

EXOMOL line lists – LXVII: empirical magnetic dipole and electric quadrupole spectra of the infrared bands of oxygen (O₂)

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ABSTRACT

A new set of comprehensive variational line lists for all six isotopologues of molecular oxygen (¹⁶O₂, ¹⁷O₂, ¹⁸O₂, ¹⁶O¹⁷O, ¹⁶O¹⁸O, and ¹⁷O¹⁸O) covering the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ electronic states is presented as part of the EXOMOL project. The line lists, collectively named SWYT, cover the wavenumber range 0–20 000 cm^{−1} and are applicable for temperatures up to 5000 K. This is the first EXOMOL line list describing magnetic dipole (M1) and electric quadrupole (E2) transitions. The line lists were computed using the DUO program with a coupled electronic-state model including all relevant spin–orbit and electronic-angular-momentum couplings, based on high-level *ab initio* potential energy, coupling, and transition moment curves. The spectroscopic model was refined to reproduce experimental MARVEL energies of O₂ and further adjusted to match HITRAN 2024 intensities by optimizing the spin–orbit, angular-momentum, and quadrupole-moment coupling curves. The SWYT line lists provide accurate transition frequencies and intensities for M1 and E2 processes, enabling reliable modelling of O₂ opacity in a wide range of astrophysical and atmospheric environments, including exoplanets, brown dwarfs, late-type stars, and other atmospheres. The line lists, partition functions, lifetimes, DUO input files, ¹⁶O₂ opacities formatted for four radiative transfer codes, TAUREX, ARCIS, NEMESIS, and PETITRADTRANS, are available from the ExoMol data base at www.exomol.com.

Key words: molecular data – opacity – planets and satellites: atmospheres – stars: atmospheres – ISM: molecules.

1 INTRODUCTION

Molecular oxygen (O₂) is one of the most important species in planetary and astrophysical environments. On Earth, it constitutes about 21 per cent of the atmosphere and plays a central role in photochemical, biological, and geophysical processes. Beyond the terrestrial context, O₂ is a key molecule in planetary atmospheres, icy satellites, and cometary comae, and its detection serves as a potential indicator of photochemical activity or biological processes on exoplanets (V. S. Meadows et al. 2018; C. M. Lisse et al. 2020; J. Krissansen-Totton et al. 2021). The presence of O₂ in an exoplanetary atmosphere would thus represent one of the most important atmospheric diagnostics, motivating the need for reliable spectroscopic data across a wide range of temperatures and wavelengths relevant to current and future astronomical facilities, including *James Webb Space Telescope*, *Ariel*, and *Extremely Large Telescope* (T. P. Greene et al. 2016; M. López-Morales et al. 2019; J. Krissansen-Totton et al. 2022).

The spectroscopy of O₂ is complex owing to its homonuclear character and high molecular symmetry. The ground and low-lying electronic states of O₂ – $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ – all possess gerade symmetry, resulting in the absence of allowed electric dipole (E1) transitions among them. Consequently, the infrared

and visible spectra of O₂ are governed instead by higher order magnetic dipole (M1) and electric quadrupole (EQ; E2) mechanisms. These transitions give rise to the well-known atmospheric A, B, and γ bands of O₂ (K. J. Ritter & T. D. Wilkerson 1987; I. E. Gordon, L. S. Rothman & G. C. Toon 2011), as well as numerous weaker features that have been the focus of experimental and theoretical investigations for decades (H. D. Babcock & L. Herzberg 1948; J. W. Brault 1980; A. Goldman, J. Reid & L. S. Rothman 1981; B. J. Drouin et al. 2010; M. Toureille et al. 2020). Accurate modelling of these transitions requires an explicit treatment of spin–orbit and angular-momentum couplings between the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states and a manifold of excited ungerade electronic terms – most notably the $I^1\Pi_u$, $II^1\Pi_u$, $I^3\Pi_u$, and $II^3\Pi_u$ states – that mediate intensity borrowing (E. B. Sveshnikova & B. F. Minaev 1983; W. Somogyi, S. N. Yurchenko & G.-S. Kim 2024).

Very recently, an accurate EQ line list for the ground electronic state of ¹⁶O₂ was computed (M. Gancewski et al. 2025) based on an effective Hamiltonian (EH) model for energies, a high-level *ab initio* EQ curve and the so-called intermediate coupling method (L. S. Rothman & A. Goldman 1981). The line list covers the rotational excitations up to $J = 40$ and was shown to accurately reproduce HITRAN’s line list for ¹⁶O₂ (I. E. Gordon et al. 2022). Previous high-level *ab initio* studies of O₂ (L. Bytautas, N. Matsunaga & K. Ruedenberg 2010; H. Liu et al. 2014) have produced accurate potential energy curves (PECs), spin–orbit coupling (SOC) curves, and other coupling properties. Recently,

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W. Somogyi et al. (2024) developed a comprehensive *ab initio* spectroscopic model for O₂, combining these curves within a fully coupled-channel framework capable of predicting magnetic dipole and quadrupole line strengths. That work established the methodological foundation for constructing realistic O₂ line lists, but no complete variational data set covering astrophysical temperatures has yet been available.

In this work, we present the first EXOMOL line lists for molecular oxygen, covering all six isotopologues (¹⁶O₂, ¹⁷O₂, ¹⁸O₂, ¹⁶O¹⁷O, ¹⁶O¹⁸O, and ¹⁷O¹⁸O). The line lists, hereafter referred to as SWYT, span wavenumbers up to 20 000 cm⁻¹ and are applicable for temperatures up to 5000 K. The underlying spectroscopic model is based on the *ab initio* PECs, SOC curves, electronic-angular-momentum coupling (EAMC) curves, and electronic quadrupole moment curves (QMCs) of W. Somogyi et al. (2024), refined against the experimentally derived MARVEL (measured active rotation vibration energy levels) energies of T. Furtenbacher et al. (2019). To improve transition intensities, selected coupling curves were further adjusted to reproduce the HITRAN 2024 laboratory intensities of O₂.

A preliminary version of the present ¹⁶O₂ line list has already been successfully validated in a recent joint experiment-theory study of the O₂ A band by E. M. Adkins et al. (2025a). In that work, frequency-stabilized cavity ring-down spectroscopy measurements provided absolute line intensities for 72 transitions near 760 nm up to $J = 40$ with relative combined standard uncertainties of about 0.15 per cent, and these measurements were combined with variational DUO-based *ab initio* intensities to constrain the rotational dependence and to extrapolate a consistent A-band intensity set to $J = 60$ via a simple scaling of the theoretical model. The resulting band-integrated intensity was found to exhibit a statistically significant (negative) bias relative to several prior ‘best-estimate’ literature models, at a level several times larger than the new uncertainty, helping to tighten the intensity component of integrated A-band spectroscopic models used in atmospheric remote-sensing retrievals. These findings were subsequently incorporated into the updated oxygen compilation released with HITRAN 2024 (I. E. Gordon et al. 2026), as summarized by E. M. Adkins et al. (2025b) in their survey of the revised O₂ line list.

All calculations were performed using the DUO nuclear-motion program (S. N. Yurchenko et al. 2016). The resulting line lists contain both M1 and E2 transitions across the X-a-b system and provide, for the first time, a complete description of O₂ opacity suitable for modelling planetary and stellar atmospheres at high temperatures. The SWYT data sets, including state lifetimes, partition functions, and the full DUO input files defining the spectroscopic model, are available from the EXOMOL data base (www.exomol.com).

2 SPECTROSCOPIC MODEL

We use the diatomic code DUO (S. N. Yurchenko et al. 2016) to compute rovibronic energies and intensities of O₂. DUO solves a system of coupled Schrödinger equations variationally and computes transition probabilities using a given so-called spectroscopic model, i.e. a set of PECs, SOC, electronic angular momentum, dipole moment, quadrupole moment, and other curves. For this work, our starting spectroscopic model consists of *ab initio* curves of O₂ reported by W. Somogyi et al. (2024), with PECs, QMCs, SOCs, and EAMCs obtained with the MOLPRO program (H.-J. Werner et al. 2012) using the MRCI/aug-cc-pV5Z level

of theory. Some of the curves were improved through analytic interpolations.

In order to improve the initial *ab initio* spectroscopic model described, and to more confidently predict the line position and intensity of absorption lines of O₂, the spectroscopic model (analytic PECs and couplings) must be empirically refined. The DUO program’s fitting routine allows one to perform a least-squares fit of the calculated rovibronic state energies to accurately known state energies, usually derived from experimental data and requires the refined curves to be represented as parametrized analytic functions. In the following, the analytic representations used to refine the *ab initio* spectroscopic model of O₂ are introduced.

2.1 Potential energy curves

Our empirical spectroscopic model consists of seven electronic states, $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $I^3\Pi_g$, $I^1\Pi_g$, $\Pi^3\Pi_g$, and $\Pi^1\Pi_g$, shown in Fig. 1. For the five bound electronic states $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $\Pi^3\Pi_g$, and $\Pi^1\Pi_g$ the Morse/long-range (MLR) potential energy function was used

$$V(r) = T_e + (A_e - T_e) \left(1 - \frac{u(r)}{u(r_e)} e^{-\beta(r)y_p^{\text{ref}}(r)} \right)^2, \quad (1)$$

with T_e the potential minimum and A_e the dissociation energy, relative to the zero-point energy (ZPE). The polynomial function $\beta(r)$ and the long-range function $u(r)$ ensure the function has the correct long-range behaviour,

$$\beta(r) = y_p^{\text{ref}}(r)\beta_\infty + [1 - y_p^{\text{ref}}(r)] \sum_{i=0}^{N_\beta} \beta_i (y_q^{\text{ref}}(r))^i, \quad (2)$$

$$y_p^{\text{ref}}(r) = \frac{r^p - r_x^p}{r^p + r_x^p}, \quad (3)$$

where p is an integer greater than 1, the value of which is a hyperparameter of the fitting procedure. The long-range function is $u(r) = \sum_n \frac{C_n}{r^n}$, where one or more of the coefficients C_n may be equal to zero. In the limit $r \rightarrow \infty$, the function approaches the $\beta_\infty = \ln \left(\frac{2D_e}{u(r_e)} \right)$ where r_e is the equilibrium bond length, and r_{ref} is some reference geometry. In all fits $r_{\text{ref}} \equiv r_e$ is selected for simplicity. The MLR form introduced by R. J. Le Roy, Y. Huang & C. Jary (2006) and later refined by R. J. Le Roy et al. (2009) improves on the well-known Morse potential by accounting for the long-range behaviour of molecular potential energy surfaces.

For the two dissociative potentials ($I^1\Pi_g$ and $I^3\Pi_g$, see Fig. 1) the following repulsive potential in the form of a Laurent power series in the radial distance was used

$$V(r) = T_e + \sum_i \frac{a_i}{r^i}, \quad (4)$$

where a_i are the fitted coefficients. For each of the bound potentials we set a single dispersion parameter, namely C_6 , to be non-zero and fix the value as $C_6 = 2.95 \times 10^5 E_h \text{ cm}^{-6}$ (W. Rijks, M. van Heeringen & P. E. S. Wormer 1989). The equilibrium bond length is bounded to remain within the range 0.9–3.0 Å, and the dissociation and excitation energies are bounded in the range of positive real numbers.

2.2 Spin-orbit coupling, quadrupole, and angular momentum curves

For all SOCs, EAMCs, and EQMCs used in this work (see Figs 1–3), a polynomial-decay expansion (L. Prajapat et al. 2017)

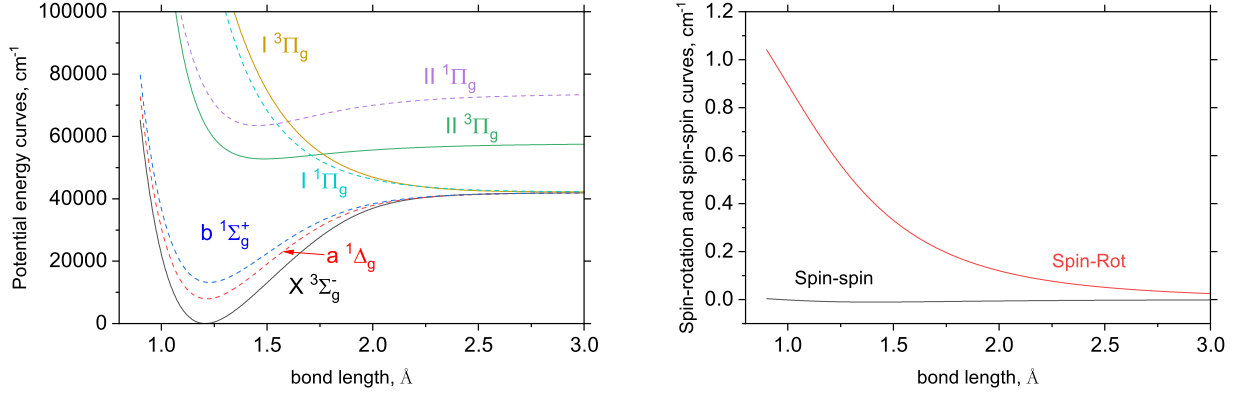


Figure 1. Potential energy, spin-spin, and spin-rotation curves of ¹⁶O₂ representing our final empirical spectroscopic model.

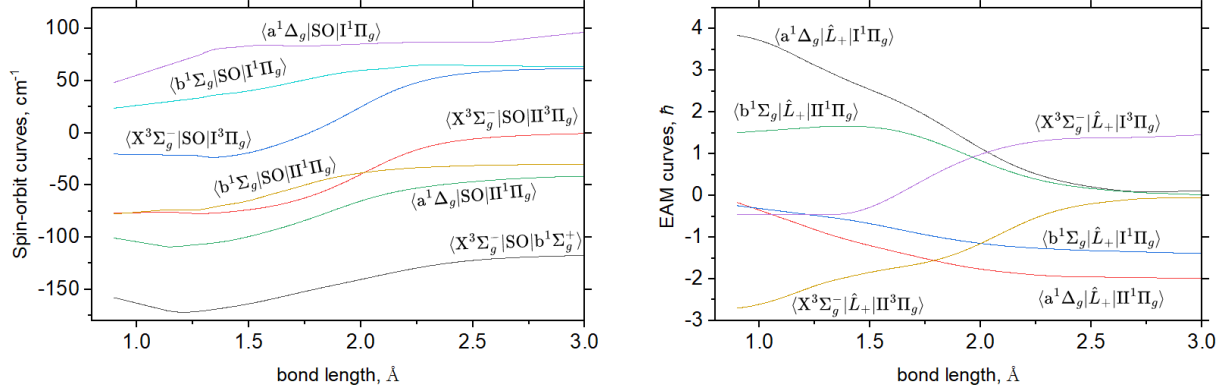


Figure 2. Empirical spin-orbit and electronic-angular-momentum curves of ¹⁶O₂.

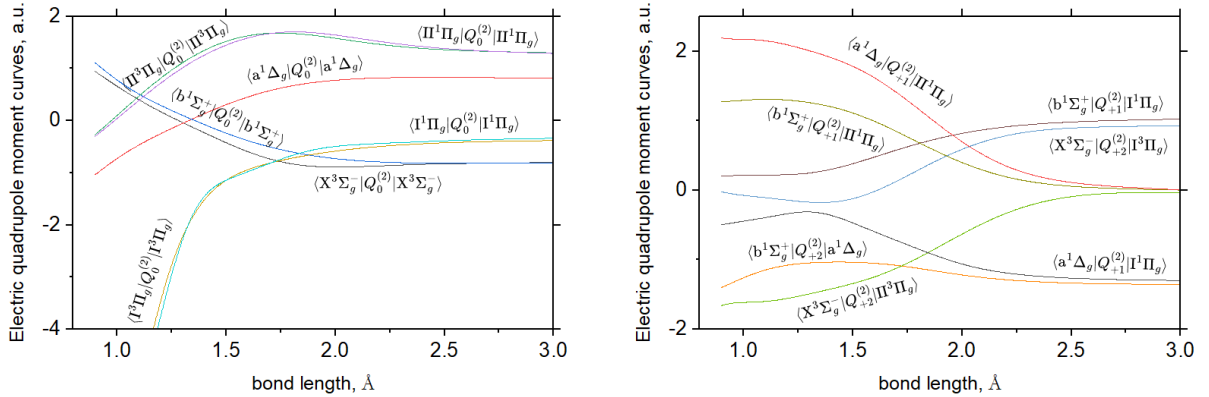


Figure 3. EQ moment curves of O₂.

was used (see also M. Semenov et al. 2022 or S. N. Yurchenko et al. 2022)

$$F(r) = \sum_{i=0}^{N_B} B_i z^i (1 - y_p^{\text{ref}}) + y_p^{\text{ref}} B_{\infty}, \quad (5)$$

where y_p is the Šurkus variable defined by equation (3), and z is taken as the damped coordinate

$$z = (r - r_{\text{ref}}) e^{-\beta_2(r-r_{\text{ref}})^2 - \beta_4(r-r_{\text{ref}})^4} \quad (6)$$

with r_{ref} taken close to the equilibrium bond length of X³Σ_g[−] of O₂, 1.21 Å.

2.3 Spin-spin curves

In addition to the curves given above, it is important to account for the spin splitting of the X³Σ_g[−] state, crucial for the b¹Σ_g⁺ – X³Σ_g[−] magnetic dipole transitions, see W. Somogyi et al. (2024). The magnitude of its spin splitting was estimated to be about 1.17 cm^{−1} (M. Tinkham & M. W. P. Strandberg 1955a, b). In DUO, it can be introduced through the phenomenological spin-spin operator (S. N. Yurchenko et al. 2016). In the absence of *ab initio* data, it is usually obtained by fitting a functional form to experimental data. Here, we use a Šurkus polynomial to represent the

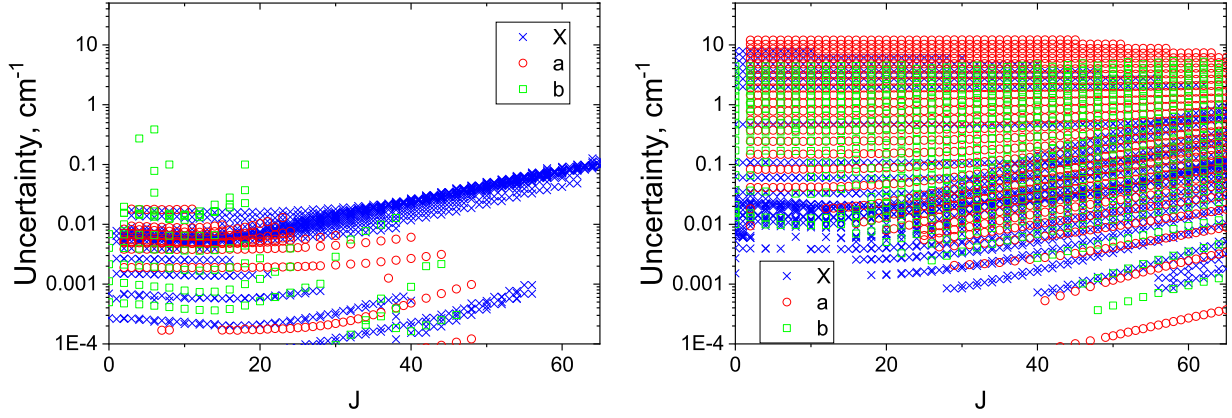


Figure 4. Distribution of uncertainties associated with the energy levels in the $^{16}\text{O}_2$ data base of T. Furtenbacher et al. (2019). Left display: experimentally determined MARVEL levels only. Right display: MARVEL levels of T. Furtenbacher et al. (2019) including those obtained from an EH.

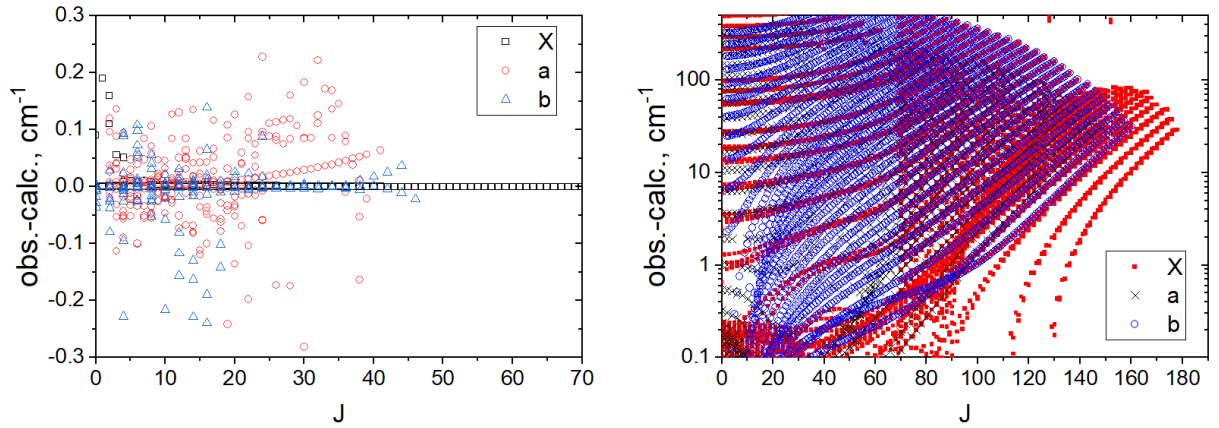


Figure 5. Residuals between the MARVEL energy term values (obs.) (T. Furtenbacher et al. 2019) of $^{16}\text{O}_2$ and the calculated values using the refined spectroscopic model (calc.). Left display: residuals for the experimentally determined MARVEL levels only. Right display: residuals for all MARVEL levels of T. Furtenbacher et al. (2019) including those based on the data produced using an EH.

Table 1. Nuclear spin statistical weights g_{ns} for O_2 isotopologues. These factors are applied in partition function calculations and line intensity normalization.

		g_{ns}		
Ortho/para	Parity	$^{16}\text{O}_2$	$^{18}\text{O}_2$	$^{17}\text{O}_2$
Ortho	1	1	1	21
Ortho	-1	1	1	21
Para	-1	0	0	15
Para	1	0	0	15
		$^{16}\text{O}^{17}\text{O}$	$^{16}\text{O}^{18}\text{O}$	$^{17}\text{O}^{18}\text{O}$
	1	6	1	6
	-1	6	1	6

spin-spin curve in the following form

$$F(r) = (1 - y_p^{r_{\text{ref}}}) \sum_{i=0}^{N_A} A_i (y_p^{r_{\text{ref}}})^i + y_p^{r_{\text{ref}}} A_{\infty} \quad (7)$$

where $y_p^{r_{\text{ref}}}$ is given by equation (3) with $r_{\text{ref}} = r_e$, the equilibrium bond length. Initially, the leading parameter A_0 was set to 1.17 cm^{-1} .

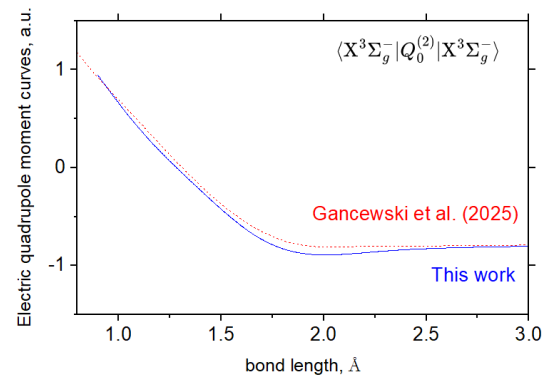


Figure 6. Comparison of two *ab initio* permanent EQ moments of O_2 , from this work (solid line) and by M. Gancewski et al. (2025, dashed line). The latter was adopted for our SWYT line list.

3 EXPERIMENTALLY DERIVED (MARVEL) ENERGIES OF $^{16}\text{O}_2$

The task of producing an accurate spectroscopic model for $^{16}\text{O}_2$ is greatly aided by the work of T. Furtenbacher et al. (2019) which contains a data base of some 15 946 rovibronic energy levels for

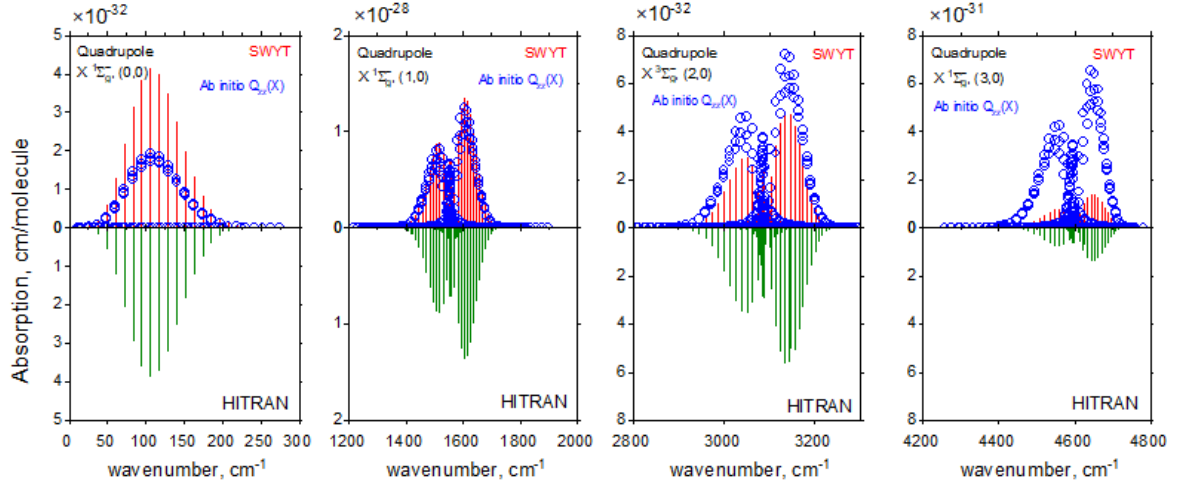


Figure 7. E2 intensities of $^{16}\text{O}_2$ at $T = 296\text{ K}$ for four lowest vibrational bands of $X^3\Sigma_g^-$ computed using two *ab initio* permanent EQ moments, from this work (blue circle) and by M. Gancewski et al. (2025, red sticks) illustrating the underlying quality of the EQ curve used. The latter was adopted for our SWYT line list. HITRAN 2024 (I. E. Gordon et al. 2026) recommended values are also given for comparison.

Table 2. Number of states and lines in the SWYT line lists for six isotopologues of O₂.

Iso	N_{states}	$N_{\text{trans}}^{(\text{M1})}$	$N_{\text{trans}}^{(\text{E2})}$
66	10 882	12 27 360	21 60 759
67	22 387	25 67 450	45 17 420
68	23 005	26 77 755	47 11 290
77	23 098	26 92 108	47 37 025
78	23 742	28 09 341	49 43 214
88	12 225	14 65 990	25 80 734

the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^+$, $A^3\Sigma_u^+$, $A'^3\Delta_u$, and $B^3\Sigma_u^-$ states. These energy levels were largely produced through the MARVEL procedure (T. Furtenbacher, A. G. Császár & J. Tennyson 2007), which derives energies within experimental uncertainties using the (W. Ritz 1908) principle by inverting experimental transition frequencies (line positions). The MARVEL program (T. Furtenbacher et al. 2007) is able to invert a so-called spectroscopic network (SN), a self-consistent undirected weighted graph in which state energies are the graph nodes, and transition frequencies are the edges, to obtain state energies from experimentally measured transition frequencies. Crucially, the MARVEL code is also able to assign uncertainties to the state energies, based on the uncertainty of the transition frequencies used to reconstruct the energy. This is invaluable for the purpose of empirically refining the spectroscopic model as it allows the data points in the fit to be weighted according to their accuracy.

Apart from the 4279 highly accurate rovibrational energies of $^{16}\text{O}_2$, supported by the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ electronic states considered here, the larger fraction of the Furtenbacher data set comes from two additional methods.

The first additional source of energy levels is an EH. In addition to the energy levels obtained by applying the usual MARVEL methodology to experimental line positions, the data base was supplemented by 11 667 energy levels determined from EHs for the $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^+$, $A^3\Sigma_u^+$, and $A'^3\Delta_u$ electronic states. These EH levels were included to aid the calculation of partition and thermochemical functions. Crucially, they favoured

completeness over accuracy for this purpose. As a result, their EHs were parametrized by the spectroscopic constants presented by M.-F. Mérienne et al. (2001), which may be less accurate than parameters with less coverage from other authors, such as K. Yoshino et al. (2000).

Many of the EH state energies have large estimated uncertainties associated with them and these are illustrated in Fig. 4. More than 70 per cent of the energies have an associated uncertainty greater than 1 cm^{-1} , with more than 60 per cent greater than 10 cm^{-1} . Large uncertainties tend to destabilize the refinement procedure. Our initial attempt to include these EH energies in the T. Furtenbacher et al. (2019) data base in the empirical refinement was unsuccessful. We therefore decided to exclude the EH energies from the refinement procedure.

The second technique employed by T. Furtenbacher et al. (2019) to improve the connectivity of their SN was the introduction of so-called Magic numbers as artificial transitions to the data base. These are transitions that were reconstructed from the energy levels of S. Yu, B. J. Drouin & C. E. Miller (2014) by taking their difference from the ground $(J, N, v) = (0, 1, 0)$ $X^3\Sigma_g^-$ state. The artificial transitions were included to connect disjoint networks (so-called orphans) and thus to increase the size of the SN for the three lowest electronic states, which in turn allowed them to determine the energies of the highly excited electronic levels. Of the 30 671 transitions that contributed to the MARVEL SN, 6295 are so-called artificial transitions. As a consequence, these artificial transitions do not have associated intensities, but their frequencies generally have a small uncertainty due to the accurate energy levels used to produce them. These artificial transitions are retained in the fitting procedure.

The majority of energy levels that appear in the data base presented by T. Furtenbacher et al. (2019) are those of highly excited ungerade electronic states $A^3\Sigma_u^+$, $A'^3\Delta_u$, $B^3\Sigma_u^-$, and $c^1\Sigma_u^+$. Since these states are fully uncoupled from the gerade states $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ and thus do not play a role in the infrared EQ and magnetic dipole spectra, they are of little value in refining the *ab initio* spectroscopic model. Only 11 335 of their energy levels correspond to states relevant to the refinement procedure, and all of these are for $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$. The primary

Table 3. Extract from the states file of the line list for $^{16}\text{O}_2$. States files of other isotopologues have the same structure except for the last two columns, which are present only for $^{16}\text{O}_2$.

i	Energy (cm ⁻¹)	g_i	J	Unc	τ	Parity	State	ν	Ω	N	Ma/Ca	Energy (cm ⁻¹)
122	10832.682377	5	2	0.206000	1.2004E+04	+ e	a1Deltag	2	2	2	Ca	10832.682377
123	11802.904466	5	2	0.806000	1.1951E+07	+ e	X3Sigmag−	8	0	1	Ca	11802.904466
124	11815.918460	5	2	0.324500	9.3993E+06	+ e	X3Sigmag−	8	1	3	Ma	11815.867388
125	12263.887473	5	2	0.306000	1.2484E+04	+ e	a1Deltag	3	2	2	Ca	12263.887473
126	13130.353067	5	2	0.000044	1.0881E+01	+ e	b1Sigmag +	0	0	2	Ma	13130.349316
127	13175.094297	5	2	0.906000	1.0500E+07	+ e	X3Sigmag−	9	0	1	Ca	13175.094297
128	13187.880757	5	2	0.260400	8.4903E+06	+ e	X3Sigmag−	9	1	3	Ma	13187.909652
129	13669.015844	5	2	0.406000	1.2498E+04	+ e	a1Deltag	4	2	2	Ca	13669.015844
130	14524.458056	5	2	0.292700	9.3736E+06	+ e	X3Sigmag−	10	0	1	Ma	14524.632294
131	14534.979892	5	2	0.000007	1.1111E+01	+ e	b1Sigmag +	1	0	2	Ma	14534.976825
132	14537.297756	5	2	0.360300	6.3954E+06	+ e	X3Sigmag−	10	1	3	Ma	14537.300521

Notes: i : state counting number.

$\bar{E}$: state energy term values in cm^{-1} , MARVEL or calculated (DUO).

g_i : total statistical weight, equal to $g_{\text{ns}}(2J + 1)$.

J : total angular momentum.

unc: uncertainty, cm^{-1} .

τ : total lifetime, including E2 and M1 (s).

+/-: total parity.

e/f: rotationless parity.

State: electronic state.

v : state vibrational quantum number.

Ω : projection of the total angular momentum, $\Omega = \Lambda + \Sigma$.

N : rotational quantum number.

Label: 'Ma' is for MARVEL and 'Ca' is for calculated.

Energy: state energy term values in cm^{-1} , calculated (DUO).

Table 4. Extract from the transitions file of the line list for $^{16}\text{O}_2$.

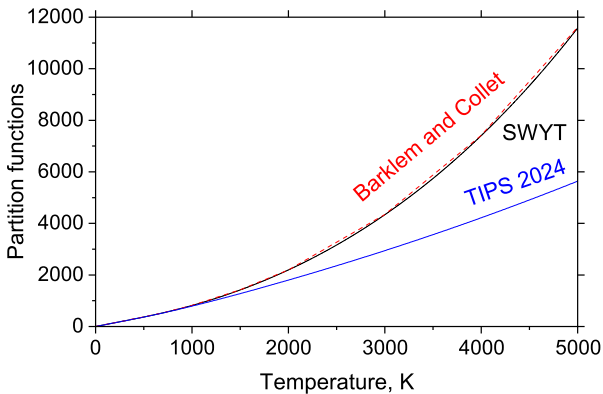
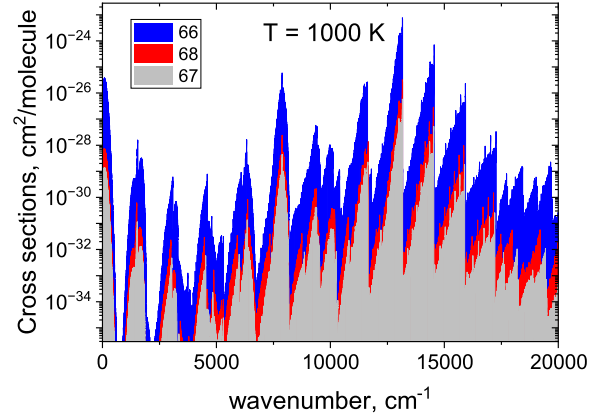
f	i	$A_{fi} (\text{s}^{-1})$	$\bar{\nu}_{fi}$
921	1123	9.4563E−34	0.139060
923	1125	7.8288E−34	0.140489
925	1127	6.2537E−34	0.141820
2646	2842	9.2405E−33	0.142375
927	1129	4.7953E−34	0.143055
803	1006	9.5826E−35	0.143227
929	1131	3.4899E−34	0.144193
3421	3230	1.6909E−33	0.144487

Notes: f : upper state counting number.

i : lower state counting number.

A_{fi} : Einstein-A coefficient in s^{-1} .

$\bar{\nu}_{fi}$: transition wavenumber in cm^{-1} .

**Figure 8.** Partition functions of $^{16}\text{O}_2$: SWYT (this work), P. S. Barklem & R. Collet (2016) and TIPS 2024 (R. R. Gamache et al. 2025).**Figure 9.** Absorption spectra of the three main isotopologues, $^{16}\text{O}_2$, $^{16}\text{O}^{17}\text{O}$, and $^{16}\text{O}^{18}\text{O}$, scaled by their natural abundances. A Gaussian line profile of half-width-half-maximum (HWHM) of 1 cm^{-1} was used.

limitation of the data base presented by T. Furtenbacher et al. (2019) is thus the absence of energies for any rovibronic levels of the four $^3\Pi_g$ and $^1\Pi_g$ states. Moreover, to the best of our knowledge, there is no experimental data for transitions involving these Π states, and thus their inclusion in any SN is not possible at present.

However, because these levels contribute to the energy and intensity of the infrared bands only indirectly, we argue that obtaining accurate PECs for these highly excited states is not essential to the production of an accurate line list. Instead, the required corrections to the state energies can usually be absorbed into the empirical refinement of the coupling terms (namely spin-orbit) that connect the Π states to the lower electronic levels.

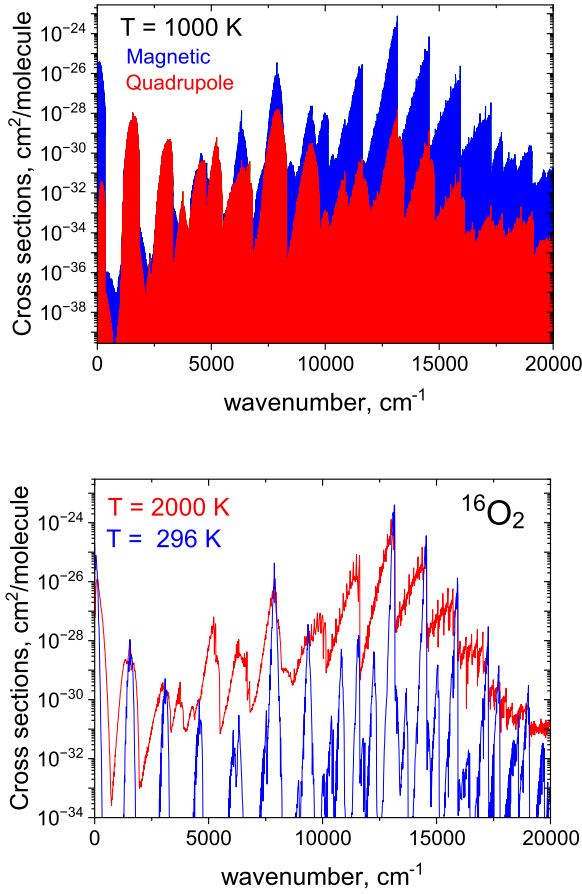


Figure 10. Intensities (cross-sections) of O₂ computed using the SWYT line list. Top display: the M1 and E2 contributions to the cross-sections of ¹⁶O₂ at T = 1000 K. A Gaussian line profile of HWHM of 1 cm⁻¹ was used. Bottom display: absorption spectra of ¹⁶O₂ at T = 296 K and 2000 K.

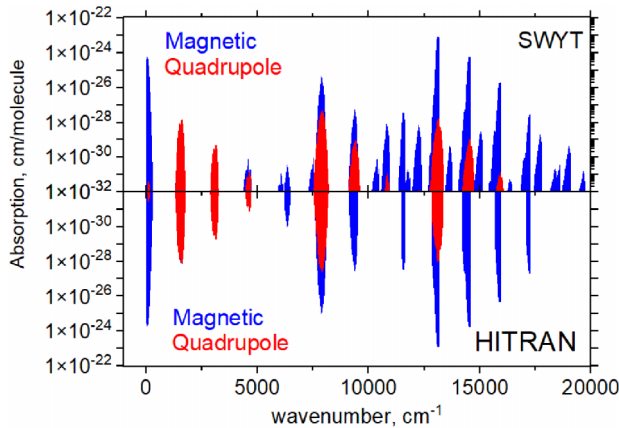


Figure 11. An overview of magnetic dipole (M1) and EQ (E2) intensities of ¹⁶O₂ at T = 296 K computed using SWYT (upper panel) and from HITRAN (lower panel).

3.1 Refinement of the spectroscopic model

The empirical refinement of *ab initio* curves takes two forms. For many curves, it is possible to perform a straightforward fit of some analytic function that completely parametrizes the energy levels; this is usually the case when the curve in question has good support in the data set being used to perform the fitting. When this is not the case, and the data set is insufficient to constrain an analytic function, a so-called morphing function can be parametrized instead. In this case the fitted function is convolved with the *ab initio* data to produce an empirical curve that can improve the calculated energies. The advantage of the latter approach is that it allows for additional support for the empirical model to come from the *ab initio* data when there is insufficient coverage in the state energy data set.

The empirical model is obtained by performing a weighted non-linear least-squares fit of the state energies predicted by DUO to those contained in the MARVEL spectroscopic data base outlined above. The least-squares fit is weighted according to the uncertainties of the energy levels produced by MARVEL as part of the inversion procedure.

Due to the large number of total parameters available across all PECs and couplings, and the high degree of correlation between them, it is not usually possible to perform a simultaneous fit of all the curves. Instead each curve or a small subset of the curves is usually fitted sequentially on a carefully selected subset of the data set that provides the greatest support for the selected curve. Once a reasonable fit has been obtained across multiple curves, the parameters can be freely varied together for a simultaneous fit of two or more curves in order to obtain a high-quality self-consistent model.

3.1.1 Potential energy curves

The three low-lying electronic states, $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$, are parametrized in the empirical model using the same MLR function that was introduced in equation (1). Initial parameters were obtained by fitting to the *ab initio* data. The dissociation energy of these states is well quantified by experimental data, and so the value of D_e , the dissociation energy relative to the ZPE of the $X^3\Sigma_g^-$ state is initially fixed according to the value provided by B. Ruscic et al. (2004). Similarly the minimum electronic energies of the $a^1\Delta_g$ and $b^1\Sigma_g^+$ states, and the equilibrium bond lengths of the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states are initially fixed at the values provided by P. H. Krupenie (1972) and K. P. Huber & G. Herzberg (1979). The remaining parameters are allowed to vary freely in the non-linear least-squares fit. The dispersion coefficient C_6 is similarly held constant at the value $C_6 = 2.95 \times 10^5 E_h \text{ cm}^{-6}$ introduced above. Once a stable parametrization of the polynomial coefficients β_i is obtained, further curves are fitted, as outlined below, and finally the parameters r_e , D_e , and T_e are allowed to vary freely only after no further improvement in the residuals can be achieved by varying other, empirically determined, parameters. We note that the final parametrization of the state $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$, is remarkably consistent with the parametrization obtained from the *ab initio* data, with a mean difference in the absolute value of the potential across the 1001 vibrational grid-points of just 0.0022 per cent, 0.13 per cent, and 0.18 per cent for the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states, respectively.

As outlined previously, the MARVEL data set used to perform the empirical refinement contains no data about the Π states. The PECs for these states must therefore be excluded from the

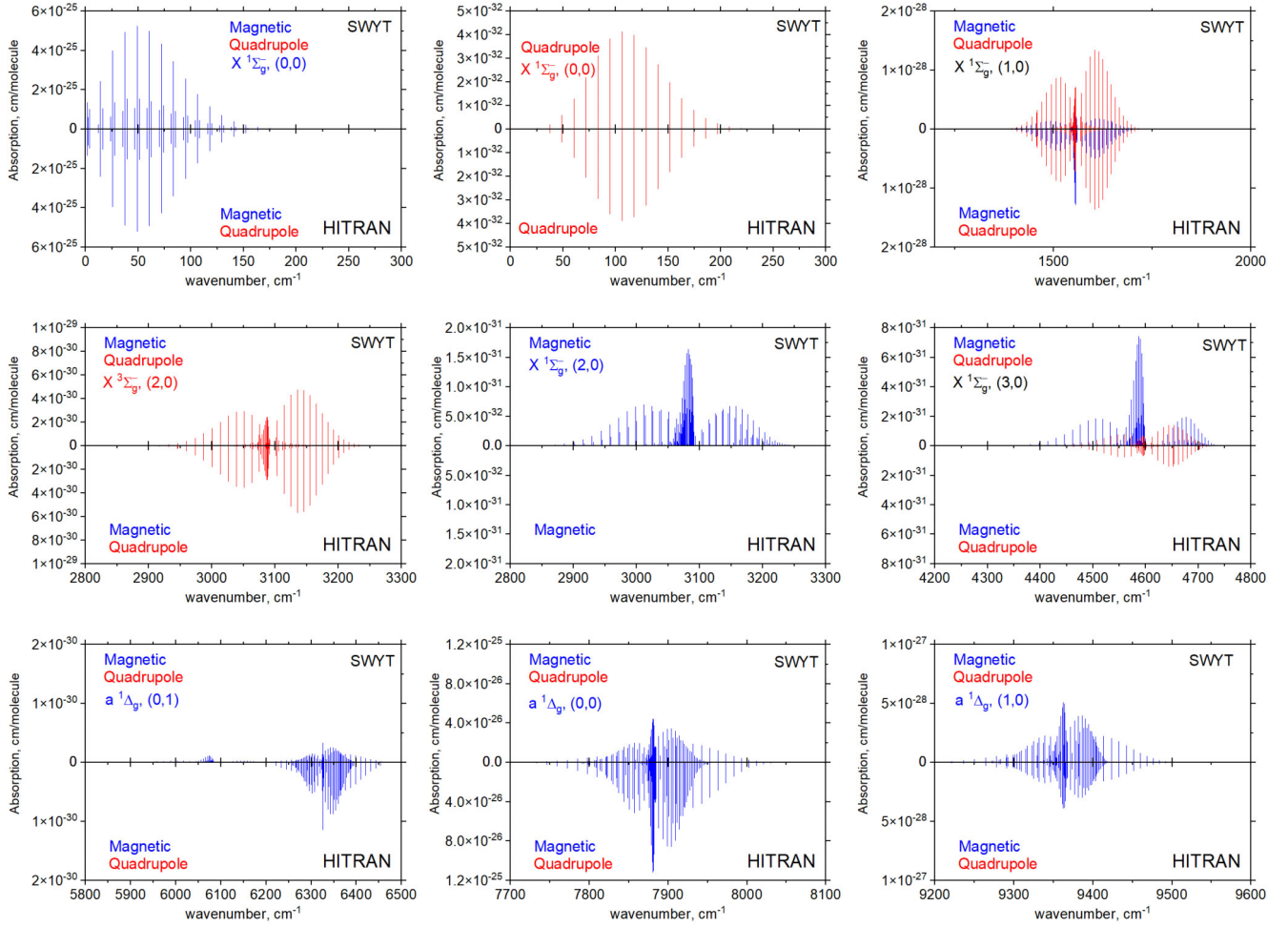


Figure 12. Magnetic and quadrupole intensities at $T = 296$ K: SWYT versus HITRAN 2024 (I. E. Gordon et al. 2026).

refinement procedure, and they are represented in the empirical model by the same PECs presented above. The close agreement of the empirical and *ab initio* PECs for the three low-lying states suggests that the Multireference Configuration Interaction (MRCI) calculations provide an accurate characterization of these properties. We can reasonably expect the parametrization of the $I^1\Pi_g$, $\Pi^1\Pi_g$, $I^3\Pi_g$, and $\Pi^3\Pi_g$ to be similarly accurate. Moreover, none of the bands of interest involve the Π states directly, and so we expect that small errors in their energies will not significantly impact the predicted line positions.

3.1.2 Spin-spin curves

Once a reasonable fit to the state energies has been obtained by varying the parameters of the MLR PECs, one can begin to refine the model by varying the parameters of some coupling curves that contribute to the state energies. Particularly important in predicting the line positions of the $X^3\Sigma_g^-$ state rovibronic transitions is the magnitude of the spin splitting for this state. To obtain a good qualitative characterization of the spin splitting in the $X^3\Sigma_g^-$, the parameters of this coupling curve can be varied freely whilst fitting exclusively the energies of the spin sublevels in the $X^3\Sigma_g^-$ state. Since the MARVEL data set includes only the quantum numbers J , N , and v , the assignment of the Σ quantum

numbers, which are required to perform the DUO refinement, is done according to the energy ordering of the three spin sublevels for a given J state. To obtain good agreement with the MARVEL data set, a first-order Šurkus polynomial of the form given by equation (7) is used.

3.1.3 Spin-orbit curves

The SOC plays an important role in determining both the energy levels and transition intensities of the $^{16}\text{O}_2$ infrared system. This is especially true of the $X^3\Sigma_g^- - b^1\Sigma_g^+$ SOC, which has a strong effect on the energies of the $X^3\Sigma_g^-$ and $b^1\Sigma_g^+$ states, and on the intensity of the $\Delta M = 0$ $X^3\Sigma_g^- - b^1\Sigma_g^+$ band (W. Somogyi et al. 2024). A good fit is found without recourse to varying the parameters of the spin-orbit curves relative to those obtained by fitting to the *ab initio* data, see Fig. 2.

3.1.4 Electronic-angular-momentum curves

The primary role of the L_x and L_y EAMCs in the infrared system of $^{16}\text{O}_2$ is their contribution to the intensities of these transitions via the magnetic dipole moments outlined above. However, they also play a role in determining the energy of the states involved.

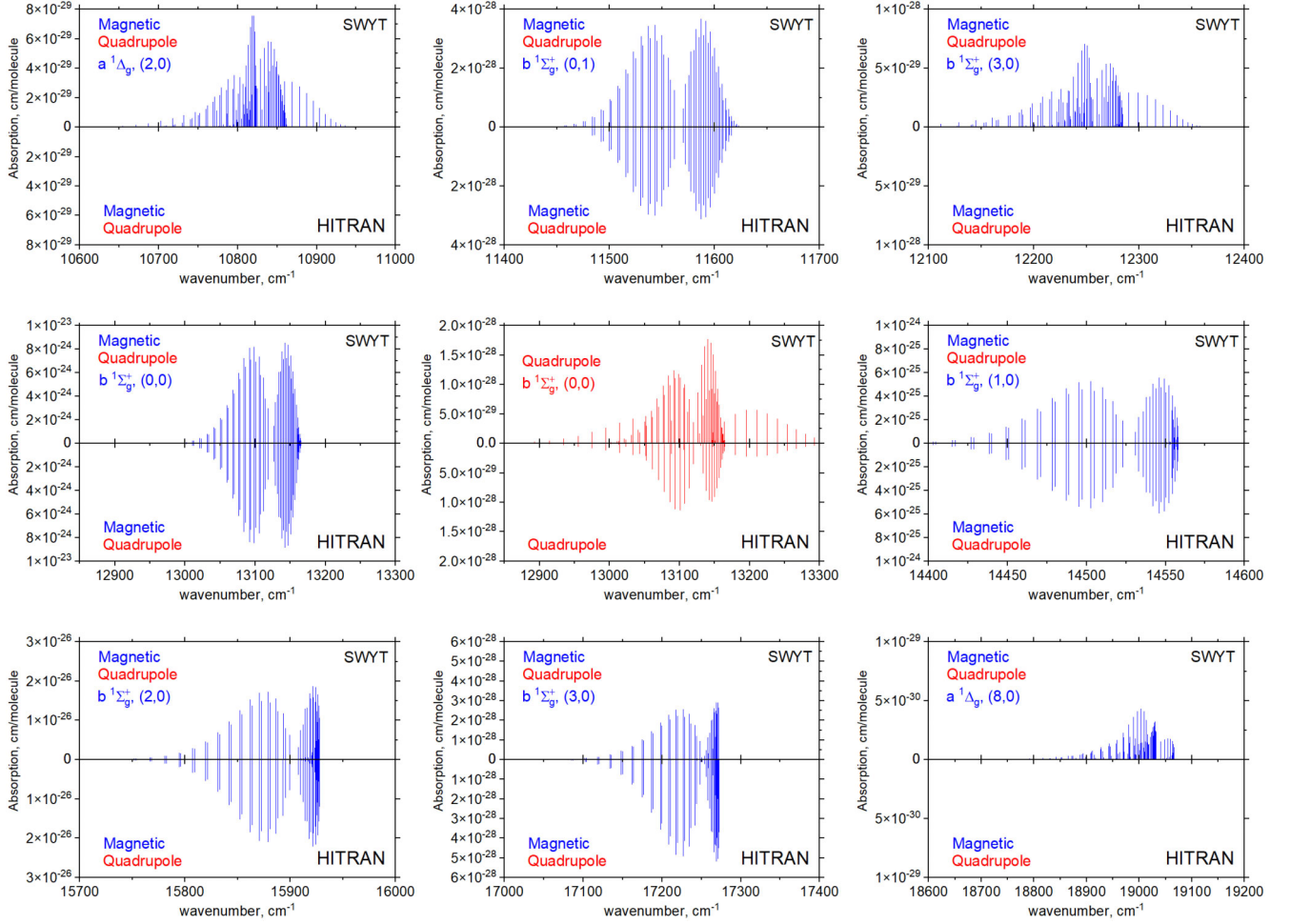


Figure 13. Magnetic and quadrupole intensities at $T = 296$ K: SWYT versus HITRAN 2024 (I. E. Gordon et al. 2026).

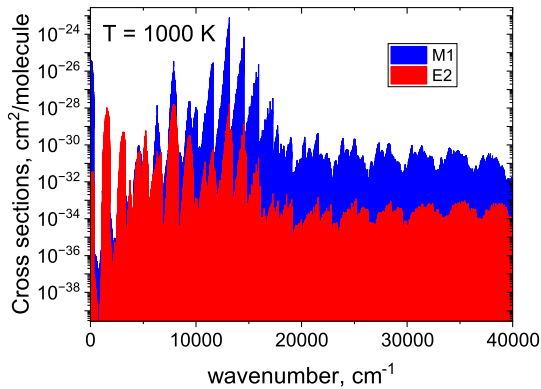


Figure 14. Illustration of the plateau in the absorption E2 and M1 intensities of ¹⁶O₂ computed using the SWYT line list (the X, a, and b system) at $T = 1000$ K appearing at high excitation overtones above $20\,000\text{ cm}^{-1}$.

Specifically, the coupling of the electronic orbital angular momentum with the rotational motion of the nuclei results in so-called Λ -doubling, in which the $\pm\Lambda$ degeneracy of states with $|\Lambda| > 0$ is lifted. In the case of ¹⁶O₂, this Λ -doubling effect is small, particularly for the $a^1\Delta_g$ state (I. V. Khudiyakov & B. F.

Minaev 2021). None the less, it is important to highlight the dual role that these coupling curves play in the spectroscopic model, as it means that changes to the EAMCs in order to improve the prediction of state energies will also have implications for the intensity calculations, and vice versa. The EAMCs of O₂ are shown in Fig. 2.

Our final refined spectroscopic model reproduces the 1855 MARVEL rovibronic energies for $J \leq 86$ with a root-mean-square (rms) error of 0.26 cm^{-1} with 32 parameters varied. A visual representation of the quality of the fit is given in Fig. 5, where the individual obs. – calc. residuals (cm^{-1}) grouped by their electronic states are plotted against the rotational quantum number J . It is important to recall that our spectroscopic model was obtained by fitting to the MARVEL energy values based on the pure experimental transition data with a limited coverage of rotational and vibrational excitations, supplemented with a few ‘Magic numbers’ (see Section 3), i.e. with no EH-based energies included. In Fig. 5, we also compare our calculated term values with the extended set of MARVEL energies from T. Furtenbacher et al. (2019), which contains a large portion of values based on the EH data of ¹⁶O₂ with a much more extended coverage of vibrations and rotations. The EH-based MARVEL values rather badly diverge from our calcula-

tions, up to hundreds of wavenumbers especially at high v and J excitations.

All potential parameters as well as other parameters defining the refined spectroscopic model of $^{16}\text{O}_2$ and discussed below are given in the supplementary material in the form of a DUO input file.

4 INTENSITY CALCULATIONS

4.1 Selection rules

The rovibronic selection rules for the magnetic dipole transitions are

$$\Delta J = J_f - J_i = 0, \pm 1, \quad (8)$$

while the EQ transitions satisfy

$$\Delta J = J_f - J_i = 0, \pm 1, \pm 2. \quad (9)$$

In both cases, the parity selection rules are

$$p' = +1 \leftrightarrow p'' = +1, \quad p' = -1 \leftrightarrow p'' = -1, \quad (10)$$

$$g \leftrightarrow g \quad u \leftrightarrow u. \quad (11)$$

Our spectroscopic model consists of gerade (g) electronic states only. In terms of the rotationless parities e/f , the selection rules are

$$\Delta J = -2, 0, 2 \text{ (O, Q, S)} : e \leftrightarrow e \text{ or } f \leftrightarrow f \quad (12)$$

$$\Delta J = -1, 1 \text{ (P, R)} : e \leftrightarrow f \text{ or } f \leftrightarrow e. \quad (13)$$

For symmetric isotopologues of oxygen with zero oxygen nuclear spin ($^{16}\text{O}_2$ and $^{18}\text{O}_2$), only ortho $\leftrightarrow$ ortho transitions occur with the corresponding nuclear statistics factor $g_{\text{ns}} = 0$ for the non-existent ‘para’ states, see Table 1, while for $^{17}\text{O}_2$ with a non-zero oxygen nuclear spin, the nuclear-spin selection rules become:

$$\text{ortho} \leftrightarrow \text{ortho}, \quad \text{para} \leftrightarrow \text{para}.$$

For asymmetric isotopologues, the e/f selection rule is general for all M1 and E2 allowed transitions and therefore still holds. The nuclear-spin degeneracy factors for the isotopologues considered in this work are summarized in Table 1.

4.2 Empirical adjustment of intensities

As part of the building of the empirical spectroscopic model, we aim to improve the calculated intensities of $^{16}\text{O}_2$. Toward this end and with the intention to introduce as little modifications to the *ab initio* curves as possible, we apply a non-uniform morphing to the EQMC and EAMC curves involved. For the morphing function, the form given by equation (5) is used with single expansion parameters B_0 , which are manually adjusted band-by-band by comparing the calculated intensities with the intensity from HITRAN 2024 (I. E. Gordon et al. 2026, $T = 296$ K). The morphing function specified by these parameters has the essential effect of scaling the curve around the equilibrium bond length, with the scaling approaching unity away from this point. The DUO program does not currently provide support for fitting curves to the transition intensities, and so the morphing expansion parameters were chosen manually to reproduce the expected intensity of known transitions.

The EQ moment intensities are formed by the quadrupole moments (diagonal and non-diagonal) as well as different SOCs. The final adjustment is summarized as follows: the diagonal EQ

matrix elements of $a^1\Delta_g$ and $b^1\Sigma_g^+$ were reduced by a factor of 1.5; the non-diagonal EQ matrix element $\langle b^1\Sigma_g^+ | Q_{+2}^{(2)} | a^1\Delta_g^- \rangle$ was scaled by 1.4.

M. Gancewski et al. (2025) recently reported an accurate *ab initio* permanent EQ curve for the $X^3\Sigma_g^-$ of O_2 computed using a high level of theory (MRCI/d-aug-cc-pV6Z), which is compared to our *ab initio* EQ curve in Fig. 6. Their EQ was shown to accurately reproduce the E2 intensities of $^{16}\text{O}_2$ from the HITRAN 2020 data base (I. E. Gordon et al. 2022). In Fig. 7, we compare E2 intensities of $^{16}\text{O}_2$ for four lowest vibrational bands computed using our EQ curve and that by M. Gancewski et al. (2025) as well as to the intensities from HITRAN 2024 (I. E. Gordon et al. 2026). Even a relatively small difference in the EQ curves leads to drastic changes of the E2 intensities. Considering that the EQ curve of M. Gancewski et al. (2025) gives better agreement with the E2 intensities for these bands, we have used this EQ moment as part of the SWYT spectroscopic model. Before inclusion into the DUO model, this EQ curve was represented by an analytic function of the polynomial decay type as in equation (5).

For the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ M1 band, the main contributions to the magnetic dipole line strengths are composed of spin and orbital angular momenta (W. Somogyi et al. 2024), including $\langle X^3\Sigma_{g,0}^- | H_{\text{SO}} | b^1\Sigma_g^+ \rangle$, $\langle \zeta^1\Pi_g | H_{\text{SO}} | X^3\Sigma_{g,1}^- \rangle$, $\langle b^1\Sigma_g^+ | \hat{L}_{\pm 1} | \zeta^1\Pi_g \rangle$, $\langle \xi^3\Pi_{g,0} | H_{\text{SO}} | b^1\Sigma_g^+ \rangle$, and $\langle \xi^3\Pi_{g,0} | \hat{L}_{\pm 1} | X^3\Sigma_{g,1}^- \rangle$, where $\zeta = \text{I or II}$. One of the dominant contributions here is the spin matrix element $\langle X^3\Sigma_{g,0}^- | \hat{S}_{\pm 1} | X^3\Sigma_{g,1}^- \rangle$ corresponding to the spin-flip transitions between the $\Sigma = 0$ and ± 1 sublevels of the $X^3\Sigma_g^-$ state through SOC between the $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ states $\langle X^3\Sigma_{g,0}^- | H_{\text{SO}} | b^1\Sigma_g^+ \rangle$. The *ab initio* EAMCs presented above indicate that the strongest EAM contribution to the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ magnetic dipole bands arises from the magnetic moment between the $X^3\Sigma_g^-$ and $\Pi^3\Pi_g$ states, which lends intensity via the strong SOC between the $\Pi^3\Pi_g$ and $b^1\Sigma_g^+$ states. The initial *ab initio* model of O_2 underestimates the strength of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ magnetic dipole transitions, see W. Somogyi et al. (2024). The magnetic dipole band $a^1\Delta_g - X^3\Sigma_g^-$ band is considerably weaker and is mainly govern by the EAMCs $\langle a^1\Pi_g | \hat{L}_{\pm 1} | \zeta^1\Pi_g \rangle$ and $\langle \zeta^3\Pi_g | \hat{L}_{\pm 1} | X^3\Sigma_g^- \rangle$ ($\zeta = \text{I or II}$).

The $X^3\Sigma_g^- - X^3\Sigma_g^-$ magnetic dipole line strength is a result of two magnetic dipole moments $\langle X^3\Sigma_{g,1}^- | \hat{S}_{\pm 1} | X^3\Sigma_{g,0}^- \rangle$ and $\langle X^3\Sigma_{g,\Omega}^- | \hat{S}_z | X^3\Sigma_{g,\Omega}^- \rangle$ (W. Somogyi et al. 2024), both originate from matrix elements of the spin operator $\hat{S}$ on the rovibronic eigenfunctions. Thus, the $X^3\Sigma_g^- - X^3\Sigma_g^-$ M1 intensities only indirectly depend on the spectroscopic model through the associated wavefunctions and are difficult to modify. We therefore do not perform any scaling of the model to improve the M1 intensities of the $X^3\Sigma_g^- - X^3\Sigma_g^-$ system.

After testing different scaling factors, the closest match with HITRAN 2024 was achieved by setting B_0 for two EAMCs $\langle a^1\Delta_g | \hat{L}_+ | \Pi^1\Pi_g \rangle$ and $\langle X^3\Sigma_g^- | \hat{L}_+ | \Pi^3\Pi_g \rangle$ in equation (5) to 1.4.

5 LINE LIST PRODUCTION

Using our empirical spectroscopic model of $^{16}\text{O}_2$, which includes refined, scaled and non-scaled *ab initio* curves detailed above, rovibronic line lists SWYT for $^{16}\text{O}_2$ and its five isotopologues

(¹⁷O₂, ¹⁸O₂, ¹⁶O¹⁷O, ¹⁶O¹⁸O, and ¹⁷O¹⁸O) covering the infrared and visible region and transitions between three electronic states $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ were computed using the DUO functionality for the EQ (W. Somogyi, S. N. Yurchenko & A. Yachmenev 2021) and magnetic dipole (W. Somogyi et al. 2024) spectra and the empirical spectroscopic model constructed above. The line lists include transitions between all states with energy below 20 000 cm⁻¹ and the rotational excitations up to $J = 180$. In solving the nuclear Schrödinger equation, a vibrational sinc-DVR (Discrete Variable Representation) basis set for each electronic state is defined on a grid of 1001 points in the range 0.90–3.00 Å. The vibronic basis sets are then truncated to the lowest 40 vibrational levels in the case of the $X^3\Sigma_g^-$, $a^1\Delta_g$, and $b^1\Sigma_g^+$ states, and to the lowest 100 vibrational levels for the $\Pi^1\Pi_g$, $\Pi^3\Pi_g$, $I^1\Pi_g$, and $I^3\Pi_g$ states. A large number of vibrational basis functions in the weakly bound and dissociative Π states are required to represent the coupling to the continuum states above the dissociation energy (W. Somogyi et al. 2024). These were important both for the M1 and E2 intensities.

Table 2 provides statistics for the line lists produced showing the number of states and lines in each isotopologue line list. An ExoMOL line list consists of a States file (see an extract for ¹⁶O₂ in Table 3) containing rovibronic energy term values, quantum numbers, lifetimes and uncertainties, Transition files, containing Einstein A coefficients (see an extract in Table 4) and a partition function file containing temperature-dependent values of the partition function. The magnetic dipole and EQ transitions are computed and stored in two separate files, distinguished by suffixes in the filenames __M1 and __E2, respectively.

The ¹⁶O₂ partition function computed using the energies from the SWYT line list using the standard methodology of Boltzmann summed populations of states is shown in Fig. 8, where it is compared to a very recent partition function of R. R. Gamache et al. (2025) used for the HITRAN 2024 compilation and a partition function by P. S. Barklem & R. Collet (2016). The SWYT partition function matches closely the latter, while TIPS 2024 appears to significantly underestimate the SWYT values at high temperatures (above 1000 K). Such behaviour is usually a reflection of the incompleteness of the states used to evaluate the partition function; similar behaviour has been noted for other TIPS partition sums (R. Wang et al. 2023).

Opacities for ¹⁶O₂ and its minor isotopologues were computed for the four radiative transfer codes ARCIS (M. Min et al. 2020), TAUREX (A. F. Al-Refaie et al. 2021), NEMESIS (P. G. J. Irwin et al. 2008), and PETITRADTRANS (P. Mollière et al. 2019) using the EXOMOLOP procedure (K. L. Chubb et al. 2021) and are available from the EXOMOL data base at www.exomol.com.

6 SPECTROSCOPIC ILLUSTRATIONS

In the following, we present O₂ spectra computed using the SWYT line lists. Fig. 9 illustrates the relative importance of the spectral contributions of three main O₂ isotopologues in the region below 20 000 cm⁻¹ when using their natural abundances at $T = 1000$ K as an example. For ¹⁶O¹⁸O (the second most abundant isotopologue), the intensities are about 1000 times weaker than those of ¹⁶O₂ at terrestrial abundances.

Fig. 10 compares the M1 and E2 contributions to the cross-sections of O₂ computed at $T = 1000$ K for ¹⁶O₂ and also illustrates the temperature dependence of the O₂ absorption by showing cross-sections of ¹⁶O₂ at $T = 296$ K and 2000 K.

In order to illustrate the accuracy of the SWYT line list, both in terms of its intensities and line positions, Fig. 11 compares room temperature ($T = 296$ K) M1 and E2 spectra computed using SWYT to the known accurate data from the HITRAN 2024 data base (I. E. Gordon et al. 2026) covering the region below 20 000 cm⁻¹. There is generally good agreement with HITRAN both for E2 and M1 although some weaker bands require more work. More detailed, band-by-band, comparisons of these $T = 296$ spectra are presented in Figs 12 and 13, showing spectral shapes for individual strong spectral features. While the shapes and orders of magnitude are reasonably well reproduced, the majority of the highly excited overtones require improvement of the associated magnetic dipole and EQ moment curves. This work is ongoing.

It is interesting that for ¹⁷O₂, the lowest energy, or ZPE, is in the $J = 1$ para state ($v = 0$, $\Omega = 0$, $f, p = -1$), while for ¹⁶O₂ and ¹⁸O₂, for which para states do not exist, ZPE corresponds to the $J = 0$ ortho state ($v = 0$, $\Omega = 0$, $e, p = +1$). The ZPE states of ¹⁶O¹⁷O, ¹⁶O¹⁸O, and ¹⁷O¹⁸O are $J = 1 f$ ($v = 0$, $\Omega = 0$, $p = -1$).

Fig. 14 shows E2 and M1 spectra at $T = 1000$ K for ¹⁶O₂ for high overtone excitations ($v < 40$) covering the wavenumber range up to 40 000 cm⁻¹ (≥ 250 nm). The spectra exhibit the plateau-like behaviour above 20 000 cm⁻¹ which is usually considered an indication of numerical errors (E. S. Medvedev et al. 2016). Following the general recommendations to deal with such errors, we have converted all relevant curves into analytic functions, but with no significant impact on these intensities. We have also applied a cut-off of 10^{-8} ea₀² to all EQ transition matrix elements and a cut-off of 10^{-8} $\hbar$ to the ‘transition’ matrix elements of EAMs, also with no significant impact. The intensities were found to be affected by the integration range: changing $r_{\max}$ from 3 to 10 Å led to a significant increase of the plateaued E2 intensities by about three orders of magnitude.

7 CONCLUSIONS

We present SWYT, a new set of comprehensive variational line lists for all six isotopologues of molecular oxygen (¹⁶O₂, ¹⁷O₂, ¹⁸O₂, ¹⁶O¹⁷O, ¹⁶O¹⁸O, and ¹⁷O¹⁸O) generated as part of the EXOMOL project. The line lists cover the wavenumber range 0–20 000 cm⁻¹ and are designed for applications at temperatures up to 5000 K. To our knowledge, SWYT represents the first EXOMOL release to provide a full treatment of oxygen opacity driven by magnetic dipole (M1) and EQ (E2) transitions, delivering a unified description of the infrared bands of the O₂ $X^3\Sigma_g^-$ – $a^1\Delta_g$ – $b^1\Sigma_g^+$ system.

The line lists were computed using a fully coupled multistate model implemented in the nuclear-motion program DUO. Our starting point was a high-level *ab initio* set of potential energy, coupling, and transition-moment curves, including the excited Π -state manifold responsible for intensity borrowing in the infrared bands. The spectroscopic model was empirically refined to reproduce experimentally derived MARVEL energies for the X, a, and b states, yielding an accurate description of rovibronic term values across a wide range of v and J . In addition, key coupling and quadrupole-moment curves were adjusted to reproduce laboratory intensities from HITRAN 2024 (I. E. Gordon et al. 2026), providing improved line strengths for the principal infrared bands at room temperature while retaining a physically motivated model for extrapolation to high temperatures.

We provide partition functions, state lifetimes, and complete DUO input files alongside the transition and states files, ensur-

ing full reproducibility and facilitating future refinement as new laboratory or astronomical constraints become available. The resulting SWYT line lists enable robust modelling of O₂ absorption in diverse environments, including planetary and exoplanetary atmospheres, brown dwarfs and late-type stars, and other high-temperature astrophysical settings where oxygen may contribute to the opacity through weak but pervasive M1 and E2 features. For some of the terrestrial atmospheric applications with more stringent requirements for the accuracy of intensities, our spectroscopic model and the associated line lists for O₂ will require further work.

Future work should focus on further improving the weakest bands and on extending the experimental constraints that underpin intensity borrowing, in particular through new high-accuracy measurements and analyses of transitions that probe the coupling to the excited Π states. The SWYT data sets reported here provide a comprehensive baseline for these developments and are available from the EXOMOL data base (www.exomol.com).

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CONFLICTS OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY

The states, transitions, opacity, and partition function files for the O₂ line lists can be downloaded from www.exomol.com. The open access programs DUO and EXOCROSS are available from github.com/exomol. Other data are contained within the article and its supplementary material.

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SUPPLEMENTARY MATERIAL

Supplementary material is available at *MNRAS* online.

This includes (i) the spectroscopic model in the form of the DUO input file, containing all the curves and parameters as well

as the experimentally derived energy term values of ¹⁶O₂ used in the fit.

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