

ExoMol line lists – LXX. The CO fourth positive band system

Chenyi Tao ¹, Nariman Abu El Kher,² Nayla El-Kork,² Sergei N. Yurchenko ¹ and Jonathan Tennyson ¹★

¹Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

²Department of Physics, Khalifa University, Abu Dhabi, PO. Box 127788, United Arab Emirates

Accepted 2026 May 20. Received 2026 May 18; in original form 2026 March 29

ABSTRACT

A high-temperature line list is provided for the $^{12}\text{C}^{16}\text{O } A^1\Pi-X^1\Sigma^+$ electronic band system, commonly referred to as the fourth positive (4thplus) system, the most extensively studied excited electronic system of carbon monoxide (CO). A new high-accuracy spectroscopic model for the ground $X^1\Sigma^+$ and excited $A^1\Pi$ states is presented, based on *ab initio* calculations performed at the aug-cc-pV5Z CASSCF/icMRCI+Q level of theory. The resulting potential energy curves and transition dipole moment functions were further refined using the DUO program in conjunction with available MARVEL (measured active rotational–vibrational energy levels) empirical energy levels to improve the accuracy of the final line list. Using the refined .states and .trans files, the comprehensive 4thplus line list contains CO 4thplus transitions and updated rotation–vibration transitions within the $X^1\Sigma^+$ ground state. Comparisons with several high-resolution experimental spectra demonstrate very good agreement in both line positions and band structures, confirming the reliability of the present spectroscopic model. The 4thplus line list is available from www.exomol.com.

Key words: molecular data – opacity – stars: atmospheres – ultraviolet: general.

1 INTRODUCTION

Carbon monoxide (CO) is the second most abundant molecule detected in the Universe after H_2 and plays a fundamental role in astrophysics, cosmology, molecular physics, and the chemistry of planetary atmospheres. Many accurate line lists are available that represent CO spectroscopy at long wavelengths where transitions involve vibrational and/or rotational excitations within the $X^1\Sigma^+$ electronic ground state of the molecule. However, while some older, partial line lists exist (S. G. Tilford & J. D. Simmons 1972; D. C. Morton & L. Noreau 1994), there remains a surprising lack of reliable line lists for the electronic (rovibronic) transitions in CO, which lie in the ultraviolet. Here, we provide a comprehensive line list for the so-called fourth positive (4thplus) band of CO, which is given by the fundamental (lowest allowed) electronic transition in CO, the $A^1\Pi-X^1\Sigma^+$ band system. This line list is integrated with a newly calculated rovibrational line list comprising $X^1\Sigma^+-X^1\Sigma^+$ infrared transitions. We call this new line list 4thplus. We note that during the completion of this work, two *ab initio* line lists considering CO vibronic transitions, due to B. Shang et al. (2026) and S. Zhang, W. Chen & L. Liu (2026), were published; these line lists will be considered further below.

Emissions by the $A^1\Pi-X^1\Sigma^+$ band system are known to follow electron collisions with the CO molecule (R. A. Lee et al. 2021). This leads to such transitions being commonly observed in plasmas (S. D. McGuire et al. 2020), from which the band gets the

name 4thplus. This process also leads to observable $A^1\Pi-X^1\Sigma^+$ emissions in both Venus and Mars (P. D. Feldman et al. 2000) and it is a focus of current space-based observations of Mars’ atmospheric spectrum (F. H. Lootah et al. 2022; J. S. Evans et al. 2024). $A^1\Pi-X^1\Sigma^+$ absorption spectra have been observed against starlight in the interstellar medium (Y. Sheffer et al. 1992) and the Red Rectangle (R. J. Glinski et al. 1996). CO is a major component of cool star atmospheres; its $A^1\Pi-X^1\Sigma^+$ spectrum is prominent in the Sun’s atmosphere and in penumbra (G. D. Sandlin et al. 1986); it has been extensively studied in the atmospheres of cooler stars using the *Hubble Space Telescope* (T. Pal et al. 2023) and the *International Ultraviolet Explorer* (T. R. Ayres 1986). The $A^1\Pi-X^1\Sigma^+$ band system has also been proposed as suitable for studying cosmological drift in the proton–electron mass ratio by E. J. Salumbides et al. (2012).

The electronic spectrum of CO has been very extensively studied in the laboratory. We have recently completed a comprehensive MARVEL (measured active rotational–vibrational energy levels) analysis of rovibronic spectra involving states lying below the CO dissociation limit, which includes the $A^1\Pi$ state (N. El-Kork et al., in preparation); this work provides a comprehensive summary of these laboratory studies, some of which are considered below.

Here we extend the ExoMol database (J. Tennyson et al. 2024) by considering the $A^1\Pi-X^1\Sigma^+$ 4thplus band of $^{12}\text{C}^{16}\text{O}$. Recently, M. Khalil et al. (2024) produced an extensive set of *ab initio* potential energy curves (PECs) and associated dipole transition moments for the low-lying electronic states of CO; this work explicitly focused on the four lowest allowed electronic bands of CO.

* E-mail: j.tennyson@ucl.ac.uk

Here we adopt their $A^1\Pi$ curves as the starting point of our treatment of the $A^1\Pi$ - $X^1\Sigma^+$ band. At the same time, we have taken the opportunity to improve our representation of infrared transitions within the $X^1\Sigma^+$ state of $^{12}\text{C}^{16}\text{O}$. Currently, the ExoMol project uses the calculated line list of G. Li et al. (2015). While this line list is generally considered to be very reliable, there has been considerable work improving both the $X^1\Sigma^+$ PEC (V. V. Meshkov et al. 2018, 2022; H.-j. Chen, W. Fang & J.-w. Zhang 2023; J. Koput 2024; D. P. Usov et al. 2024) and associated dipole moment curve (DMC; K. Bielska et al. 2022; E. S. Medvedev & V. G. Ushakov 2022; V. V. Meshkov et al. 2022; A. A. Balashov et al. 2023; J. Koput 2025; J.-K. Li et al. 2025; N. F. Zobov et al. 2025). Comprehensive MARVEL studies have also recently been performed for the $X^1\Sigma^+$ energy levels of $^{12}\text{C}^{16}\text{O}$ (S. Mahmoud et al. 2025) as well as its isotopologues (T. Grigorev et al. 2026). We have therefore taken the opportunity to update our $X^1\Sigma^+$ - $X^1\Sigma^+$ line list, allowing us to present a new combined line list suitable for studying $^{12}\text{C}^{16}\text{O}$ transitions in the infrared and for the $A^1\Pi$ - $X^1\Sigma^+$ band system; we call this new line list 4thplus.

2 THEORY AND METHODS

2.1 *Ab initio* calculations

As in previous work (L. Peng-Fei et al. 2013; D.-H. Shi et al. 2013; M. Zhang & D. Shi 2021; V. V. Meshkov et al. 2023; M. Khalil et al. 2024; P. Wei et al. 2024; I. M. Savelyev et al. 2025), PECs and transition dipole moments (TDMs) are utilized to determine the rovibronic eigenstates and spectral properties of the CO molecule. In this study, MOLPRO is used to obtain a comprehensive description of the electronic structure of CO. In more detail, all PECs and TDMs were computed using the MOLPRO 2020.2 program package. In principle, CO belongs to the $C_{\infty v}$ point group. However, as MOLPRO supports only abelian point group symmetries, calculations for molecules possessing degenerate electronic states must be carried out using an appropriate abelian subgroup (D.-H. Shi et al. 2013). Consequently, all MOLPRO calculations in this work were performed employing the C_{2v} point group symmetry.

The PECs and TDMs for each electronic state were primarily computed using the complete active space self-consistent field (CASSCF) method within the MOLPRO framework. The CASSCF wavefunctions were used as reference functions for subsequent Davidson-corrected internally contracted multireference configuration interaction (MRCI+Q) calculations. The MRCI approach has been demonstrated to provide reliable results for a wide range of diatomic molecules and has been successfully applied in numerous recent studies (D.-H. Shi et al. 2010, 2011a, b, c; X. Zhang et al. 2011). Despite the overall robustness of this methodology, discontinuities and non-smooth behaviour were observed in some regions of the calculated PECs. These artefacts are most likely associated with changes in the character of the active orbitals as the internuclear separation increases, leading to orbital reordering (orbital swapping) during the calculations (A. Dora & J. Tennyson 2020; M. Khalil et al. 2024).

For the MOLPRO electronic structure calculations, an appropriate atomic basis set must be specified. In this work, we consider eight low-lying electronic states of CO and additionally compute the spin-orbit coupling curves between these states, which were not included in the study of M. Khalil et al. (2024). These couplings are required for constructing a fully coupled spectroscopic model within DUO. Although this study focuses on uncoupled-state calculations, the spin-orbit coupling curves were gener-

ated in preparation for future multistate modelling. Two atomic basis sets were employed: the augmented correlation-consistent polarized valence double-zeta (aug-cc-pVDZ) basis set and the augmented correlation-consistent polarized valence quintuple-zeta (aug-cc-pV5Z) basis set. The aug-cc-pVDZ and aug-cc-pV5Z basis sets differ primarily in their level of completeness, with the aug-cc-pV5Z providing a significantly more flexible and accurate description of the electronic wavefunction compared to the aug-cc-pVDZ. Both basis sets were applied consistently to the carbon and oxygen atoms. The present electronic structure calculations therefore provide a consistent set of PECs and coupling matrix elements required for subsequent spectroscopic modelling and comparison with experimental data, including the MARVEL energy levels used in this work (S. Mahmoud et al. 2025; N. El-Kork et al., in preparation). The aug-cc-pVDZ basis set was initially adopted to conserve computational resources and to ensure the stability and correctness of the calculations prior to extending the study to the larger and higher-quality aug-cc-pV5Z basis set. To mitigate the issues associated with orbital reordering discussed above, only the s , p , and d orbital functions were included in the active space. This restriction not only improves the smoothness of the resulting PECs but also significantly reduces the computational cost.

Using these basis sets, a total of eight electronic states of CO were investigated, namely $X^1\Sigma^+$, $A^1\Pi$, $I^1\Sigma^-$, $d^1\Delta$, $a'^3\Sigma^+$, $a^3\Pi$, $d^3\Delta$, and $e^3\Sigma^-$. All calculations were carried out within the C_{2v} point group symmetry, for which the electronic states were assigned to the irreducible representations A_1 , B_1 , B_2 , and A_2 . Within this symmetry framework, states of Σ^+ symmetry correlate with the A_1 irreducible representation, while Σ^- states correspond to A_2 . Electronic states that are doubly degenerate under the full $C_{\infty v}$ symmetry, such as Π , Δ , and higher angular momentum states, must be represented as combinations of one-dimensional irreducible representations in C_{2v} . Accordingly, Π states are described by the direct sum $B_1 + B_2$, while Δ states correlate with $A_1 + A_2$.

Starting from the closed-shell ground-state electronic configuration ($1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$), the electronic structure calculations were performed within the C_{2v} point group. In the CASSCF calculations, the electrons originate from the $1s^2 2s^2 2p^2 3s 3p$ shells of carbon and the $1s^2 2s^2 2p^4$ shells of oxygen. The $1s$ orbitals of both atoms were kept doubly occupied in all configurations and treated within the frozen-core approximation. This corresponds to four electrons occupying two orbitals, represented by the frozen-core occupation vector $[2, 0, 0, 0]$. The remaining 10 valence electrons were distributed among 12 active MOs (molecular orbitals), corresponding to the orbital set $[6a_1, 3b_1, 3b_2, 0a_2]$ in the C_{2v} symmetry used by MOLPRO. These orbitals mainly correspond to the valence and near-valence σ and π orbitals derived from the C and O $2s$ and $2p$ atomic orbitals. All excited-state electronic configurations were generated relative to the closed-shell reference configuration in the subsequent CASSCF and MRCI calculations (L. Peng-Fei et al. 2013). This active space, therefore, includes all valence and near-valence orbitals required for an accurate description of the electronic states considered in this work.

To obtain accurate and reliable PECs, the internuclear grid must be sufficiently dense to capture all relevant features of the electronic potentials. In this work, the MOLPRO calculations were performed over an internuclear distance range from 1.0 to 3.0 Å, using a uniform step size of 0.04 Å. This internuclear dis-

tance range was chosen based on previous *ab initio* investigations of CO PECs reported by M. Khalil et al. (2024). Comparison with earlier studies shows that the PECs of the eight electronic states considered here exhibit consistent long-range behaviour, converging smoothly and collectively at internuclear separations of approximately 3.0 Å. As a result, extending the calculations beyond this range would not provide additional physical insight while incurring unnecessary computational cost. The resulting *ab initio* PECs and TDMs obtained from the aug-cc-pV5Z basis set therefore provide a consistent and reliable foundation for the subsequent rovibrational calculations and spectroscopic analysis presented in this study.

2.2 Nuclear motion calculations

Once the electronic structure calculations were completed with MOLPRO, the spectroscopic analysis was performed based on the resulting *ab initio* data. This stage employed the program DUO (S. N. Yurchenko et al. 2016), which computes rovibrational and rovibronic transitions for diatomic molecules by solving the coupled-channel nuclear-motion Schrödinger equation. Here, DUO was used to refine the PECs and generate the molecular line list for the $A^1\Pi-X^1\Sigma^+$ electronic transition. The coupled Schrödinger equation was solved on a uniform grid of 441 points using the sinc DVR (discrete variable representation) basis set, which is the default choice in DUO. The calculations covered an internuclear distance range from 0.8 to 3.0 Å. The upper energy limit was set to 100 000 cm⁻¹, with vibrational quantum numbers up to $v = 50$ included for both the X and A electronic states. Rotational levels were considered for total angular momentum quantum numbers in the range $J = 0-146$.

The PECs of both electronic states form the main input to DUO. For the ground $X^1\Sigma^+$ state, the PEC was represented using the Morse/Lennard–Jones (MLJ) oscillator form. This functional form provides a flexible and physically motivated description of diatomic molecular potentials and has been widely used in high-accuracy spectroscopic studies (J. A. Coxon & P. G. Hajigeorgiou 2004). The MLJ potential is defined as

$$V(R) = T_e + (A_e - T_e) \left[1 - \left(\frac{R_e}{R} \right)^n \exp \{ -\phi(R) z(R, R_e) \} \right]^2, \quad (1)$$

where T_e is the minimum of the PEC, $A_e - T_e (= D_e)$ represents the depth of the potential well, R is the internuclear distance, and R_e denotes the equilibrium bond length. The exponent n is an integer chosen to reflect the leading inverse-power term governing the long-range interaction. The functions $\phi(R)$ and $z(R, R_e)$ control the detailed shape of the potential and are defined below:

$$\phi(R) = f_{sw}(R) \sum_{m=0}^{\infty} \phi_m z^m + [1 - f_{sw}(R)] \phi(\infty), \quad (2)$$

$$z(R, R_e) = 2 \frac{R - R_e}{R + R_e}. \quad (3)$$

In this formulation, $\phi(R)$ is expressed as a function of the dimensionless Morse-like variable $z(R, R_e)$. The polynomial expansion $\sum_m \phi_m z^m$ describes the short- to intermediate-range behaviour of the potential, while $\phi(\infty)$ enforces the correct asymptotic limit at large internuclear separations. The smooth transition between these two regimes is governed by the switching function $f_{sw}(R)$:

$$f_{sw}(R) = (1 + e^{\delta(R-R_{1/2})})^{-1}. \quad (4)$$

This Fermi–Dirac-type switching function varies continuously between 0 and 1. The parameter δ controls the sharpness of the

transition, while $R_{1/2}$ denotes the internuclear distance at which the switching function reaches 50 per cent:

$$\phi(\infty) = \frac{1}{2} \ln \left(\frac{2D_e R_e^n}{C_n} \right), \quad (5)$$

where D_e is the dissociation energy and C_n is the long-range coefficient, a molecular constant that determines the asymptotic behaviour of the potential at large R .

In general, the initial coefficients of the MLJ potential can be obtained by fitting the *ab initio* PECs calculated in the previous section within the DUO framework. However, in this case, the ground-state PEC of CO has already been modelled with high accuracy by J. A. Coxon & P. G. Hajigeorgiou (2004) using a robust theoretical framework. Accordingly, this study adopts the MLJ coefficients reported in that work as an initial reference. Additionally, the rotational Born–Oppenheimer breakdown (BOB) term was modelled using the DUO polynomial-decay form (L. Prajapat et al. 2017)

$$F(R) = \sum_{k=0}^N B_k z^k (1 - y_p) + y_p B_\infty, \quad (6)$$

with the Šurkus variable y_p defined by

$$y_p(R) = \frac{R^p - R_e^p}{R^p + R_e^p}. \quad (7)$$

The damped coordinate z is given by

$$z = (R - R_e) \exp \left[-\beta_2 (R - R_e)^2 - \beta_4 (R - R_e)^4 \right], \quad (8)$$

where β_2 and β_4 are two damping parameters and B_∞ is constrained to 0. The resulting model reproduces the MARVEL energy levels of $X^1\Sigma^+$ (S. Mahmoud et al. 2025) with a root-mean-square (rms) error of 0.0014 cm⁻¹ and is provided as the Supplementary Material as part of the DUO input file.

A similar fitting strategy was employed for the excited $A^1\Pi$ state; however, in this case, the PEC was represented using the extended Morse oscillator (EMO) functional form, as recommended in previous studies (E. G. Lee et al. 1999; S. N. Yurchenko et al. 2016). The EMO potential is defined as

$$V(R) = T_e + (A_e - T_e) [1 - \exp(-\beta(R)(R - R_e))]^2, \quad (9)$$

where the distance-dependent Morse parameter $\beta(R)$ is expressed as

$$\beta(R) = \sum_{i=0}^{\infty} a_i y_p(R)^i, \quad (10)$$

with the Šurkus variable defined by equation (7). Here, A_e denotes the asymptotic energy limit of the potential, a_i are the expansion coefficients of the power series, and p is an integer parameter controlling the mapping of the internuclear coordinate. The EMO form retains the general structure of a Morse potential while introducing a distance-dependent exponent, thereby providing additional flexibility for accurately describing excited-state PECs.

The procedure used to determine the EMO coefficients was conceptually similar to that adopted for the ground state: the potential was first fitted to the *ab initio* PECs and subsequently refined using the latest MARVEL energy levels. However, unlike the ground-state case, no sufficiently reliable pre-existing analytical model for the $A^1\Pi$ state was available in the literature. As a result, the EMO parameters were initially optimized using a custom PYTHON fitting routine, after which the resulting coefficients

were transferred to DUO for further refinement. Despite this strategy, achieving a satisfactory fit required considerable effort. The final EMO model reproduces the experimental energy levels with an overall rms deviation of approximately 0.82 cm^{-1} for levels up to $v = 20$ and $J = 20$. The main contributions to this deviation arise from two sources. First, spin-orbit interactions affecting the lowest two vibrational levels are not included in the present fitting model, which introduces systematic discrepancies for these states. Secondly, inspection of the MARVEL data set indicates that several energy levels around $v = 14$ are associated with relatively large uncertainties due to the limited number of experimental sources available for these assignments. The optimized EMO coefficients are provided in the Supplementary Material as part of the DUO input file.

Once analytical potential models had been constructed for both electronic states, additional coupling interactions were introduced within the DUO framework to account for effects that arise in the physical system. For the $A^1\Pi-X^1\Sigma^+$ transition, the dominant coupling mechanisms are Λ -doubling and spin-orbit coupling. However, since this study focuses specifically on the $A^1\Pi-X^1\Sigma^+$ transition and spin-orbit interactions, which are strongly influenced by couplings with neighbouring electronic states, spin-orbit coupling is not included in the current model. A comprehensive treatment incorporating spin-orbit effects and additional electronic states will be presented in a subsequent publication.

Accordingly, only Λ -doubling effects were considered here for the $A^1\Pi$ state. Inspection of the MARVEL energy-level data set reveals small but systematic splittings between levels of opposite parity, with typical magnitudes of approximately 0.01 cm^{-1} . To reproduce this behaviour, a q -type Λ -doubling interaction was included, as this term provides the dominant contribution for $^1\Pi$ states. The resulting parity splitting is approximately given by

$$\Delta E \approx qJ(J+1), \quad (11)$$

where q determines the magnitude of the e/f parity separation. Within DUO, the Λ -doubling parameter $q(R)$ was represented as a polynomial expansion in the displacement from the equilibrium bond length,

$$q(R) = A_0 + A_1(R - R_e) + A_2(R - R_e)^2 + \dots, \quad (12)$$

allowing sufficient flexibility to reproduce the observed parity splittings across the relevant vibrational range. The optimized coefficients defining $q(R)$ are provided in the Supplementary Material.

At this stage, all models, including the PEC models for the $X^1\Sigma^+$ and $A^1\Pi$ states as well as the Λ -doubling treatment, were combined with the TDM curve adopted from J. Cheng, H. Zhang & X. Cheng (2018). This procedure yields the 4thplus line list consisting of two key output files in the ExoMol format (J. Tennyson, C. Hill & S. N. Yurchenko 2013; J. Tennyson et al. 2024): the `.states` file, which contains rovibronic energy levels, uncertainties, lifetimes and quantum numbers, and the `.trans` file, which lists the corresponding transition probabilities in the form of Einstein A coefficients.

Following the generation of these files, further post-processing was carried out to enhance the overall accuracy of the data set. The $X^1\Sigma^+$ rovibronic energy levels calculated in this work were compared with the updated theoretical ground-state line list reported by V. G. Ushakov & E. S. Medvedev (2025), showing excellent agreement with differences typically in the range $0.001\text{--}0.005 \text{ cm}^{-1}$. Further improvement of the present line lists was achieved

through the incorporation of experimental data. The $X^1\Sigma^+$ data set was then systematically compared with experimentally derived energy levels from the MARVEL database (S. Mahmoud et al. 2025) for states with identical quantum numbers, and the corresponding levels were replaced wherever reliable MARVEL values were available. The same procedure was also applied to the $A^1\Pi$ state. In such cases, both the energy levels and their associated uncertainties were taken from the MARVEL data set in place of the theoretical values. This hybrid strategy preserves the predictive capability of the underlying spectroscopic model while incorporating the most accurate experimental information currently available. The average uncertainty of the final calculated energy levels for the $X^1\Sigma^+$ state is approximately 0.002 cm^{-1} , while the mean uncertainty for the $A^1\Pi$ state is about 4.99 cm^{-1} , for levels up to vibrational quantum number $v = 49$ and rotational quantum number $J = 146$.

As part of the 4thplus line list, the partition function of CO as provided is generated as

$$Q(T) = \sum_n g_n^{\text{tot}} e^{-(c_2 \bar{E}_n)/T}, \quad (13)$$

where g_n^{tot} is the total degeneracy of the n th rovibronic level, given by $g_n^{\text{tot}} = g^{\text{ns}}(2J_n + 1)$. Here, g^{ns} is the nuclear-spin statistical weight factor, which equals unity for $^{12}\text{C}^{16}\text{O}$, J_n is the rotational quantum number of the corresponding level, $\bar{E}_n = E_i/(hc)$ is the energy term value expressed in cm^{-1} , $c_2 = hc/k_B$ is the second radiation constant (in cm K), and T is the temperature in Kelvin.

The radiative lifetime of an excited state i is defined as the inverse of the total spontaneous emission probability from that state to all energetically lower states:

$$\tau_i = \left(\sum_f A_{if} \right)^{-1}, \quad (14)$$

where τ_i is the radiative lifetime of state i (can be computed by EXOCROSS), and A_{if} denotes the Einstein A coefficient for spontaneous emission from the initial state i to a lower lying final state f . The summation runs over all dipole-allowed transitions originating from state i , including all accessible rovibronic levels of lower energy.

The Einstein A coefficients are determined from the transition DMCs and the rovibronic wavefunctions obtained from the DUO calculations. As a result, the computed radiative lifetimes provide a sensitive test of both the quality of the electronic TDM and the accuracy of the nuclear-motion wavefunctions. Radiative lifetimes derived in this manner are therefore valuable observables for validating the spectroscopic model against experimental measurements. Furthermore, the calculated lifetimes show good agreement with those obtained using an alternative approach based on the approximate sum rule of A. V. Stolyarov & V. I. Pupyshev (1994).

3 RESULTS AND DISCUSSION

3.1 Potential energy curves

As described in Section 2.1, the *ab initio* PECs were computed using the icMRCI+Q approach implemented in the MOLPRO program package. The resulting PECs were subsequently visualized using PYTHON and are presented in Fig. 1. The calculations span an internuclear distance range from 1.00 to 3.00 Å and include a total of eight electronic states of CO; the corresponding potential

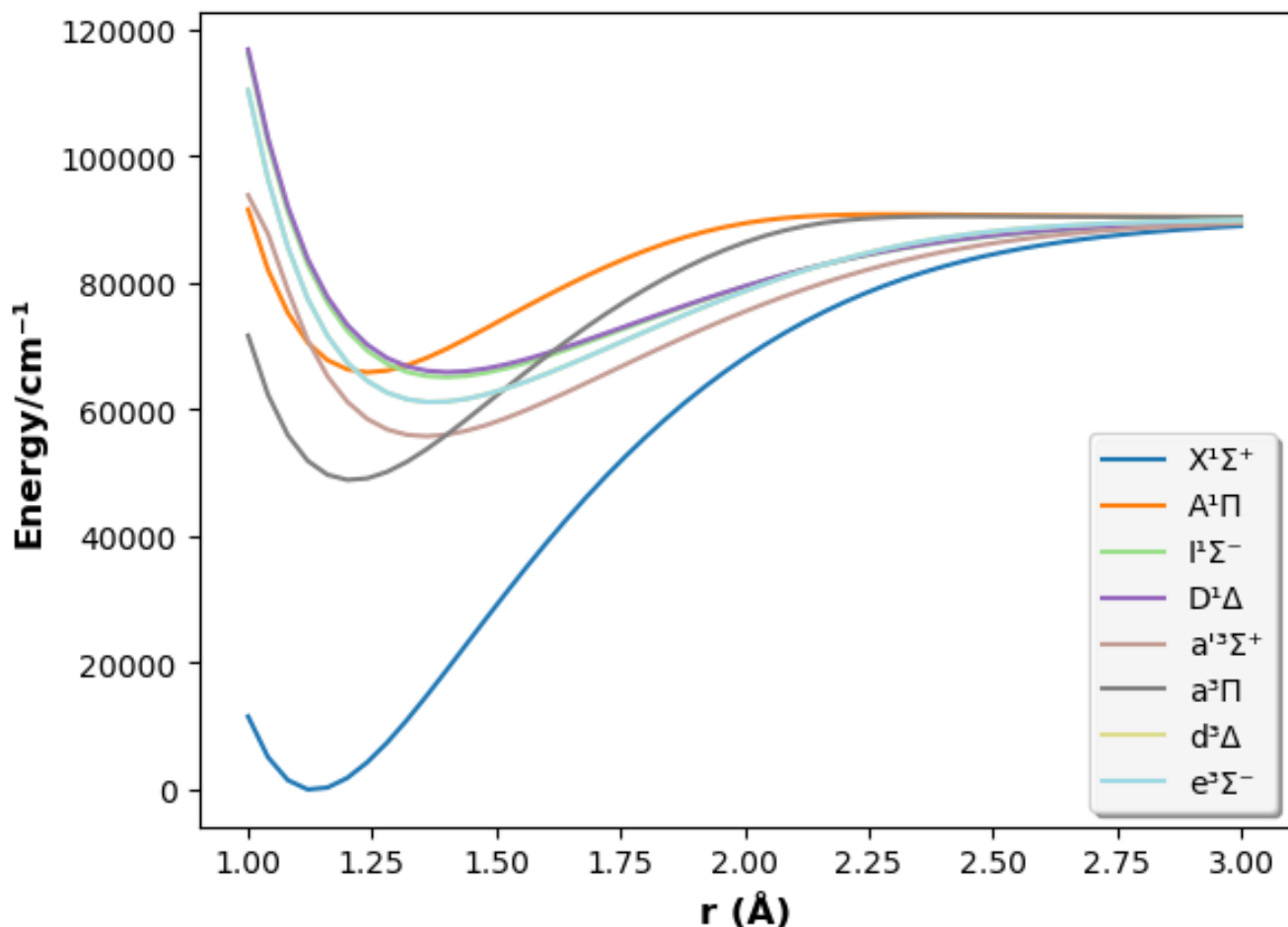


Figure 1. *Ab initio* PECs of the four singlet and four triplet electronic states of CO.

energy values at the selected internuclear distances are provided in the Supplementary Material. As shown in Fig. 1, all PECs exhibit similar qualitative behaviour, characterized by Morse-like potential profiles that converge exponentially towards their respective dissociation limits at large internuclear separations.

By extracting the PECs of the $X^1\Sigma^+$ and $A^1\Pi$ states from Fig. 1, the corresponding curves are shown in Fig. 2. The *ab initio* PECs shown in Fig. 2 indicate that both the X and A states approach the same asymptotic dissociation limit as the internuclear distance increases, with the curves already showing clear convergence around $R \approx 3.0$ Å. At larger internuclear separations, the behaviour of the potentials remains consistent with previously reported *ab initio* calculations (M. Khalil et al. 2024; B. Shang et al. 2026; S. Zhang et al. 2026), indicating that both states continue to approach the correct dissociation limit without introducing additional crossings or irregular features. Motivated by this behaviour, a common dissociation energy was adopted for both states in the construction of the initial fitted PEC models. The initial value of the dissociation energy was taken from the *ab initio* calculations of V. V. Meshkov et al. (2022), yielding $D_e = 90\,679.1$ cm $^{-1}$. The initial MLJ parameters of the $X^1\Sigma^+$ states were taken from J. A. Coxon & P. G. Hajigeorgiou (2004) and then fitted to the MARVEL energies (S. Mahmoud et al. 2025) together with the BOB term introduced above. The optimised MLJ parameters were found to be in close agreement with those reported by J. A. Coxon & P. G.

Hajigeorgiou (2004), thereby reaffirming the robustness and accuracy of their ground-state PEC model. As a result, the ground-state PEC adopted in this work closely follows the functional form and parametrization proposed by J. A. Coxon & P. G. Hajigeorgiou (2004).

The initial work by M. Khalil et al. (2024) involved shifting the PECs prior to their incorporation into DUO. As an improvement, this procedure was omitted in favour of using a refined approach that retains the same basis sets while adopting a different active space. Consequently, the previously published PEC was not adopted, and a new spectroscopic model for the $A^1\Pi$ state was constructed. Using the same dissociation energy as in the ground-state MLJ model did not yield satisfactory agreement with the MARVEL experimental energy levels, suggesting the presence of a finite offset between the asymptotic limits of the $X^1\Sigma^+$ and $A^1\Pi$ states. This offset is consistent with the fine-structure splitting of the $C + O$ dissociation limit.

Accordingly, the dissociation energy of the $A^1\Pi$ state was allowed to exceed that of the ground state. By increasing the asymptotic energy of the $A^1\Pi$ state by several hundred wavenumbers and subsequently refitting the EMO model, a substantial improvement in the agreement with the MARVEL data was achieved. The rms deviation was thereby reduced from approximately 8.24 to 0.82 cm $^{-1}$ for energy levels with vibrational and rotational

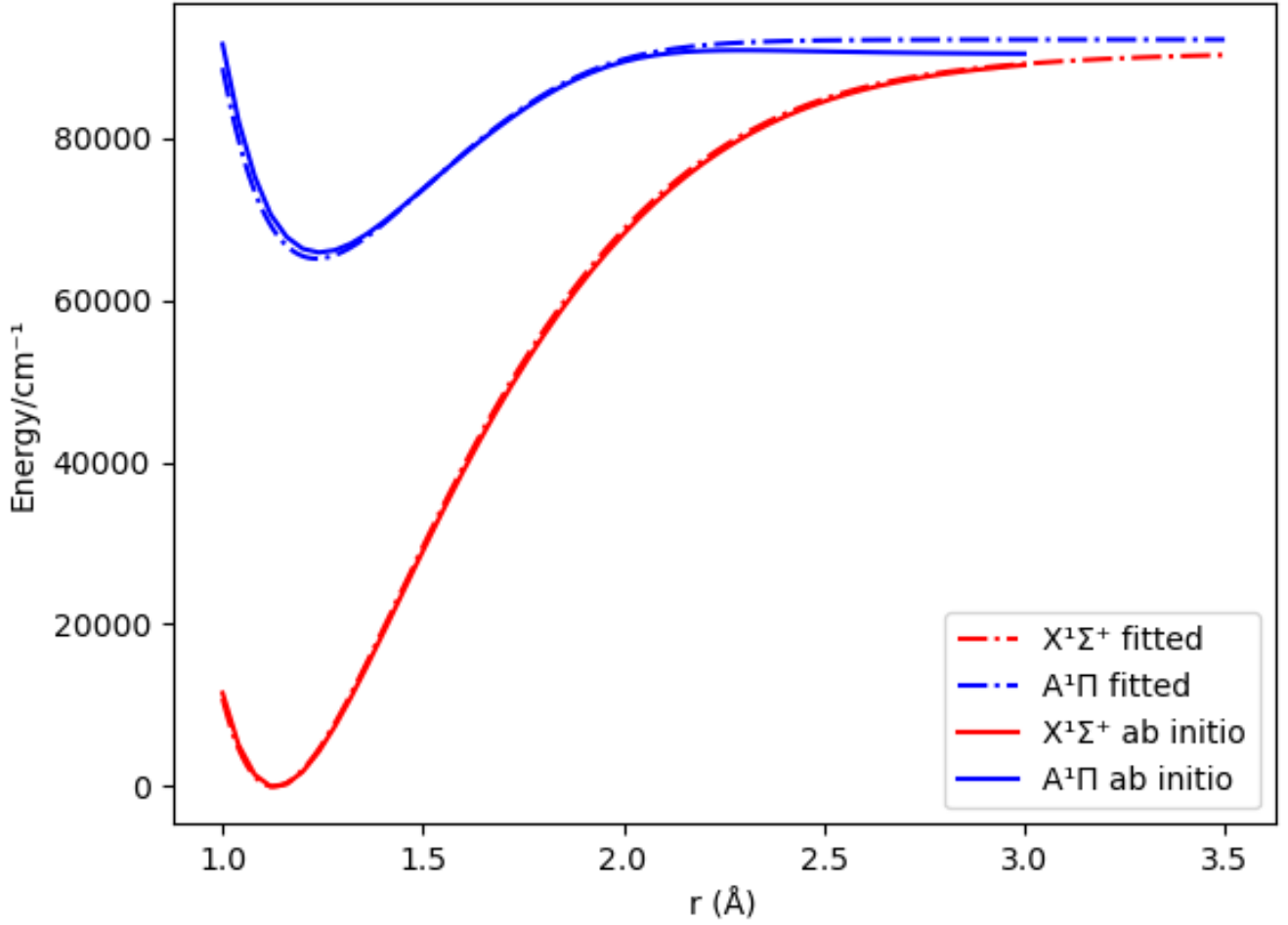


Figure 2. Comparison between the *ab initio* PECs and the experimentally refined PECs of CO obtained by fitting rovibrational energy levels using the DUO program for the $X^1\Sigma^+$ and $A^1\Pi$ electronic states.

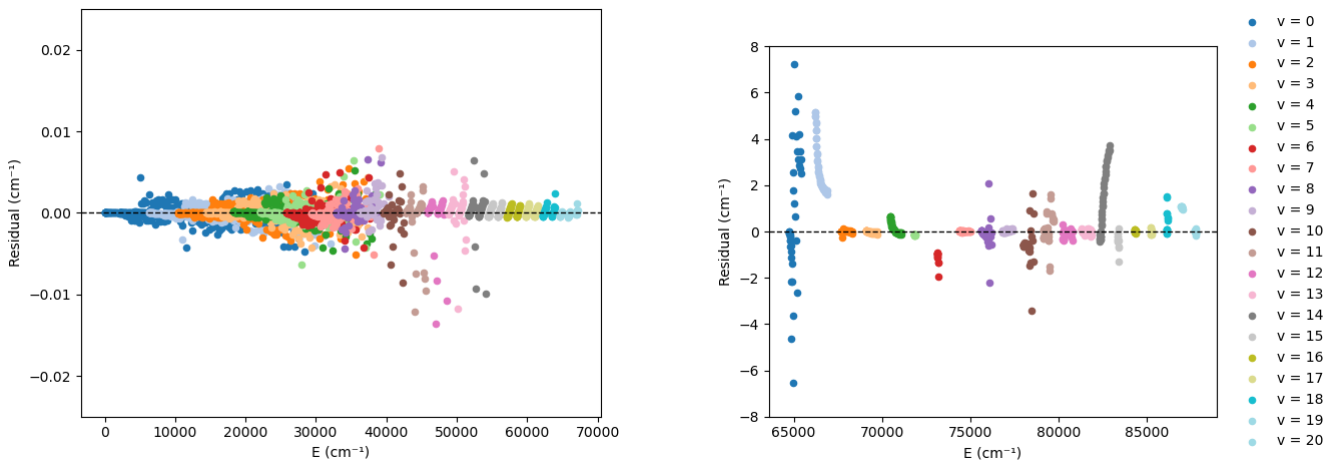


Figure 3. Residuals (observed minus calculated) between calculated and experimental rovibrational energy levels for the $X^1\Sigma^+$ (left) and $A^1\Pi$ (right) electronic states of CO. The results are shown as a function of energy, both expressed in units of cm^{-1} . Different colours denote energy levels associated with different vibrational quantum numbers.

quantum numbers up to $v = 20$ and $J = 20$, respectively. The resulting fitted PECs are shown by the dashed curves in Fig. 2.

The residuals for the $X^1\Sigma^+$ and $A^1\Pi$ electronic states are presented in Fig. 3. For the ground $X^1\Sigma^+$ state, the residuals remain small across the full range of fitted energy levels, demonstrating excellent agreement between the calculated and experimental MARVEL energy levels of ^{12}CO . As shown in Fig. 3 (left), the majority of residuals are confined to a narrow band centred around zero. Although several outliers are visible, the residuals for experimentally observed levels up to $v = 41$ and $J = 123$ remain within approximately 0.02 cm^{-1} with an rms error of 0.0014 cm^{-1} , confirming the reliability of the ground-state model over the full experimentally accessible range of the CO $X^1\Sigma^+$ state. An additional feature evident in Fig. 3 (left) is the nearly symmetric distribution of points above and below the $y = 0$ line, indicating that the current ground-state model has largely eliminated systematic deviations and that the remaining scatter is primarily associated with experimental uncertainties. Overall, the residual distribution demonstrates the robustness of the MLJ+BOB correction function adopted for the ground state, which closely follows the well-established model of J. A. Coxon & P. G. Hagiogriou (2004). It also confirms that refinement using recent MARVEL data introduces only minor corrections while preserving the high overall accuracy of the potential.

In contrast, the residuals for the excited $A^1\Pi$ state exhibit a larger dispersion, although most of them remain within acceptable limits for high-resolution spectroscopic modelling. The refined EMO potential substantially reduces the systematic deviations present in the initial *ab initio* model, as indicated by the near-random distribution of residuals about zero following refinement. Inspection of Fig. 3 (right) reveals that the largest residuals are associated with the lowest two vibrational levels ($v = 0$ and 1). In comparison, the residuals for higher vibrational states are significantly smaller and display improved agreement with the experimental data. This behaviour suggests that the enhanced residuals at low vibrational excitation are unlikely to arise from deficiencies in the PEC model itself, but instead reflect the influence of additional coupling effects not included in the present calculations. For the $A^1\Pi$ state, the most important missing interaction is the spin-orbit coupling with the nearby triplet states, which is deliberately neglected in this work as we do not include these triplet states in our spectroscopic model. Support for this interpretation is provided by the MARVEL energy levels (N. El-Kork et al., in preparation), which show relatively large parity-dependent splittings for the lowest vibrational levels. Nevertheless, despite these localized discrepancies, the refined EMO model shows overall good agreement with the experimental data, indicating that it provides a reliable representation of the $A^1\Pi$ state. The model is therefore suitable for generating accurate rovibrational energy levels and transition intensities for the 4thplus system of CO. The robustness of the model is further supported by the calculated partition function values. These were compared with previously published results by G. Li et al. (2015), available on the ExoMol website over the same temperature range. Excellent agreement between the two data sets is observed, as illustrated in Fig. 4.

3.2 Transition dipole moment

The TDM treatment in this study encompasses both the $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ and $A^1\Pi \rightarrow X^1\Sigma^+$ transitions. For the $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ transition, the dipole moment function reported by N. F. Zobov

et al. (2025) was initially considered. This function, expressed in a simple polynomial analytic form, is suitable for short-range internuclear separations, especially within $2.0\text{ \AA}$. However, as this work requires coverage up to $3.0\text{ \AA}$, this representation was ultimately deemed inadequate and therefore not adopted.

Instead, a more general dipole moment function with improved long-range behaviour, as reported by V. V. Meshkov, E. A. Pazyuk & A. V. Stolyarov (2026), was adopted. The parametrization of the ground-state dipole moment function is taken directly from V. V. Meshkov et al. (2026) without modification; the corresponding parameters are implemented explicitly in the DUO input file provided in the Supplementary Material, ensuring full reproducibility of the present calculations.

The use of this analytic representation within DUO yields a more physically consistent description of the dipole moment over the extended internuclear distance range considered here. In particular, the plateau feature in the cross-section profile at 2000 K reported by G. Li et al. (2015) is effectively removed. This improvement is attributed to the more reliable long-range behaviour of the adopted dipole moment function and is discussed in further detail in Section 3.4.1.

The TDM curve for the $A^1\Pi \rightarrow X^1\Sigma^+$ system of CO obtained in this work is presented in Fig. 5 as a function of the internuclear separation. Overall, the present TDM shows good agreement with most previously reported theoretical results across the range from 1.0 to $3.0\text{ \AA}$. However, a noticeable discrepancy is observed when comparing these theoretical curves with the available experimental dipole moment data. As illustrated in Fig. 5, none of the theoretical TDM curves fully reproduce the experimental behaviour, with the exception of the results reported by J. Cheng et al. (2018), which exhibit significantly better agreement.

Given this situation, this study adopts the TDM from J. Cheng et al. (2018) for subsequent calculations, as it provides a more reliable representation of the experimental trend. Consequently, the *ab initio* TDM computed in this work is not used in the final spectroscopic modelling. This choice is motivated by the primary objective of this study, namely the generation of highly accurate and reliable line lists for the CO 4thplus band system, for which an experimentally consistent dipole moment function is essential.

3.3 Rovibronic energy levels

The complete rovibronic energy-level data set presented in this work comprises contributions from both the $X^1\Sigma^+$ and $A^1\Pi$ systems. Ground-state energy levels associated with the $X^1\Sigma^+$ state were calculated using the refined MLJ model within the DUO framework. These are represented by the entries labelled ‘Ca’ in the final `.states` file, as illustrated in Table 1.

To assess the reliability of the calculated energy levels, comparisons were carried out against the line list of V. G. Ushakov & E. S. Medvedev (2025). Overall, the differences between the present results and those of V. G. Ushakov & E. S. Medvedev (2025) are small, typically on the order of fractions of a wavenumber. Although the discrepancies increase for states with high vibrational (v) and rotational (J) quantum numbers, they remain modest, with an average relative uncertainty of approximately 0.003 per cent for the $X^1\Sigma^+$ levels. This data set, therefore, provides a high-level reference for highly excited states and serves as a valuable benchmark for validating and refining the present ground-state energy levels.

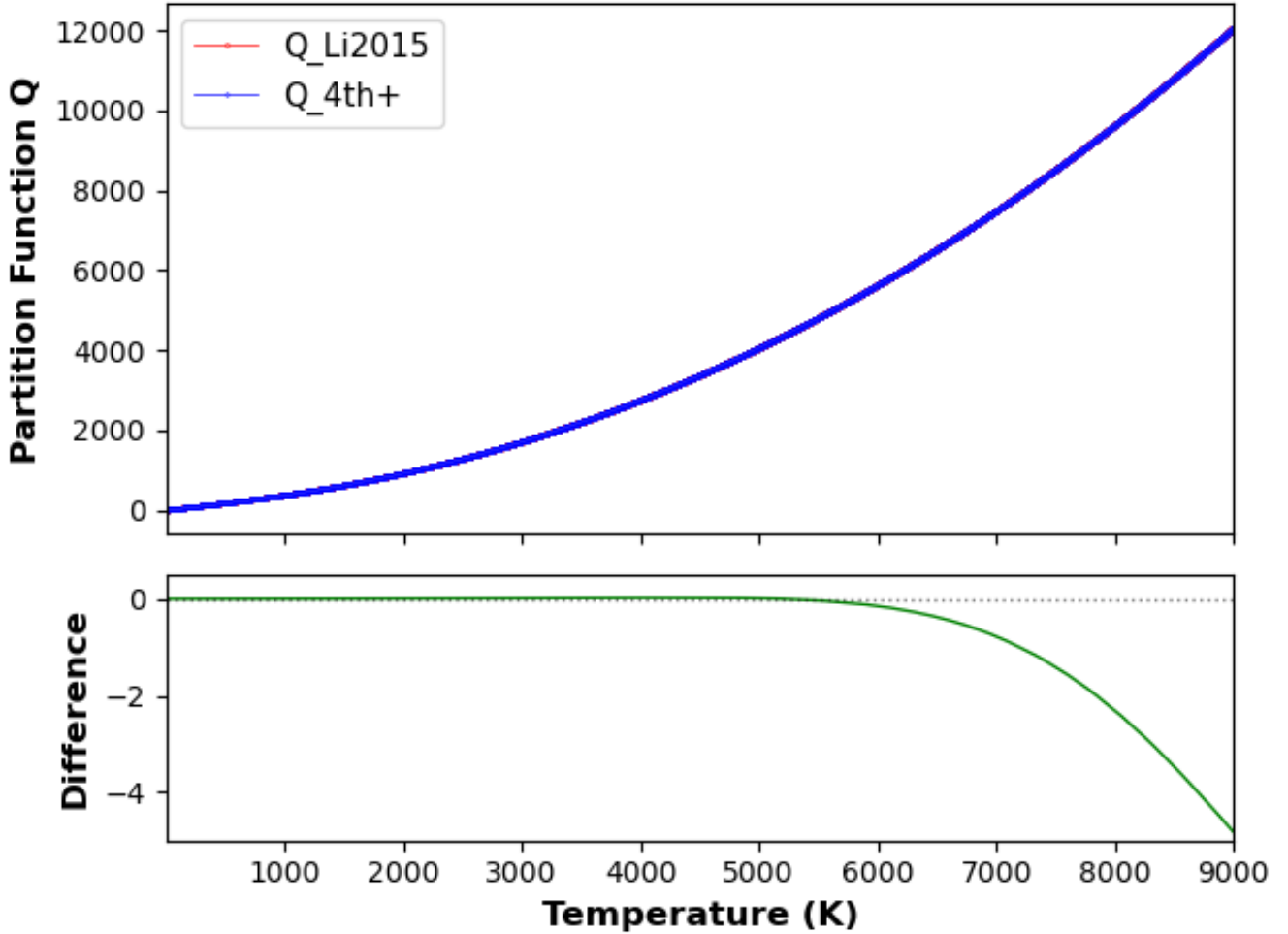


Figure 4. The partition function calculated in this study is compared with that of G. Li et al. (2015); at elevated temperatures, the partition function of G. Li et al. (2015) is slightly larger than the present values.

Experimental energy levels from the MARVEL database (S. Mahmoud et al. 2025) were subsequently incorporated into the $X^1\Sigma^+$ data set wherever available, thereby improving the overall accuracy.

For the excited $A^1\Pi$ state, a similar post-processing MARVELization strategy was employed. The complete set of rovibronic energy levels is provided in the ExoMol .states file format, with a representative sample shown in Table 1. This table contains the full set of quantum number assignments, term energies, and degeneracies for each rovibronic state.

Following the ExoMol approach (J. Tennyson et al. 2024), the experimental energy levels from the MARVEL data set of ^{12}CO (S. Mahmoud et al. 2025; N. El-Kork et al., in preparation) were incorporated into the .states file through the so-called MARVELization procedure. The original calculated energies are retained alongside the refined values to allow direct comparison between theoretical predictions and experimental measurements. Energy levels marked with ‘Ma’ in the ‘Abbr’ column indicate that the calculated values have been replaced by corresponding MARVEL energies to improve spectral accuracy, whereas entries labelled ‘Ca’ correspond to states for which no experimental data are currently available and for which the DUO-calculated energies are retained.

In addition to the .states file, DUO produces the .trans file, which is essential for computing rovibronic spectra of the $X^1\Sigma^+-X^1\Sigma^+$ and $A^1\Pi-X^1\Sigma^+$ systems. This file contains radiative transitions between energy levels, including transition wavenumbers, Einstein A coefficients, and indices of the upper and lower states. The .trans file follows the ExoMol format, and a representative excerpt is shown in Table 2. As with the .states file, the .trans file was refined using the MARVEL data set, with experimental transition energies replacing corresponding theoretical values wherever available.

Tables 1 and 2 present representative excerpts from the .states and .trans files, respectively, illustrating the structure and content of the computed rovibronic data set. These files together underpin the construction of a comprehensive line list for the $X^1\Sigma^+-X^1\Sigma^+$ and $A^1\Pi-X^1\Sigma^+$ systems, which is subsequently processed using EXOCROSS to generate the spectral data discussed in the following subsection.

3.4 Radiative lifetimes of $A^1\Pi$

The radiative lifetimes of the $A^1\Pi$ state were calculated using the TDM from J. Cheng et al. (2018). Since the same TDM is employed, the lifetimes obtained in this work might be expected

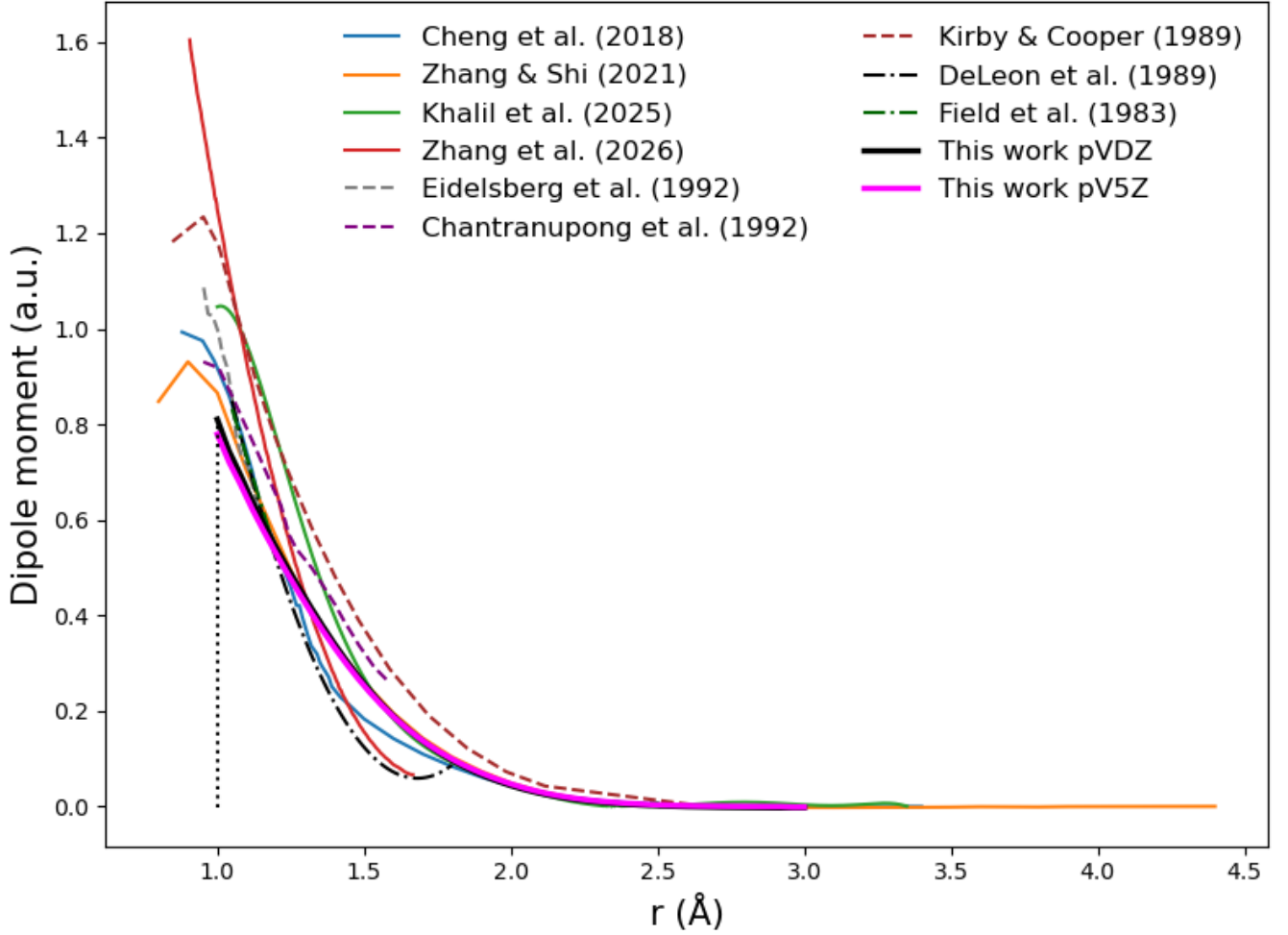


Figure 5. TDM curves for the $A^1\Pi-X^1\Sigma^+$ system of CO as a function of internuclear separation, compared with results from theoretical studies (K. Kirby & D. L. Cooper 1989; L. Chantranupong et al. 1992; J. Cheng et al. 2018; M. Zhang & D. Shi 2021; M. Khalil et al. 2024; S. Zhang et al. 2026) and experimental studies (R. W. Field et al. 1983; R. L. DeLeon 1989; M. Eidelsberg et al. 1992). The vertical dashed line denotes the starting point of the present TDM data.

to closely match those reported by J. Cheng et al. (2018). However, as shown in Table 3, systematic differences of approximately 0.6 ns exist between the two sets of theoretical results, presumably due to the use of different PECs and here wavefunctions.

Several factors account for these discrepancies despite the use of the same TDM. Differences in vibrational wavefunctions affect the Franck–Condon overlaps and transition matrix elements. The sum over lower vibrational levels and the ν^3 scaling of transition frequencies also influence the total decay rate. Additionally, the numerical implementation of the r -dependent TDM and perturbations from nearby electronic states (e.g. $d^1\Delta$) can produce ν' -dependent variations. Furthermore, spin–orbit coupling is not considered in this study.

The present lifetimes show good general agreement with the experimental data of R. W. Field et al. (1983) for low ν' , while deviations from J. Cheng et al. (2018) are within expected uncertainties. For $\nu' \geq 10$, the lifetimes increase gradually, consistent with the trends reported in other theoretical studies (N. Mosyagin et al. 2021). Overall, our lifetimes are slightly shorter than the observed ones but are likely to increase slightly once coupling with the nearby triplet states is included.

3.5 Spectra and line positions

3.5.1 X–X spectra

The 4thplus .states and .trans files were used as input for the program EXOCROSS, which was employed to generate theoretical spectra and absorption cross-sections over user-defined temperature and energy ranges (S. N. Yurchenko, A. F. Al-Refaie & J. Tennyson 2018). The line intensity (absorption coefficient, in units of cm molecule^{-1}) for a transition from an initial state i to a final state f is given by

$$I(f \leftarrow i) = \frac{g_f^{\text{tot}} A_{fi} \exp[-(c_2 \tilde{E}_i)/T] [1 - \exp(-(c_2 \tilde{\nu}_{fi})/T)]}{8\pi c \tilde{\nu}_{fi}^2 Q(T)}, \quad (15)$$

where A_{fi} is the Einstein A coefficient for spontaneous emission (in s^{-1}), $\tilde{\nu}_{fi}$ is the transition wavenumber (in cm^{-1}), $\tilde{E}_i = E_i/(hc)$ is the lower state energy expressed in cm^{-1} , and $Q(T)$ denotes the molecular partition function.

As the .states and .trans files include both X–X and A–X transitions, the corresponding line lists and spectra for the X–X transition are also generated in this work. These are expected to

Table 1. Sample rovibronic energy levels extracted from the ExoMol .states file for the 4thplus line list for $^{12}\text{C}^{16}\text{O}$.

<i>i</i>	$\tilde{E}$ (cm^{-1})	<i>g</i>	<i>J</i>	Unc (cm^{-1})	τ (s)	+/-	<i>e/f</i>	State	ν	Λ	Σ	Ω	Abbr	$\tilde{E}_0$ (cm^{-1})
48	73293.644019	1	0	0.001055	2.0234E-03	+	<i>e</i>	$X^1\Sigma^+$	47	0	0	0	Ca	73293.644019
49	74262.672266	1	0	0.001077	2.0411E-03	+	<i>e</i>	$X^1\Sigma^+$	48	0	0	0	Ca	74262.672266
50	75206.525162	1	0	0.001098	2.0598E-03	+	<i>e</i>	$X^1\Sigma^+$	49	0	0	0	Ca	75206.525162
51	64747.982889	3	1	0.005006	9.3142E-09	+	<i>f</i>	$A^1\Pi$	0	1	0	1	Ma	64747.979199
52	66236.229292	3	1	0.005006	9.2506E-09	+	<i>f</i>	$A^1\Pi$	1	1	0	1	Ma	66231.060038
53	67678.892467	3	1	0.010000	9.1119E-09	+	<i>f</i>	$A^1\Pi$	2	1	0	1	Ma	67678.889584

Notes: *i*: state counting number; $\tilde{E}$: state energy in cm^{-1} ; *g*: state degeneracy; *J*: total angular momentum; Unc: energy uncertainty in cm^{-1} ; τ : radiative lifetime in s; +/-: total parity; *e/f*: rotationless parity; State: electronic state label; ν : state vibrational quantum number; Λ : projection of the electronic angular momentum; Σ : projection of the electronic spin; $\Omega = \Lambda + \Sigma$, projection of total angular momentum; Abbr: abbreviation giving source of state energy; $\tilde{E}_0$: original (calculated) state energy in cm^{-1} .

provide an improvement over the X-X line list reported by G. Li et al. (2015), and may be of particular value for future studies of the ground electronic state.

Fig. 6 compares CO ground-state cross-sections of G. Li et al. (2015), previously recommended by both ExoMol and HITRAN, and the updated HITRAN 2024 (I. E. Gordon et al. 2026) values. The spectra computed using the 4thplus line list remove the artificial plateau, which was a feature of the earlier study, and maintain good agreement with the revised HITRAN 2024 data. The plateauing of calculated intensities at high overtones is a well-documented issue (E. S. Medvedev et al. 2016). In this study, this problem is mitigated through the use of an improved dipole moment function derived from the DMC of V. V. Meshkov et al. (2026) within the DUO framework. In particular, the plateau previously observed near 15000 cm^{-1} in Fig. 6 is removed, and the simulated spectra instead display a more physically realistic decay at higher wavenumbers.

Furthermore, investigations conducted after the work of G. Li et al. (2015) suggested that the intensities reported for the important 1–0 fundamental band were underestimated by approximately 2 per cent (N. F. Zobov et al. 2025; G. Li et al. 2026). This issue is also improved in this work through the adoption of the more recent DMC. Temperature-dependent spectra for the $X^1\Sigma^+ \rightarrow X^1\Sigma^+$ transition were additionally computed and are presented in Fig. 7, demonstrating the expected variation of cross-sections with temperature.

3.5.2 A-X spectra and line position

Using the .states and .trans files as input to EXOCROSS, the 4thplus line list for the CO fourth positive system ($A^1\Pi-X^1\Sigma^+$) was used to generate simulated spectra. The resulting spectra are shown in Fig. 8 over the range $60000\text{--}80000\text{ cm}^{-1}$. In the left panel, each peak corresponds to a vibronic band; from left to right, these bands represent the (0, 0), (1, 0), (2, 0) transitions and higher members of the progression. For comparison, Fig. 8 also includes the simulated spectrum reported by B. Shang et al. (2026) at 296 K. A further comparison at the same temperature with the simulated spectrum from S. Zhang et al. (2026) is presented in Fig. 9, shown over a narrower spectral region corresponding to the (1, 0) band. A noticeable shift between the data sets is observed in both figures. As illustrated in Fig. 8 (right) and Fig. 9, the spectrum obtained in this work shows closer agreement with the results reported by S. Zhang et al. (2026). To determine which spectrum is more accurate, a direct comparison with experimental data was performed. By overlaying our simulated spectra with the experimental spectra of M. L. Niu et al. (2013) and M. Niu et al. (2015), as shown in Figs 10 and 11, excellent agreement is achieved on the finer scale of individual bands, demonstrating the accuracy of the present calculations. The shift observed in the larger-scale spectra of Fig. 8 highlights that the line positions from this work provide a much more reliable representation of the $^{12}\text{C}^{16}\text{O } A^1\Pi-X^1\Sigma^+$ system than the *ab initio* studies of B. Shang et al. (2026) and S. Zhang et al. (2026).

Figs 3 and 11 illustrate the agreement of the 4thplus energy levels with experiment. The residual differences between the calculated and observed spectra are minimal, demonstrating that our rovibronic model reliably reproduces the experimental energy levels. Moreover, the band shape of the (0, 0) transition in this work closely resembles the non-perturbative band profile reported by J. Cheng et al. (2018), further validating the accuracy of

Table 2. Sample transitions extracted from the ExoMol .trans file for 4thplus for $^{12}\text{C}^{16}\text{O}$.

i	f	$A_{fi} \text{ (s}^{-1}\text{)}$	$\tilde{\nu}_{fi} \text{ (cm}^{-1}\text{)}$
113	37	1.2616E-06	2.5849E+00
112	36	1.2410E-06	2.6203E+00
111	35	1.2159E-06	2.6557E+00
110	34	1.1862E-06	2.6909E+00
109	33	1.1525E-06	2.7261E+00
108	32	1.1149E-06	2.7613E+00
107	31	1.0740E-06	2.7963E+00
4117	3999	2.4367E-13	2.8293E+00
106	30	1.0299E-06	2.8314E+00
105	29	9.8321E-07	2.8664E+00
104	28	9.3416E-07	2.9013E+00

Notes: i : upper state index;

f : lower state index;

A : Einstein A coefficient for spontaneous emission in s^{-1} ;

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

the theoretical model. Fig. 12 presents absorption cross-sections for the $A^1\Pi-X^1\Sigma^+$ band system in the range of 0–100 000 cm^{-1} at three temperatures (296, 1000, and 5000 K) using a Doppler line profile. To enhance visibility, the cross-sections are plotted on a logarithmic scale.

Compared with previous theoretical line lists, such as those of B. Shang et al. (2026), the present calculations provide a notable improvement in line positions and band alignment. Refinement using MARVEL experimental energy levels ensures that both rovibrational energies and transition frequencies more closely reproduce the observed values. For example, the rms deviation of the calculated line positions relative to experiment is significantly reduced, particularly for low- and mid-vibrational bands, where earlier models exhibited systematic shifts. This improved agreement is evident in the alignment between simulated and experimental spectra shown in Figs 10 and 11. However, the theoretical spectra presented here do not perfectly reproduce the experimental spectra for all bands, especially those associated with relatively large residuals in Fig. 3. As shown in Fig. 3 (right), the $v = 0$ and $v = 1$ levels exhibit the largest deviations, indicating that

coupling effects are particularly significant in this energy region. As discussed in Section 3.1, these discrepancies are likely due to spin-orbit interactions involving this electronic state. According to D. C. Morton & L. Noreau (1994), the deviations observed for $v = 0$ (i.e. the (0, 0) band) arise from coupling of the $A^1\Pi$ state with the $e^3\Sigma^-$ and $d^3\Delta$ states, while those for $v = 1$ (the (1, 0) band) are attributed to interactions with the $d^3\Delta$ state; none of these couplings are included in the present model. Although additional coupling interactions may affect higher energy levels, their impact on the overall spectral accuracy is comparatively small. These effects will be incorporated in future work aimed at developing a higher-resolution spectroscopic model. Consequently, the present line list provides a reasonably high-accuracy description of the $A^1\Pi-X^1\Sigma^+$ transition and improves the reliability of derived spectral quantities, such as absorption cross-sections and temperature-dependent line intensities.

4 CONCLUSION

In conclusion, high-accuracy empirical PECs for the $X^1\Sigma^+$ and $A^1\Pi$ electronic states of CO were generated by fitting to experimental MARVEL energies of ^{12}CO (S. Mahmoud et al. 2025; N. El-Kork, in preparation). The ground-state PEC, based on the model of J. A. Coxon & P. G. Hajigeorgiou (2004) and represented by an MLJ function, exhibits excellent agreement with previous theoretical studies. The excited-state $A^1\Pi$ PEC was modelled with an EMO function, achieving an rms deviation of 0.82 cm^{-1} relative to MARVEL energy levels (N. El-Kork, in preparation). Residual analysis indicates that the rovibronic models accurately reproduce both low- and high-energy states, with minor discrepancies likely arising from unaccounted-for effects such as spin-orbit coupling, which will be addressed in future work.

Using these refined PECs, coupling models and accurate (T)DM functions from the literature (J. Cheng et al. 2018; V. V. Meshkov et al. 2026), rovibronic energy levels and transition probabilities were calculated with DUO, producing .states and .trans files in the ExoMol format. These line lists were further adjusted with MARVEL data to enhance accuracy. Comparison with experimental spectra and prior theoretical studies confirms that the present model reliably reproduces both line positions and

Table 3. Calculated radiative lifetimes τ_r of CO $A^1\Pi$ compared with experimental results and theoretical calculations.

v'	Experimental						Theory	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	This work
0	10.69 ± 0.3	11.5 ± 0.5	15.9 ± 0.5		11.9 ± 0.7	10.8 ± 0.1	9.96	9.38
1	10.37 ± 0.3	10.9 ± 0.2	16.2 ± 0.8	10.4 ± 0.8	12.3 ± 0.5	10.45 ± 0.1	9.99	9.31
2	9.34 ± 0.25	10.5 ± 1.0	16.6 ± 1.0	8.5 ± 1.0	12.0 ± 0.5	9.75 ± 0.1	9.81	9.17
3	8.97 ± 0.35	10.5 ± 0.2	16.1 ± 0.6		12.5 ± 0.5	9.6 ± 0.1	9.60	8.94
4	9.67 ± 0.4	10.4 ± 0.3	15.0 ± 0.6		13.3 ± 0.6	9.5 ± 0.1	9.42	8.75
5	9.75 ± 0.5	10.2 ± 0.2	14.3 ± 0.8		13.5 ± 0.9	9.2 ± 0.1	9.25	8.59
6	10.45 ± 0.65					10.85 ± 0.1	9.13	8.55
7						8.95 ± 0.1	9.05	8.55
8							8.93	8.54
9							8.86	8.59
10							8.83	8.66
11							8.78	8.73
12							8.72	8.85
13	11.9 ± 1 (8)						8.71	8.99

Notes. (1) R. Imhof & F. Read (1971); (2) J. E. Hesser (1968); (3) J. G. Chervenak & R. A. Anderson (1971); (4) R. L. Burnham, R. C. Isler & W. C. Wells (1972); (5) T. A. Carlson et al. (1978); (6) R. W. Field et al. (1983); (7) J. Cheng et al. (2018); (8) H. Hallstadius & H. Lundberg (1989).

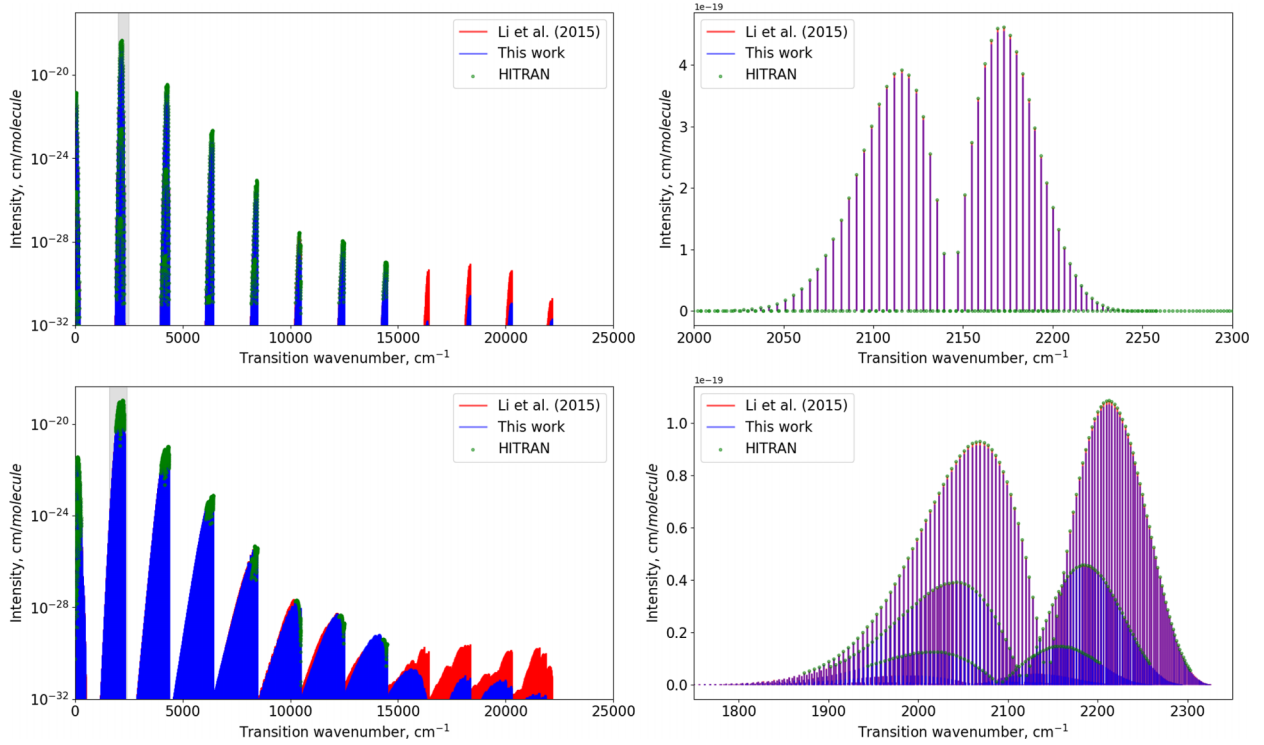


Figure 6. Absorption cross-sections for the $^{12}\text{C}^{16}\text{O } X^1\Sigma^+-X^1\Sigma^+$ system at temperatures of 296 K (top row) and 2000 K (bottom row), compared with the spectra calculated by G. Li et al. (2015) and the HITRAN 2024 database (I. E. Gordon et al. 2026) over the spectral range 0–25 000 cm^{-1} . The corresponding zoomed-in spectra for the (1, 0) band at both temperatures, displayed on a linear intensity scale, are shown alongside the full-range cross-sections presented on a logarithmic scale.

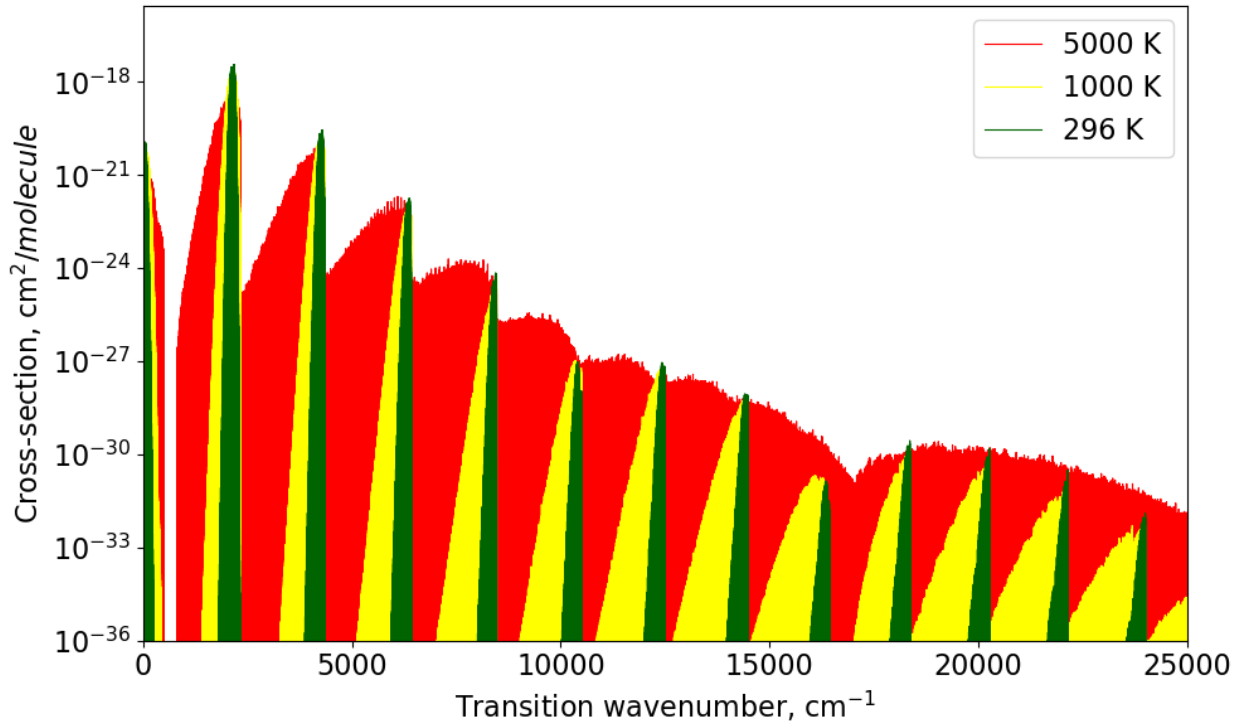


Figure 7. The cross-section for the $^{12}\text{C}^{16}\text{O } X^1\Sigma^+-X^1\Sigma^+$ band at $T = 296, 1000,$ and 5000 K, computed using Doppler broadening.

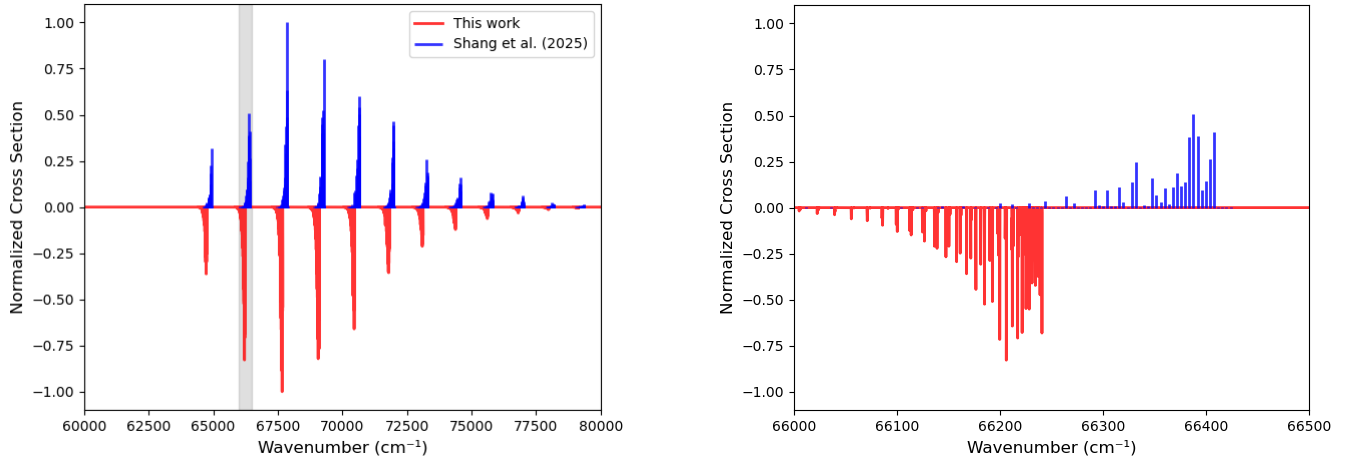


Figure 8. Comparison of the theoretical room-temperature spectra for $A^1\Pi-X^1\Sigma^+$: 4thplus (this work) and B. Shang et al. (2026). Left: Full spectral range. Right: Enlarged view of the shaded region in the left panel, highlighting the (1, 0) band.

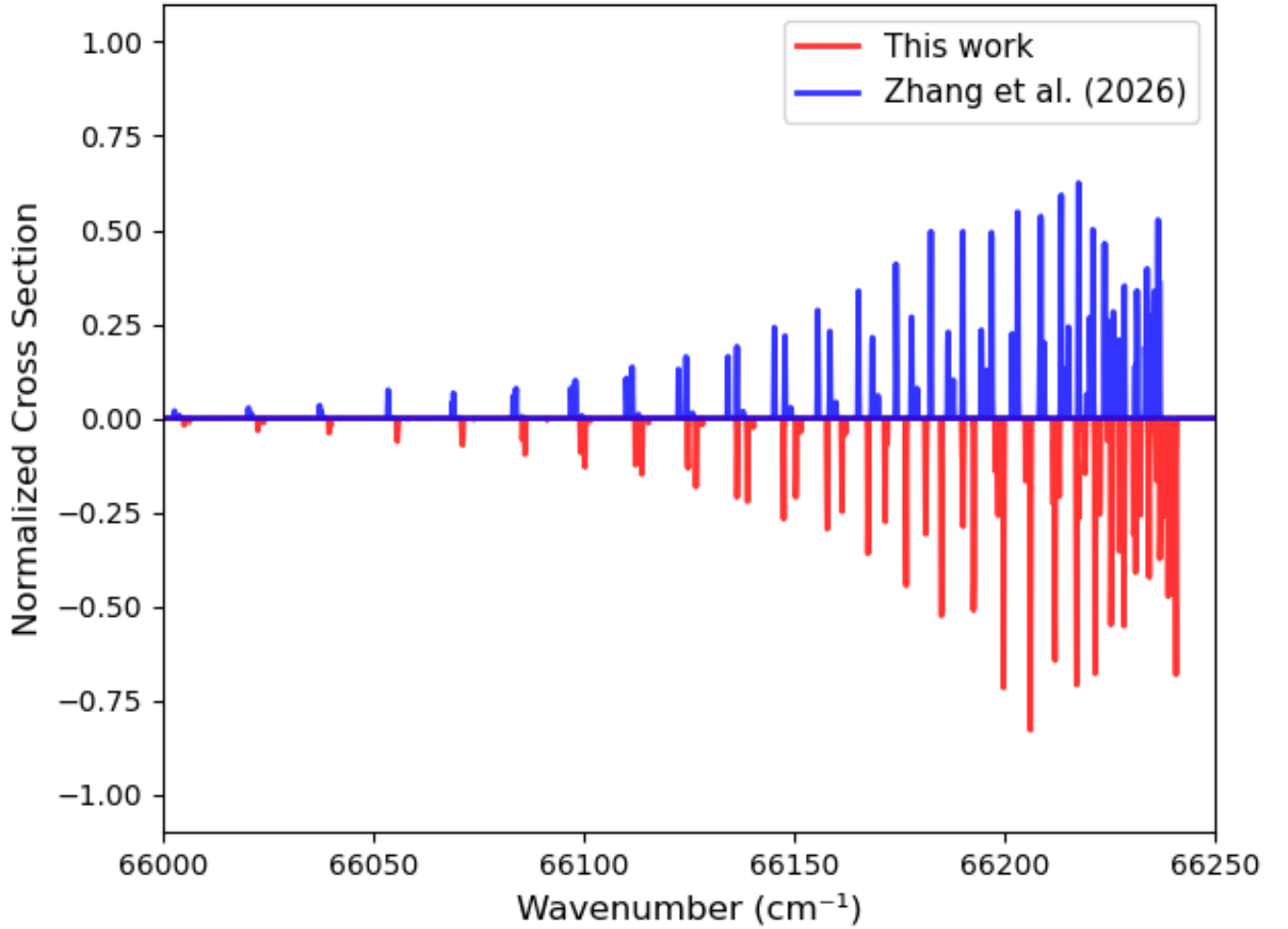


Figure 9. The theoretical room temperature spectrum of $A^1\Pi-X^1\Sigma^+$: 4thplus compared with the theoretical spectra obtained from the work of S. Zhang et al. (2026).

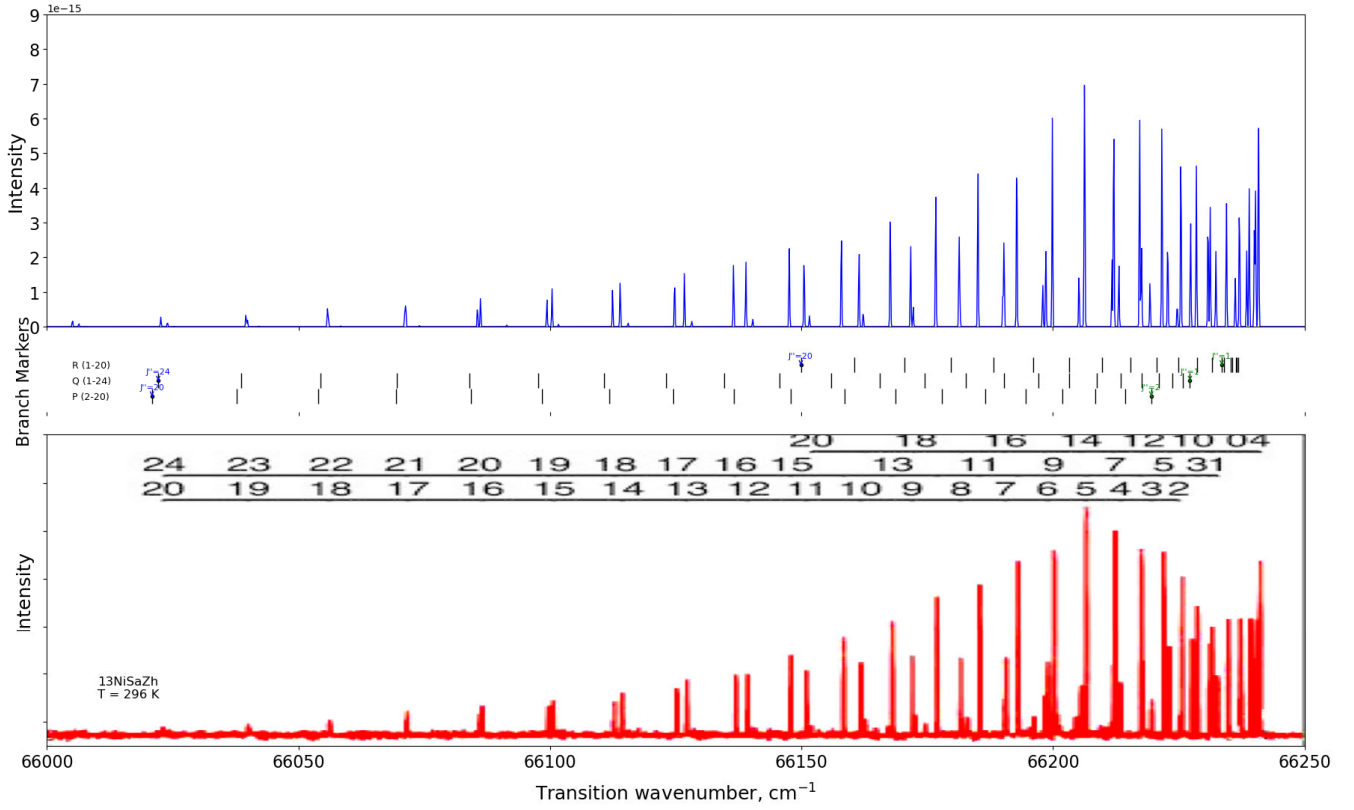


Figure 10. The spectrum of CO band (1,0) compared with the experimental spectrum observed by Niu et al. (2013).

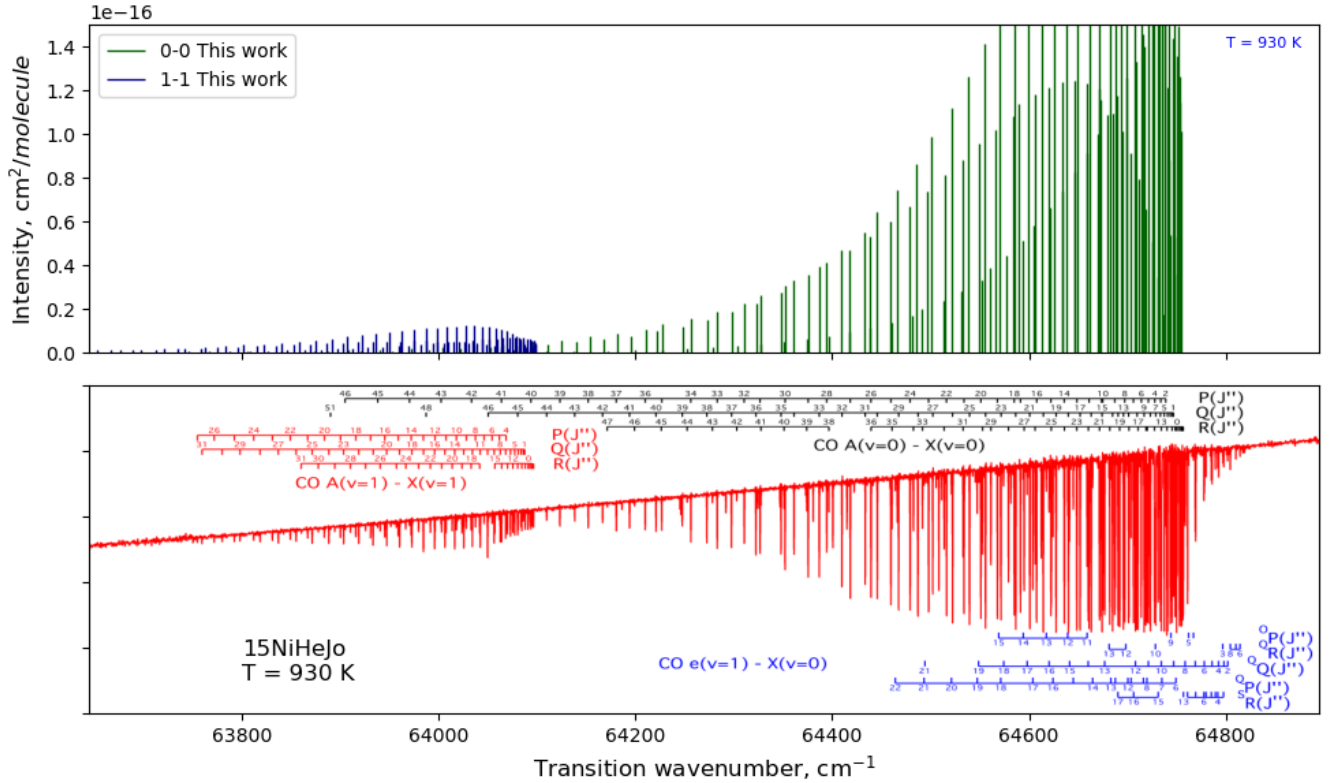


Figure 11. The spectrum of the CO band (0, 0) and (1, 1) compared with the experimental by M. Niu et al. (2015); when T is set to the experimental value of 930 K.

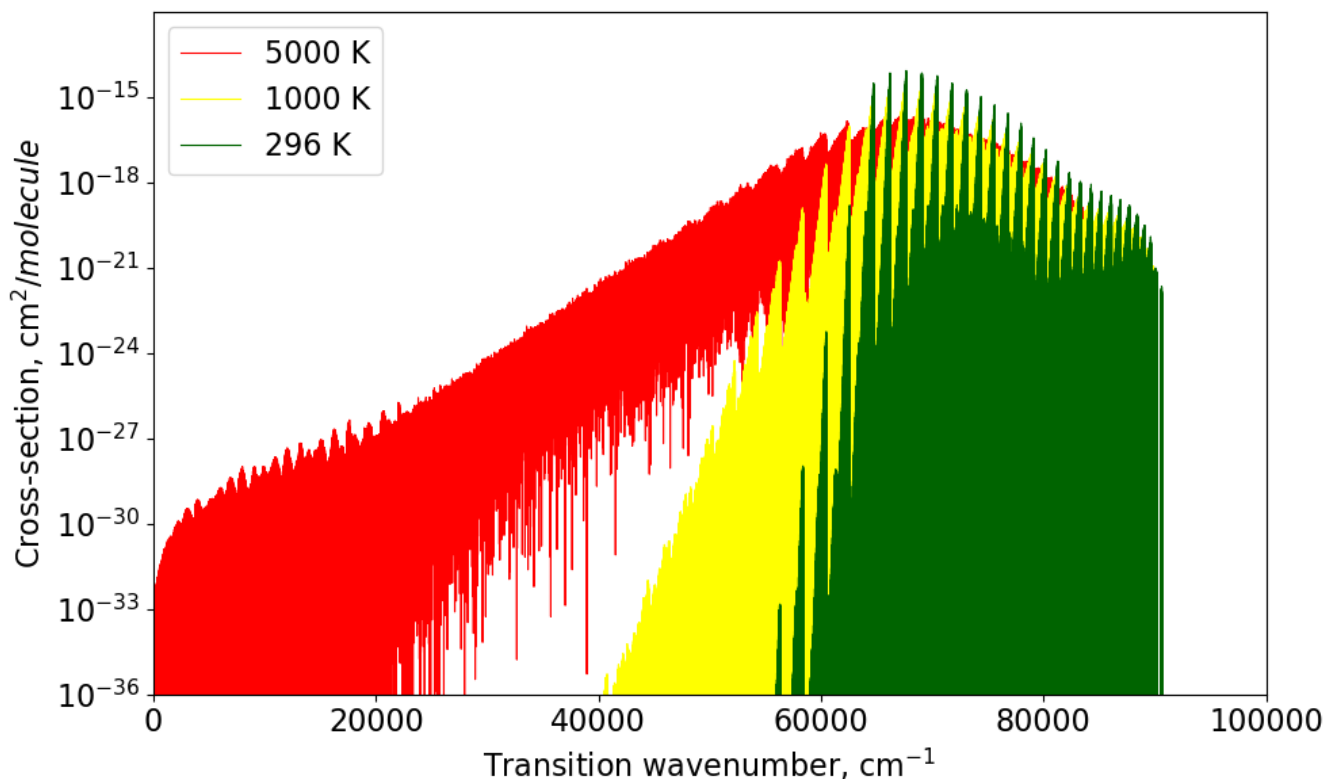


Figure 12. The cross-sections for the $^{12}\text{C}^{16}\text{O}$ $A^1\Pi-X^1\Sigma^+$ band at $T = 296, 1000,$ and 5000 K were computed using Doppler broadening.

band shapes for the 4thplus system of ^{12}CO . Calculated absorption cross-sections at multiple temperatures further demonstrate the robustness of the model for astrophysical and laboratory applications.

Overall, the integration of high-level *ab initio* calculations, empirical refinement, and rigorous spectroscopic modelling has yielded a comprehensive and reliable 4thplus line list for the $X^1\Sigma^+-X^1\Sigma^+$ and $A^1\Pi-X^1\Sigma^+$ systems of ^{12}CO , representing a significant improvement over previous line lists of $X^1\Sigma^+-X^1\Sigma^+$ and available purely *ab initio* studies of $A^1\Pi-X^1\Sigma^+$. These results provide a valuable reference for high-resolution spectroscopy, astrophysical modelling, and future investigations of molecular transitions in diatomic species. The $A^1\Pi-X^1\Sigma^+$ band system is one of many important rovibronic bands for ^{12}CO . We plan to systematically provide line lists for all of those of astronomical importance.

CONFLICT OF INTEREST

There are no conflicts to declare.

ACKNOWLEDGEMENTS

This work was supported by Khalifa University Research and Innovation Grant under Award No. RIG 2024-053; by the European Research Council (ERC) under the European Union's Horizon 2020 Framework Programme through an Advanced Grant number 883830 and by the STFC Projects No. ST/Y001508/1 and UKRI/ST/B001183/1.

DATA AVAILABILITY

The DUO and EXOCROSS program packages are freely available from the ExoMol GitHub repository at <https://github.com/ExoMol>. The input files associated with this work are available in the Supplementary Material; other data, including the line list, are available from the ExoMol website www.exomol.com.

REFERENCES

- Ayres T. R., 1986, *ApJ*, 308, 246
- Balashov A. A. et al., 2023, *J. Chem. Phys.*, 158, 234306
- Bielska K. et al., 2022, *Phys. Rev. Lett.*, 129, 043002
- Burnham R. L., Isler R. C., Wells W. C., 1972, *Phys. Rev. A*, 6, 1327
- Carlson T. A., Duric N., Erman P., Larsson M., 1978, *Z. Phys. A*, 287, 123
- Chantranupong L., Bhanuprakash K., Honigmann M., Hirsch G., Bunker R. J., 1992, *Chem. Phys.*, 161, 351
- Chen H.-j., Fang W., Zhang J.-w., 2023, *Spectrosc. Spectr. Anal.*, 43, 3380
- Cheng J., Zhang H., Cheng X., 2018, *ApJ*, 859, 19
- Chervenak J. G., Anderson R. A., 1971, *J. Opt. Soc. Am.*, 61, 952
- Coxon J. A., Hajigeorgiou P. G., 2004, *J. Chem. Phys.*, 121, 2992
- DeLeon R. L., 1989, *J. Chem. Phys.*, 91, 5859
- Dora A., Tennyson J., 2020, *J. Phys. B: At. Mol. Opt. Phys.*, 53, 195202
- Eidelsberg M., Benayoun J. J., Viala Y., Rostas F., Smith P. L., Yoshino K., Stark G., Shettle C. A., 1992, *A&A*, 265, 839
- Evans J. S. et al., 2024, *J. Geophys. Res.: Planets*, 129, e2023JE008181
- Feldman P. D., Burgh E. B., Durrance S. T., Davidsen A. F., 2000, *ApJ*, 538, 395
- Field R. W., d'Azy O. B., Lavollée M., Lopez-Delgado R., Tramer A., 1983, *J. Chem. Phys.*, 78, 2838
- Gliniski R. J., Nuth J. A., III, Reese M. D., Sitko M. L., 1996, *ApJ*, 467, L109
- Gordon I. E. et al., 2026, *J. Quant. Spectrosc. Radiat. Transf.*, 353, 109807

- Grigorev T., Dai Y., Potter M., Xiang X., Zhang K., Tennyson J., 2026, *ApJS*, 283, 39
- Hallstadius H., Lundberg H., 1989, *Phys. Scr.*, 40, 652
- Hesser J. E., 1968, *J. Chem. Phys.*, 48, 2518
- Imhof R., Read F., 1971, *Chem. Phys. Lett.*, 11, 326
- Khalil M. et al., 2024, *Phys. Chem. Chem. Phys.*, 27, 2783
- Kirby K., Cooper D. L., 1989, *J. Chem. Phys.*, 90, 4895
- Koput J., 2024, *J. Chem. Theory Comput.*, 20, 9041
- Koput J., 2025, *J. Quant. Spectrosc. Radiat. Transf.*, 347, 109673
- Lee E. G., Seto J. Y., Hirao T., Bernath P. F., Le Roy R. J., 1999, *J. Mol. Spectrosc.*, 194, 197
- Lee R. A. et al., 2021, *J. Geophys. Res.: Planets*, 126, e2020JE006602
- Li G., Gordon I. E., Rothman L. S., Tan Y., Hu S.-M., Kass S., Campargue A., Medvedev E. S., 2015, *ApJS*, 216, 15
- Li J.-K. et al., 2025, *Sci. Adv.*, 11, eadz6560
- Li G. et al., 2026, CO line intensities: Solution of the fundamental band problem by the Study of 5 Hot and Cold Bands Intensities
- Lootah F. H. et al., 2022, *Geophys. Res. Lett.*, 49, e2022GL099852
- McGuire S. D., Tibere-Inglese A. C., Mariotto P. B., Cruden B. A., Laux C. O., 2020, *J. Quant. Spectrosc. Radiat. Transf.*, 245, 106855
- Mahmoud S. et al., 2025, *ApJS*, 276, 66
- Medvedev E. S., Ushakov V. G., 2022, *J. Quant. Spectrosc. Radiat. Transf.*, 288, 108255
- Medvedev E. S., Meshkov V. V., Stolyarov A. V., Ushakov V. G., Gordon I. E., 2016, *J. Mol. Spectrosc.*, 330, 36
- Meshkov V. V., Stolyarov A. V., Ermilov A. Y., Medvedev E. S., Ushakov V. G., Gordon I. E., 2018, *J. Quant. Spectrosc. Radiat. Transf.*, 217, 262
- Meshkov V. V., Ermilov A. Y., Stolyarov A. V., Medvedev E. S., Ushakov V. G., Gordon I. E., 2022, *J. Quant. Spectrosc. Radiat. Transf.*, 280, 108090
- Meshkov V. V. et al., 2023, *Russ. J. Phys. Chem. A*, 97, 2165
- Meshkov V. V., Pazyuk E. A., Stolyarov A. V., 2026, *Mol. Phys.*, 124, e2429740
- Morton D. C., Noreau L., 1994, *ApJS*, 95, 301
- Mosyagin N., Oleynichenko A., Zaitsevskii A., Kudrin A., Pazyuk E., Stolyarov A., 2021, *J. Quant. Spectrosc. Radiat. Transf.*, 263, 107532
- Niu M. L. et al., 2013, *Mol. Phys.*, 111, 2163
- Niu M., Heays A., Jones S., Salumbides E., van Dishoeck E., De Oliveira N., Nahon L., Ubachs W., 2015, *J. Mol. Spectrosc.*, 315, 137
- Pal T., Khan I., Worthey G., Gregg M. D., Silva D. R., 2023, *ApJS*, 266, 41
- Peng-Fei L., Lei Y., Zhong-Yuan Y., Yu-Feng G., Tao G., 2013, *Commun. Theor. Phys.*, 59, 193
- Prajapat L., Jagoda P., Lodi L., Gorman M. N., Yurchenko S. N., Tennyson J., 2017, *MNRAS*, 472, 3648
- Salumbides E. J., Niu M. L., Bagdonaitė J., de Oliveira N., Joyeux D., Nahon L., Ubachs W., 2012, *Phys. Rev. A*, 86, 022510
- Sandlin G. D., Bartoe J.-D. F., Brueckner G. E., Tousey R., Vanhoosier M. E., 1986, *ApJS*, 61, 801
- Savelyev I. M., Oleynichenko A. V., Losev M. I., Zaitsevskii A., Stolyarov A. V., Meshkov V. V., Shabaev V. M., 2025, *J. Chem. Phys.*, 163, 194309
- Shang B., Chen G., Li X., Liu L., Dai S., Li F., Bai T., 2026, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, 348, 127148
- Sheffer Y., Federman S. R., Lambert D. L., Cardelli J. A., 1992, *ApJ*, 397, 482
- Shi D.-H., Liu H., Sun J.-F., Liu Y.-F., Zhu Z.-L., 2010, *J. Mol. Spectrosc.*, 264, 55
- Shi D.-H., Zhang X., Sun J.-F., Zhu Z.-L., 2011a, *Mol. Phys.*, 109, 1453
- Shi D.-H., Liu H., Sun J.-f., Zhu Z.-L., Liu Y.-f., 2011b, *J. Quant. Spectrosc. Radiat. Transf.*, 112, 2567
- Shi D., Li W., Zhang X., Sun J., Liu Y., Zhu Z., Wang J., 2011c, *J. Mol. Spectrosc.*, 266, 27
- Shi D.-H., Li W.-T., Sun J.-F., Zhu Z.-L., 2013, *Int. J. Quantum Chem.*, 113, 934
- Stolyarov A. V., Pupyshv V. I., 1994, *Phys. Rev. A*, 49, 1693
- Tennyson J., Hill C., Yurchenko S. N., 2013, in Gillaspay J. D., Wiese W. L., Podpaly Y. A., eds, AIP Conf. Proc. Vol. 1545, Eighth International Conference on Atomic and Molecular Data and their Applications: ICAMDATA-2012. Am. Inst. Phys., New York, p. 186
- Tennyson J. et al., 2024, *J. Quant. Spectrosc. Radiat. Transf.*, 326, 109083
- Tilford S. G., Simmons J. D., 1972, *J. Phys. Chem. Ref. Data*, 1, 147
- Ushakov V. G., Medvedev E. S., 2025, *J. Mol. Spectrosc.*, 413, 112037
- Usov D. P. et al., 2024, *Phys. Rev. A*, 109, 042822
- Wei P., Huang C., Cheng X., Zhang H., 2024, *Chin. Phys. B*, 33, 043101
- Yurchenko S. N., Lodi L., Tennyson J., Stolyarov A. V., 2016, *Comput. Phys. Commun.*, 202, 262
- Yurchenko S. N., Al-Rafaie A. F., Tennyson J., 2018, *A&A*, 614, A131
- Zhang M., Shi D., 2021, *Comput. Theor. Chem.*, 1202, 113302
- Zhang X., Shi D.-H., Sun J.-F., Zhu Z.-L., 2011, *Mol. Phys.*, 109, 1627
- Zhang S., Chen W., Liu L., 2026, *Phys. Chem. Chem. Phys.*, 28, 3734
- Zobov N. F., Ovsyannikov R. I., Rogov M. A., Lebedev E. I., Tennyson J., Polyansky O. L., 2025, *J. Quant. Spectrosc. Radiat. Transf.*, 325, 109510

SUPPORTING INFORMATION

Supplementary data are available at *MNRAS* online.

The data and input files supporting the findings of this study are available in the repository folder entitled `A_X_4th_noSOC`. This archive contains the following materials:

- (i) Grids of PECs and TDM functions extracted from the MOLPRO output files, provided as `CO_pv5z_Ec.xlsx` and `CO_pv5z_Ec.xlsx`, respectively.
- (ii) The DUO input file containing the fitted parameters for the $X^1\Sigma^+$ and $A^1\Pi$ electronic states, along with the experimentally refined energy levels derived from the MARVEL data set.
- (iii) Absorption cross-section files at three different temperatures, corresponding to the results shown in Figs 9 and 12, provided in `.xsec` format.

Please note: Oxford University Press is not responsible for the content or functionality of any supporting materials supplied by the authors. Any queries (other than missing material) should be directed to the corresponding author for the article.

This paper has been typeset from a $\text{\LaTeX}$ file prepared by the author.