = 0), *R* ≡ (Δ = +1), *P* ≡ (Δ = -1), *S* ≡ (Δ = +2) and *O* ≡ (Δ = -2). The strongest rotational transitions occur for Δ*N* = Δ*J*, while for Δ*N* = Δ*J* ± 1 and Δ*N* = Δ*J* ± 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 cm⁻¹ ≡ 4 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 Δ*ν* via:

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

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

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 Δ*N* = 0, Δ*J* = ±2, transitions, i.e. the *QO* 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 *S**R*(1, 1). The line at 5896.55 Å is a blend of *S**S*(1, 1), *S**S*(2, 1) and the very weak *S**Q*(2, 1). The line at 5897.23 Å is a blend of *S**S*(0, 1) and *S**R*(2, 1). For *N* ≥ 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 *S**S*(*J*, *N*) lines and the very weak *S**Q*(*N* + 1, *N*) line. The weak satellites are from *S**R*(*N*, *N*) and *S**R*(*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 O₂ 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.

^{ΔN} ΔJ(<i>J</i> , <i>N</i>)	Δ <i>ν</i> [cm ⁻¹]	anti-Stokes [Å]	Stokes [Å]
<i>QS</i> (4, 5)	0.0239	5891.58	5891.60
<i>QO</i> (8, 7)	0.0424	5891.58	5891.61
<i>QO</i> (10, 9)	0.0943	5891.56	5891.62
<i>QS</i> (2, 3)	0.1347	5891.54	5891.64
<i>QO</i> (12, 11)	0.1397	5891.54	5891.64
<i>QO</i> (14, 13)	0.1816	5891.53	5891.65
<i>QO</i> (16, 15)	0.2213	5891.51	5891.67
<i>QO</i> (18, 17)	0.2597	5891.50	5891.68
<i>QO</i> (20, 19)	0.2971	5891.49	5891.69
<i>QO</i> (22, 21)	0.3338	5891.48	5891.71
<i>QO</i> (24, 23)	0.3701	5891.46	5891.72
<i>QO</i> (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

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