ExoMol line lists XXXI: spectroscopy of lowest eight electronic states of \( \text{C}_2 \)

Sergei N. Yurchenko,1 István Szabó,2 Elizaveta Pyatenko1 and Jonathan Tennyson1

1Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
2Department of Chemistry, King’s College London, London SE1 1DB, UK

Accepted 2018 July 26. Received 2018 July 4; in original form 2018 May 5

ABSTRACT

Accurate line lists for the carbon dimer, \( \text{C}_2 \), are presented. These line lists cover rovibronic transitions between the eight lowest electronic states: \( X^1 \Sigma_u^+, a^3 \Pi_u, A^1 \Pi_u, b^3 \Sigma_g^-, c^3 \Sigma_g^+, d^3 \Pi_u, B^1 \Delta_u \), and \( B^1 \Sigma^+ \). Potential energy curves (PECs) and transition dipole moment curves are computed on a large grid of geometries using the aug-cc-pwCVQZ-DK/MRCI level of theory including core and core–valence correlations and scalar relativistic energy corrections. The same level of theory is used to compute spin-orbit and electronic angular momentum couplings. The PECs and couplings are refined by fitting to the empirical (MARVEL) energies of \( ^{12}\text{C}_2 \) using the nuclear-motion program DUO. The transition dipole moment curves are represented as analytical functions to reduce the numerical noise when computing transition line strengths. Partition functions, full line lists, Landé-factors, and lifetimes for three main isotopologues of \( \text{C}_2 \) (\( ^{12}\text{C}_2, ^{13}\text{C}_2 \), and \( ^{12}\text{C}^{13}\text{C} \)) are made available in electronic form from the CDS (http://cdsarc.u-strasbg.fr) and ExoMol (www.exomol.com) data bases.

Key words: molecular data – opacity – astronomical data bases: miscellaneous – planets and satellites: atmospheres – stars: low-mass.

1 INTRODUCTION

The \( \text{C}_2 \) molecule is a prominent species in a wide variety of astrophysical sources, including comets (Rousselot et al. 2012), interstellar clouds (Hupe, Sheffer & Federman 2012), translucent clouds (Sonnentrucker et al. 2010), protoplanetary nebulae (Wehres et al. 2010), cool carbon stars (Goorvitch 1990), high-temperature stars (Vartya 1970), and the Sun (Lambert 1978; Brault et al. 1982). Indeed \( \text{C}_2 \) spectra are commonly used to determine the \( ^{12}\text{C}/^{13}\text{C} \) isotopic ratio in carbon stars (Zamora et al. 2009) and comets (Stawikowski & Greenstein 1964).

Unusually, astronomical spectra of \( \text{C}_2 \) have been observed via several different electronic bands; those considered in this work are summarized in Fig. 1. The spectroscopy of \( \text{C}_2 \) is an important tool for stellar classifications (Keenan & Morgan 1941; Vartya 1970; Fujita 1980; Keenan 1993; De Mello et al. 2009; Gonnoau et al. 2017) and determining the chemical composition of stars (Querci, Querci & Kunde 1971; Lambert et al. 1984; Goorvitch 1990; Bakker et al. 1996; Hall & Maxwell 2008; Zamora et al. 2009; Ishigaki et al. 2012; Green 2013; Schmidt et al. 2013; Gonnoau et al. 2017) and of the Sun (Lambert 1968; Grevesse & Sauval 1973; Lambert 1978; Brault et al. 1982).

The Swan bands of \( \text{C}_2 \) have long been known in cometary spectra (Meunier 1911). These bands are easily detected and have been extensively studied, see Rousselot et al. (2012), for example. The Swan bands are useful to estimate the effective excitation temperatures of \( \text{C}_2 \), see, for example Lambert & Danks (1983) and Rousselot et al. (1995). Using \( \text{C}_2 \) columns densities, Newburn & Spinrad (1984) were able to obtain \( \text{C}_2/\text{O} \) and \( \text{C}_2/\text{CN} \) ratios for 17 comets. Other observations include works on the cometary spectroscopy of \( \text{C}_2 \) by Stawikowski & Greenstein (1964), Mayer & O’dell (1968), Owen (1973), Danks, Lambert & Arpigny (1974), Johnson, Fink & Larson (1983), Lambert & Danks (1983), Newburn & Spinrad (1984), Gredel, van Dishoeck & Black (1989), and Rousselot et al. (2012).

Stawikowski & Greenstein (1964) used the \( 1, 0 \) band to determine the \( ^{12}\text{C}/^{13}\text{C} \) ratio in comet Ikeya and found it similar to that observed in the solar system, \( ^{12}\text{C}/^{13}\text{C} = 89 \). The \( 1, 0 \) band head was also used to determine the \( ^{12}\text{C}/^{13}\text{C} \) ratio in the comet Tago-Sato-Kosaka 1969 by Owen (1973) and the comet Kohoutek by Danks et al. (1974). Rousselot et al. (2012) used the \( 1, 0 \) and \( 2, 1 \) Swan bands to obtain isotope ratios for two comets (NEAT and LINEAR), which were again consistent with the terrestrial ratio, thus supporting the proposition that comets were created in our solar system and indicating that the ratio has not changed significantly since their birth (Rousselot et al. 2012).

Although \( \text{C}_2 \) had long been observed in the spectra of cool stars and comets, the first detection in the interstellar medium (ISM) was
There have been extensive theoretical studies involving the eight lowest electronic states of C$_2$. Here we discuss only the most recent works. Because of the near degeneracies among the electron configurations along the whole range of internuclear separations, the potential energy curves (PECs) lie very close together, even near the equilibrium geometry, and several PECs undergo avoided crossings. This means that traditional single-reference methods are unable to provide quantitatively acceptable results for the functions dependent upon the interatomic distance (Abrams & Sherrill 2004; Sherrill & Piecuch 2005).

Systematic high-level ab initio analysis of the $J = 0$ vibrational manifolds including also the $^{12}$C$^{12}$C and $^{13}$C$_2$ isotopologues was performed for the $A^1\Sigma_u^+$ and $X^1\Sigma_g^+$ states by Zhang et al. (2011), who computed PECs of C$_2$ at the multireference configuration interaction (MRCI; Werner & Knowles 1988) level of theory in conjunction with the aug-cc-pV6Z basis set, using complete active space self-consistent field (CASSCF; Roos & Taylor 1980; Werner & Knowles 1985) reference wavefunctions.

Highly accurate PECs, transition dipole moment functions, spectroscopic constants, oscillator strengths, and radiative lifetimes were obtained for the Phillips, Swan, Ballik-Ramsay and Duck systems by Kokkin, Bacskaï & Schmidt (2007) using the CASSCF and subsequent MRCI computational approach including higher order corrections. Schmidt & Bacskaï (2007) improved the aforementioned computational methodology by computation of MRCI transition dipole moments between these four systems. Accurate ab initio calculations of three PECs of C$_2$ at the complete basis set limit were reported by Varandas (2008).

Brooke et al. (2013) presented an empirical line list for the Swan system of C$_2$ ($d^3\Pi_u \rightarrow a^3\Pi_g$) which included vibrational bands with $\nu = 0$ to 10 and $\nu' = 0$ to 9, and rotational states with $J$ up to 96, based on an accurate ab initio (MRCI) transition dipole moment $d-a$ curve. The opacity data base of Kurucz (2011) contains a C$_2$ line list for several electronic bands; Ballik-Ramsay, Swan, Fox-Herzberg ($\varepsilon^1\Pi_u \rightarrow a^3\Pi_g$), and Phillips.

Experimental lifetimes of specific vibronic states of C$_2$ have been reported by Smith (1969), Curtis, Engman & Erman (1976), Bauer et al. (1985, 1986), Naulin, Costes & Dorthe (1988), Erman & Iwane (1995), and Kokkin et al. (2007). These observations provide an important test of any spectroscopic model for the system. Brooke et al. (2013) reported theoretical lifetimes for the Swan band which were in good agreement with experimental values.

The ExoMol project aims to provide line lists for all molecules of importance for the atmospheres of exoplanets and cool stars (Tennyson & Yurchenko 2012; Tennyson et al. 2016b). Given the astrophysical importance of C$_2$ and the lack of a comprehensive line list for the molecule, it is natural that C$_2$ should be treated as part of the ExoMol project. Here we use the program DUO (Yurchenko et al. 2016a) to produce line lists for the eight electronic states ($X^1\Sigma_g^+, A^1\Pi_u$, $B^1\Delta_g$, $B^1\Sigma_g^+, a^3\Pi_u$, $b^3\Sigma_g^+$, $c^3\Sigma_g^+$, and $d^3\Pi_u$) of three isotopologues of C$_2$. The electronic bands connecting these states are summarized in Fig. 1. The line lists are computed using high-level ab initio transition dipole moments of C$_2$, MRCI/aug-cc-pwCVQZ-DK, and empirical potential energy, spin-orbit, electronic angular momenta, Born-Oppenheimer breakdown, spin–spin, spin–rotation, and Λ-doubling curves (see below for description of the curves taken into account). These empirical curves were obtained by refining ab initio curves using a recent set of experimentally derived (MARVEL) term values of C$_2$ (Furtenbacher et al. 2016). This methodology has been used for similar studies as part of the ExoMol project including the diatomic molecules AlO (Patrascu, Tennyson & Yurchenko 2015), ScH (Lodi, Yurchenko & Tennyson 2012), and others.

---

**Figure 1.** Band systems connecting the eight lowest electronic states of C$_2$ considered in this work. The dashed lines represent intercombination bands.
Figure 2. The eight refined potential energy curves of C$_2$ (left) and the avoided crossing between the $X^1\Sigma_g^+$ and $B^1\Sigma_g^+$ states in the adiabatic representation (right).

Figure 3. Diagonal spin-orbit curves of C$_2$ between the $a^3\Pi_u$ and $d^3\Pi_g$. The ab initio curves are shown using dashed line, while the refined curves are given by solid lines. The empirical $d^3\Pi_g$ SOC was produced by morphing the ab initio curve, while the $a^3\Pi_u$ SOC was obtained by refining the ab initio parameters.

Figure 4. Ab initio $a$–$A$, $a$–$c$, $B'$–$b$, $b$–$d$, $X$–$d$, and $A$–$c$ spin-orbit curves of C$_2$. These curves were not refined.

2 THEORETICAL APPROACH

2.1 Electronic structure computations

The presence of spin, orbital, and rotational angular momentum results in complicated and extensive couplings between electronic states. How these are treated formally and their non-perturbative inclusion in the calculation of rovibronic spectra of diatomic molecules is the subject of a recent topical review by two of us (Tennyson et al. 2016a). This review provides a detailed, formal description of the various coupling curves considered below.

The PECs, spin-orbit coupling curves (SOCs), electronic angular momentum curves (EAMCs), and the transition dipole moment curves (TDMs) were computed at the MRCI level of theory, using reference wavefunctions from a CASSCF with all single and double excitations included, in conjunction with the augmented correlation-consistent polarized aug-cc-pwCVQZ-DK Dunning type basis set (Dunning 1989; Woon & Dunning 1993; Peterson & Dunning 2002), plus Douglas-Kroll corrections and core-correlation effects as implemented in MOLPRO (Werner et al. 2012). The complete active space is defined by (3, 1, 1, 0, 3, 1, 1, 0) in the D$_2h$ symmetry group employed by MOLPRO, which corresponds to the $A_g$, $B_3u$, $B_2u$, $B_1g$, $B_1u$, $B_2g$, $B_3g$, and $A_u$ irreducible representations of this group, respectively. The initial grid included about 400 points ranging from 0.7 to 10 Å. However some geometries close to the curve crossings did not converge and were then excluded. Some of the ab initio curves are shown in Figs 2–9. Our $a$–$d$ transition dipole moment curve compares well with that computed by Brooke et al. (2013) who used it to produce their C$_2$ line list for the Swan system.

2.2 Solution of the rovibronic problem

We used the program DUO (Yurchenko et al. 2016a) to solve the fully coupled Schrödinger equation for eight lowest electronic states of C$_2$, single and triplet: $X^1\Sigma_g^+$, $A^1\Pi_u$, $B^1\Delta_x$, $B'^1\Sigma_g^+$, $a^3\Pi_u$, $b^1\Sigma_g^-$, $c^1\Sigma_g^+$, and $d^3\Pi_g$. The vibrational basis set was constructed by solving eight uncoupled Schrödinger equations using the sinc DVR (discrete variable representation) method based on the grid of equidistant 401 points covering the bond lengths between 0.85 and

2015), CaO (Yurchenko et al. 2016b), PO and PS (Prajapat et al. 2017), VO (McKemmish, Yurchenko & Tennyson 2016), NO (Wong et al. 2017), NS and SH (Yurchenko et al. 2018a), SiH (Yurchenko et al. 2018c), and AlH (Yurchenko et al. 2018b).
and oscillator (EMO) functions (Lee et al. 1999) for both ab initio and EMO functions were used. The vibrational basis set sizes were 60, 30, 30, 30, 40, 40, 30, and 30 for $X^1 \Sigma_g^+$, $A^1 \Pi_u$, $B^1 \Delta_g$, $B^1 \Sigma_u^+$, $A^1 \Pi_g$, $B^1 \Sigma_g^-$, $c^1 \Sigma_u^+$, and $d^3 \Pi_g$, respectively.

DuDu employs Hund’s case a formalism: rotational and spin basis set functions are the spherical harmonics $|J, \Omega\rangle$ and $|S, \Sigma\rangle$, respectively. For the nuclear-motion step of the calculation, the electronic basis functions (State, Λ) are defined implicitly by the matrix elements of the SO, EAM coupling, and TDM as computed by MOLPRO. Note that the couplings and TDMs had to be made phase-consistent (Patrascu et al. 2014) and transformed to the symmetrized Λ-representation (see Yurchenko et al. 2016a).

2.3 Potential energy curves

Our PECs are fully empirical (reconstructed through the fit to the experimental data). To represent the PECs, the following two types of functions were used.

For the simpler PECs that do not exhibit avoided crossing ($A^1 \Pi_u$, $B^1 \Delta_g$, $a^1 \Pi_g$, $b^1 \Sigma_u^-$, and $c^1 \Sigma_g^+$) we used the extended Morse oscillator (EMO) functions (Lee et al. 1999) for both ab initio and refined PECs.

In this case a PEC is given by

$$V(r) = V_e + (A_e - V_e) \left[ 1 - \exp \left( -\sum_{k=0}^{N} B_k \xi_k^e (r - r_e) \right) \right]^2,$$

where $A_e - V_e$ is the dissociation energy, $r_e$ is an equilibrium distance of the PEC, and $\xi_k^e$ is the Škurš variable given by

$$\xi_k^e = \frac{r_e - r_0}{r_e + r_0}.$$

The corresponding expansion parameters are obtained by fitting to the empirical (MARVEL) energies from Furtenbacher et al. (2016).

For the three states with avoided crossing, $X^1 \Sigma_g^+$, $B^1 \Sigma_u^+$, and $d^3 \Pi_g$ (see Fig. 2) a diabatic representation of two coupled EMO PECs was used. In this representation the PEC is obtained as a root of a characteristic $2 \times 2$ diabatic matrix

$$\mathbf{A} = \begin{pmatrix} V_1(r) & W(r) \\ W(r) & V_2(r) \end{pmatrix},$$

where $V_1(r)$ and $V_2(r)$ are given by the EMO potential function in equation (1). The coupling function $W(r)$ is given by

$$W(r) = W_0 + \sum_{k=0}^{N} w_k (r - r_0)^k \cosh[\beta (r - r_0)],$$

where $r_0$ is a crossing point. The two eigenvalues of the matrix $\mathbf{A}$ are given by

$$V_{\text{low}}(r) = \frac{V_1(r) + V_2(r)}{2} - \frac{\sqrt{(V_1(r) - V_2(r))^2 + 4 W^2(r)}}{2},$$

$$V_{\text{upp}}(r) = \frac{V_1(r) + V_2(r)}{2} + \frac{\sqrt{(V_1(r) - V_2(r))^2 + 4 W^2(r)}}{2}.$$

For each pair of states, only one component is taken, $V_{\text{low}}$ for $X^1 \Sigma_g^+$ and $d^3 \Pi_g$ and $V_{\text{upp}}$ for $B^1 \Sigma_u^+$, and the other component is ignored. For example, the coupled $X$–$B$ system is treated as two independent diabatic systems in equation (3), as we could not obtain a consistent model with only one pair of the $X$ and $B$ curves. In case of the $X^1 \Sigma_g^+$ state, the upper component, formally representing the $B^1 \Sigma_u^+$ state, is only used as a dummy PEC. The actual $B^1 \Sigma_u^+$ PEC is taken as the upper component with different $V_{\text{low}}$. The latter is also a dummy PEC and disregarded from the rest of the calculations. In this decoupled way we could achieve a more stable fit.

The expansion parameters, including the corresponding equilibrium bond lengths $r_e$ appearing in equations (1)–(4) are obtained by fitting to the experimentally derived energies. The dissociation asymptote $A_e$ in all cases was first varied and then fixed to the value 50 937.91 cm$^{-1}$ (6.315 eV) for all but the $P^2 \Sigma_u^+$ PEC, for which it was refined to obtain 62 826.57 cm$^{-1}$ (7.789 eV) for better accuracy. To compare, the experimental value of $D_0 = 6.30 \pm 0.02$ eV ($D_e \sim 6.41$ eV) was determined by Urdahl, Bao & Jackson (1991). The best ab initio values of $D_e$ of C$_2$ from the literature include 6.197 eV by Feller & Sordo (2000) and 6.381 eV by Varandas (2008). The lowest asymptote $A_e$ correlates with the $3P3P$ limit (Martin 1992), while the next is the $3P1D$ limit (+1.26 eV). Our zero-point-value is 924.02 cm$^{-1}$.

The effect of the avoiding crossings on the shape of the $X^1 \Sigma_g^+$, $B^1 \Sigma_u^+$, and $d^3 \Pi_g$ PECs is illustrated in Fig. 2. It is clear that simple one-curve expansions would be problematic for these states. This effect has been studied in detail by Varandas (2008, 2009).
Figure 7. Empirical curves of C₂: spin–rotational (left) and spin–spin (right) curves representing the states \( a^3\Pi_u \), \( c^3\Sigma_u^+ \), and \( d^3\Pi_g \).

Figure 8. Empirical \( \Lambda \)-doubling curves used for \( a^3\Pi_u \) and \( d^3\Pi_g \) (left-hand panel) and a Born-Oppenheimer breakdown curve used for \( d^3\Pi_g \) (right-hand panel) of C₂.

Figure 9. Dipole moment curves of C₂ between the singlet states X–A, A–B, and A–B’ (left) and between triplet states \( a–d \), \( a–b \), and \( b–d \). The ab initio \( a–d \) TDMC used by Brooke et al. (2013) is also shown.

2.4 Couplings

In the refinement of the SO and EAM coupling we use the ab initio curves, which are ‘morphed’ at the ab initio grid points using the following expansion:

\[
F(r) = \sum_{k=0}^{N} B_k \xi^k (1 - \xi) + \xi B_\infty,
\]

where \( z \) is either taken as the Šurkus variable \( z = \xi \) or a damped coordinate given by

\[
z = (r - r_\text{ref}) e^{-\beta_2 (r - r_\text{ref})^2} - \beta_4 (r - r_\text{ref})^4,
\]

see also Prajapat et al. (2017) and Yurchenko et al. (2018c). Here \( r_\text{ref} \) is a reference position equal to \( r_c \) by default and \( \beta_2 \) and \( \beta_4 \) are damping factors. When used for morphing, the parameter \( B_\infty \) is usually fixed to 1. The \( B_\infty \) parameters should in principle correspond to the atomic limit of the corresponding couplings, however we have
Some of the coupling curves have complex shapes due to, for example, avoided crossings. This complexity is assumed to be covered by the morphing procedure, as morphed curves should inherit the shape of the parent function.

The \( \Lambda \)-doubling effects in \( a^3 \Pi_g \) and \( d^3 \Pi_g \) were obtained empirically using effective \( \Lambda \)-doubling functions, the \((o+p+q)\) and \((p+2q)\) coupling operators (Brown & Merer 1979) as given by

\[
\hat{R}_{opq} = \frac{1}{2} a^{LD}_{opq}(r) \left( \hat{S}_r^2 + \hat{S}_v^2 \right),
\]

\[
\hat{R}_{p2q} = -\frac{1}{2} a^{LD}_{p2q}(r) \left( \hat{J}_- \hat{S}_z + \hat{J}_+ \hat{S}_z \right).
\]

The latter operator is limited to linear \( J \)-dependence, which is justified for the heavy molecule like C\( _2 \). In this case for \( a^{LD}_{p2q}(r) \) and \( a^{LD}_{q2p}(r) \) we use the Šurkus-type expansion as in equation (7). The empirical \( \Lambda \)-doubling curves of C\( _2 \) are shown in Fig. 8. We used these couplings to improve the fit for the states \( a^3 \Pi_g \) and \( d^3 \Pi_g \).

To allow for rotational Born-Oppenheimer breakdown (BOB) effects (Le Roy 2017), the vibrational kinetic energy operator for each electronic state was extended by

\[
-\frac{\hbar^2}{2\mu r^2} \rightarrow -\frac{\hbar^2}{2\mu r^2} \left( 1 + g^{BOB}(r) \right),
\]

where the unitless BOB functions \( g^{BOB} \) are represented by the polynomial

\[
g^{BOB}(r) = \left[ 1 - \xi_\nu \sum_{k=0}^{N_\nu} A_k \xi_\nu^k + \xi_\nu A_\infty \right],
\]

where \( \xi_\nu \) is the Šurkus variable and \( p, A_\nu \), and \( A_\infty \) are adjustable parameters. This representation was used for the \( d^3 \Pi_g \) state only, which appeared to be the most difficult to fit.
Table 3. Rms errors (cm$^{-1}$) for obs.−calc. residuals achieved in the fit for individual vibronic states.

| $v$ | $X$ | $v_0$ | $A$ | $v_a$ | $b$ | $v_c$ | $v_d$ | $B$ | $v_0$ | $B'$ |
|-----|-----|-------|-----|-------|-----|-------|-------|-----|-------|------|
| 0   | 0.01| 0.16  | 0.26| 0.09  | 0.19| 0.19  | 0.01  | 0.02 |
| 1   | 0.01| 0.02  | 0.33| 0.14  | 0.74| 0.09  | 1.07  | 0.06 |
| 2   | 0.16| 0.06  | 0.35| 0.13  | 0.23| 0.17  | 0.06  | 0.31 |
| 3   | 0.33| 0.05  | 0.26| 0.07  | 0.21| 0.44  | 0.05  | 0.10 |
| 4   | 0.06| 0.08  | 0.22| 0.07  | –   | 4.33  | 4.03  | –   |
| 5   | 0.29| 0.13  | 0.22| 0.14  | –   | 5.28  | 5.01  | –   |
| 6   | 0.31| 0.08  | 0.33| 0.15  | –   | 6.70  | 6.04  | –   |
| 7   | 0.04| 0.72  | 0.07| 0.10  | –   | 7.31  | 7.04  | –   |
| 8   | 0.01| 0.67  | 0.10| 0.13  | –   | 8.48  | 8.18  | –   |
| 9   | 1.80| 0.32  | 0.20| –     | –   | –     | 9.100 | –   |
|   – |    | 10    | 0.16| 0.25  | –   | –     | 10.54 | –   |
|   – |    | 11    | 0.34| 0.29  | –   | –     | 11.82 | –   |
|   – |    | 12    | 0.80| 0.26  | –   | –     | 12.44 | –   |
|   – |    | 13    | 2.43| 0.19  | –   | –     | 13. –  | –   |

Figure 10. Obs.−calc. residuals for individual vibronic bands of C$_2$: $g$-states.

Figure 11. Obs.−calc. residuals for individual vibronic bands of C$_2$: $u$-states.

The final model comprises 89 parameters appearing in the expansions from equations (1), (4), and (7) obtained by fitting to 4900 MARVEL energy term values of $^{12}$C$_2$ using DUO. The robust weighting method of Watson (2003) was used to adjust the fitting weights. During the fit, in order to avoid unphysically large distortions, the SOC and EAMS curves were constrained to the ab initio shapes using the simultaneous fit approach (Yurchenko et al. 2003). The MARVEL energies were correlated to the theoretical values using the DUO assignment procedure, which is based on the largest basis function contribution (Yurchenko et al. 2016a). One of the main difficulties in controlling the correspondence between the theoretical (DUO) and experimental energies in case of such a complex, strongly coupled systems is that the relative order of the computed energies can change during the fit, in this case automatic assignment is especially helpful. For some C$_2$ resonance states it was necessary to use also the second largest coefficients to resolve possible ambiguities. However, even this did not fully prevent accidental re-ordering of states, especially the assignment of the different $\Omega$ components of the triplet $a$ and $d$ states appeared to be very unstable and difficult.
Table 4. Extract from the .states file for $^{12}$C$_2$.

| n | $E_0$ | $\tilde{E}$ | $\tilde{E}_0$ | $\tilde{E}_{tot}$ | $J$ | $\tau$ | $g$-Landé | $\pm$ | eff | State | $\nu$ | $\Lambda$ | $\Sigma$ | $\Omega$ | m/d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.000000 | 1 | 0 | Inf | 0.000000 | + | e | X1Sigmag+ | 0 | 0 | 0 | 0 | m |
| 2 | 1827.486182 | 1 | 0 | 1.71E+03 | 0.000000 | + | e | X1Sigmag+ | 1 | 0 | 0 | 0 | m |
| 3 | 3626.681492 | 1 | 0 | 1.08E+03 | 0.000000 | + | e | X1Sigmag+ | 2 | 0 | 0 | 0 | m |
| 4 | 5396.686466 | 1 | 0 | 1.34E+01 | 0.000000 | + | e | X1Sigmag+ | 3 | 0 | 0 | 0 | m |
| 5 | 6250.149530 | 1 | 0 | 1.81E-05 | 0.000000 | + | e | b3Sigmag- | 0 | 0 | 0 | 0 | m |
| 6 | 7136.349911 | 1 | 0 | 6.52E-01 | 0.000000 | + | e | X1Sigmag+ | 4 | 0 | 0 | 0 | m |
| 7 | 7698.252879 | 1 | 0 | 1.47E-05 | 0.000000 | + | e | b3Sigmag- | 1 | 0 | 0 | 0 | m |
| 8 | 8844.124324 | 1 | 0 | 1.94E-01 | 0.000000 | + | e | X1Sigmag+ | 5 | 0 | 0 | 0 | m |
| 9 | 9124.177468 | 1 | 0 | 1.24E-05 | 0.000000 | + | e | b3Sigmag- | 2 | 0 | 0 | 0 | m |
| ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 309 | 619.642109 | 3 | 1 | 1.22E+04 | 0.892310 | – | e | a3Piu | 0 | –1 | 0 | –1 | m |
| 310 | 655.327453 | 3 | 1 | 4.27E+04 | –0.392310 | – | e | a3Piu | 0 | –1 | 1 | 0 | m |
| 311 | 2237.606490 | 3 | 1 | 3.54E+02 | 0.889334 | – | e | a3Piu | 1 | –1 | 0 | –1 | m |
| 312 | 2253.259339 | 3 | 1 | 1.41E+03 | –0.389333 | – | e | a3Piu | 1 | –1 | 1 | 0 | m |
| 313 | 3832.261242 | 3 | 1 | 1.38E+02 | 0.886238 | – | e | a3Piu | 2 | –1 | 0 | –1 | m |
| 314 | 3847.875681 | 3 | 1 | 5.44E+02 | –0.386238 | – | e | a3Piu | 2 | –1 | 1 | 0 | m |
| 315 | 5403.597872 | 3 | 1 | 7.81E+01 | 0.883039 | – | e | a3Piu | 3 | –1 | 0 | –1 | m |
| 316 | 5419.156711 | 3 | 1 | 3.06E+02 | –0.383039 | – | e | a3Piu | 3 | –1 | 1 | 0 | m |
| 317 | 6951.569985 | 3 | 1 | 2.65E+01 | 0.879743 | – | e | a3Piu | 4 | –1 | 0 | –1 | m |
| 318 | 6976.108683 | 3 | 1 | 4.06E+01 | –0.379743 | – | e | a3Piu | 4 | –1 | 1 | 0 | m |
| 319 | 8271.609854 | 3 | 1 | 1.31E–05 | 0.500000 | – | e | a1Piu | 0 | –1 | 0 | –1 | m |

Column Notation

- $i$: State counting number
- $E$: State energy in cm$^{-1}$
- $g$: Total statistical weight, equal to $g_{ns}(2J+1)$
- $J$: Total angular momentum
- $\tau$: Lifetime (s$^{-1}$)
- $g_J$: Landé $g$-factor
- $\pm$: Total parity
- eff: Rotationless parity (Brown et al. 1975; Bernath 2005)

State:

- Electronic state
- $v$: State vibrational quantum number
- $\Lambda$: Projection of the electronic angular momentum
- $\Sigma$: Projection of the electronic spin
- $\Omega = \Lambda + \Sigma$: Projection of the total angular momentum
- m/d: $m =$ MARVEL, $d =$ Duo

Table 5. Extract from the $^{12}$C$_2$.trans file. Identification numbers $f$ and $i$ for upper (final) and lower (initial) levels, respectively, Einstein-A coefficients denoted by $A$ (s$^{-1}$) and transition frequencies $\nu$ (cm$^{-1}$).

| $f$ | $i$ | $\nu$ | $\nu$ |
|---|---|---|---|
| 2645 | 2025 | 3.2835E–10 | 140.623371 |
| 3199 | 3823 | 4.0106E–02 | 140.628688 |
| 10 456 | 10 728 | 8.7514E–07 | 140.643001 |
| 9 518 | 9 321 | 1.0017E–01 | 140.646479 |
| 12 644 | 12 248 | 8.347E–11 | 140.659142 |
| 31 380 | 31 262 | 1.9673E–02 | 140.674536 |
| 19 212 | 19 072 | 7.0890E–08 | 140.695134 |
| 31 818 | 31 381 | 3.4496E–08 | 140.710566 |
| 13 701 | 13 087 | 2.6171E–09 | 140.710707 |
| 4772 | 4972 | 6.4432E–07 | 140.723432 |
| 24 697 | 25 214 | 9.6700E–08 | 140.724596 |
| 5111 | 5398 | 2.7821E–08 | 140.725422 |
| 14 918 | 15 183 | 6.6731E–07 | 140.728046 |

In such cases, as the final resort for preventing disastrous fitting effects, states exhibiting too large errors (typically > 8 cm$^{-1}$) were removed from the fit, which, together with the second-largest-coefficient assignment feature are new implementations in DUO. One of the artefacts of the largest-contribution assignment is that it can fail for the vibrational quantum numbers at high rotational excitations $J$. Our vibrational basis functions, generated as eigensolutions of the pure, uncoupled $J = 0$, Schrödinger equations, become less efficient for high $J$ (>50). This is because of the centrifugal distortion term in the Hamiltonian, which becomes large and thus distorts the effective shape of the interaction potential substantially. The rovibronic eigenfunctions in this case are a complicated mixture of
Figure 12. Electronic bands of C$_2$ at $T = 2000$ K using a Gaussian line profile with HWHM of 5 cm$^{-1}$. The forbidden interconnection band is shown using a light (yellow) colour.

Figure 13. Temperature dependence of the C$_2$ cross-sections using the 8states line list, from bottom to top: $T = 500$, 1000, 2000, 3000, and 5000 K.

Figure 14. $\chi ^{1} \Sigma ^{\pm}_g - \alpha ^{3} \Pi _u$ intercombination band of C$_2$ in absorption at $T = 100$ K. Individual 8states lines and cross-sections obtained using Lorentzian line profile of HWHM $= 0.5$ cm$^{-1}$ are shown. The major features are assigned; numbers in square brackets represent the $\Omega$ spin components $^{3} \Pi _{\Omega}$ of the $\alpha ^{3} \Pi _u$ state.

Figure 15. 8states comparing to Kurucz's line list (Kurucz 2011) at $T = 1100$ K.

Figure 16. The C$_2$ Swan (0, 0) $P$ branch band from the spectrum of V854 Cen recorded on 1998 April 8 by Kameswara Rao & Lambert (2000) (lower trace), compared to the theoretical spectrum at $T = 4625$ K (quoted as rotation temperature by Kameswara Rao & Lambert 2000) using a Gaussian line profile with HWHM $= 0.8$ cm$^{-1}$ (upper trace). The star spectrum is red-shifted by 0.2195 nm.

Figure 17. Swan band: Carbon-star HD 92055 spectra observed by Rayner et al. (2009) at $R = 2000$ compared to cross-sections simulated using $T = 5000$ K and a Gaussian profile with HWHM $= 1$ cm$^{-1}$.
new feature in DUO implemented in order to improve the vibrational states of the same electronic term and 

\[ g(M) = \frac{\gamma}{2\pi} \]

energies in our fitting set are supported by multiple transitions and assignment of the states with high values of \( J \).

Figure 18. The Phillips band of C\(_2\) at \( T = 240 \) K using a Gaussian line profile with HWHM of 0.2 cm\(^{-1}\) (upper display) compared to the spectrum of the AGB remnants of HD 56126 observed by Bakker et al. (1996; lower display). The HD 56126 spectrum was shifted to match the Mg(I) line to 8809.8 \( \AA \). The theoretical transmittance spectrum is computed assuming the column of \( 10^{16} \) molecule cm\(^{-2}\).

Figure 19. The C\(_2\) Swan (0, 0), (1, 0), and (0, 1) bands in emission at \( T = 2700 \) K simulated using our line list and the empirical line list of Brooke et al. (2013) and a Gaussian line profile of HWHM = 0.15 cm\(^{-1}\).

4 LINE LISTS

The line lists for three isotopologues of the carbon dimer, \(^{12}\)C\(_2\), \(^{13}\)C\(_2\), and \(^{12}\)C\(^{13}\)C were computed using the refined model of the eight lowest electronic states and the ab initio transition DMCs. The line lists, called 8states, cover the wavelength region up to 0.25 \( \mu m \), \( J = 0 \ldots 190 \). The upper state energy term values were truncated at 50 000 cm\(^{-1}\). The lower state energy threshold was set to 30 000 cm\(^{-1}\) so one can assume that the other electronic states from the region below 50 000 cm\(^{-1}\) are not populated. The vibrational excitation coverage for each electronic state was defined based on the convergence and completeness to include all bound states below the first dissociation limit. We did not have problems with the numerical noise in the production of overtone intensities since they are simply forbidden, as are any transitions within the same electronic states, therefore no transition dipole moment cutoffs were applied.

The homonuclear molecule C\(_2\) belongs to the infinite point symmetry group \( D_\infty \), which also the group used in classification of the electronic terms. The total rovibronic state spans a finite symmetry group \( D_{\infty h} \) with four elements \( E \) (the identity), \( (12) \) (exchange of the identical nuclei), \( E' \) (inversion), and \( (12)' \) (Bunker et al. 1997; Bunker & Jensen 1998). The irreducible representations of \( D_{\infty h} \) are \( \Sigma^e_1 \), \( \Sigma^g_1 \), \( \Sigma^g_2 \), and \( \Sigma^e_2 \). For energy calculations DUO uses the \( C_{\infty v} \) group to symmetrize its basis both for homonuclear and heteronuclear systems. This group has two elements, \( \Sigma^e \) and \( \Sigma^g \), depending on whether the corresponding property is symmetric or antisymmetric when the molecule is inverted. In case of homonuclear \(^{12}\)C\(_2\), the missing symmetry is the permutation of the nuclei, which introduces additional elements \( g \) and \( u \). This does not affect the energy calculations as the absence of corresponding couplings between \( g \) and \( u \) is guaranteed by construction. However, it is important to use the proper symmetry for intensities mainly due to the selection rules imposed by the nuclear spin statistics associated with different irreducible representations. For the homonuclear molecules like C\(_2\), we therefore have to further classify the rovibronic states according to \( g \) and \( u \). This is done by simply adopting the corresponding symmetry of the electronic terms.
The carbon atom $^{12}$C has a zero nuclear spin. This gives rise to the zero statistical weights $g_{ns}$ for the $\Sigma_1^+$ and $\Sigma_1^-$ states, while the other two irreducible representations have $g_{ns} = 1$. The statistical weights in case of $^{13}$C$_2$ are $g_{ns} = 1, 1, 3$ and $3$ for $\Sigma_1^+$, $\Sigma_1^-$, $\Sigma_1^+$, and $\Sigma_1^-$, respectively. For $^{12}$C$^{13}$C, all states have $g_{ns} = 2$. Note ExoMol follows the HITRAN convention (Gamache et al. 2017) and includes the full nuclear-spin degeneracy in the partition function.

Other selection rules for the electronic dipole transitions are $\pm \leftrightarrow \mp$, $g \leftrightarrow u$, $J' - J'' = 0, \pm 1$.

The $^{12}$C$_2$ line list contains 44 189 states and 6080 920 transitions, while the $^{13}$C$_2$ and $^{12}$C$^{13}$C line lists comprise 94 003/13 361 992, and 91 067/1 2743 954 states/transitions, respectively.

The line lists include lifetimes and L"{a}nde–g factors. Extracts from the line lists are given in Tables 4 and 5. In the final .states file the theoretical (DUO) energy term values were replaced with the experimentally derived (MARVEL) values where available and indicated by a label $m$.

5 RESULTS AND DISCUSSION

5.1 Spectra

All spectral simulations were performed using exocross (Yurchenko, Al-Refaie & Tennyson 2018d): our open-access Fortran 2003 code written to work with molecular line lists.

Fig. 12 shows an overview of the electronic absorption spectra of $^{12}$C$_2$ at $T = 2000$ K and Fig. 13 shows the temperature dependence of C$_2$ absorption cross-sections computed using the 8states line list. The single–triplet intercombination $X^1\Sigma_g^+ - a^3\Pi_u$ band is illustrated in Fig. 12 as well as in Fig. 14. Fig. 15 compares the synthetic absorption spectra of C$_2$ at $T = 1100$ K computed using our 8states line list with that by Kurucz (2011). The agreement is very good: Kurucz (2011)’s line list has more extensive coverage, while ours is more accurate and complete below 40 000 cm$^{-1}$.

Fig. 16 shows a comparison of a Swan band-head (0, 0) calculated using our new line list and a stellar spectrum of V854 Cen (Kameswaran Rao & Lambert 2000). Fig. 17 compares the theoretical flux spectrum of C$_2$ with a stellar spectrum of the Carbon star HD 92055 (Rayner, Cushing & Vacca 2009) at the resolving power $R = 2000$. Fig. 18 shows a simulated Philips band (2, 0) compared to the spectrum of AGB remnants of HD 56126 observed by Bakker et al. (1996). Similar spectra of this band were reported by Schmidt et al. (2013) and Ishigaki et al. (2012).

Fig. 19 gives detailed, high-resolution emission spectra of the (0, 0), (1, 0), and (0, 1) Swan bands computed using our line list and the empirical line list by Brooke et al. (2013). Fig. 20 shows a simulation of the $d$–$c$ (3, 0) band of C$_2$ compared to the experiment by Nakajima & Endo (2014).

Fig. 21 shows a plasma spectrum of C$_2$ recorded by Al-Shboul et al. (2013) compared to 8states emission cross-sections at $T = 8000$ K.

Figure 20. The $d$–$c$ band of C$_2$ at $T = 300$ K using a Gaussian line profile with HWHM of 0.1 cm$^{-1}$ (lower display) compared to the experimental spectrum of Nakajima & Endo (2014; upper display).

Figure 21. Swan bands: a plasma spectrum of C$_2$ by Al-Shboul et al. (2013) and our emission spectrum (erg cm$^{-1}$ sr$^{-1}$ molecule$^{-1}$) at $T = 8000$ K for four different vibronic bands as specified in each panel. A Gaussian profile with the HWHM = 4 cm$^{-1}$ was used.
5.2 Isotopic shifts

Fig. 22 shows the effect of the isotopic substitution on the vibronic spectra of C₂ for the (1,0) Swan band of ¹²C₂, ¹²C¹³C, and ¹³C₂ at T = 6000 K compared to the experimental, laser-induced plasma spectrum of Dong et al. (2014).

5.3 Partition function

As part of the line list package and as supplementary material we also report partition functions of the three C₂ isotopologues up to 10000 K at 1 K intervals. Fig. 23 shows the partition functions of ¹²C₂ computed using our line list and compared to that by Sauval & Tatum (1984) and Barklem & Collet (2016). All three partition functions are in a good agreement.

We have also fitted the partition functions to the function form of Vidler & Tennyson (2000):

\[ \log_{10} Q(T) = \sum_{n=0}^{9} a_n \left( \log_{10} T \right)^n. \]

(13)

Table 6 gives the expansion coefficients for all three isotopologues considered, which reproduce our partition functions within 1 per cent (relative values) for T > 300 K and within ∼1 (absolute values) for T < 300 K.

5.4 Lifetime

We have computed lifetimes of C₂ for all rovibronic states below 30000 cm⁻¹. These are compared to the experimental and theoretical values by Smith (1969), Cooper & Nicholls (1975), Curtis et al. (1976), Bauer et al. (1985, 1986), Naulin et al. (1988), and Erman & Iwane (1995). The agreement is good and comparable to the previous ab initio values (Davidson corrected MRCI/aug-cc-pV6Z level) obtained by Schmidt & Bacskay (2007) and Kokkin et al. (2007). The lifetimes are also illustrated in Fig. 24. The rather unusual long lifetimes of the lower rovibronic states of \( a^3 \Pi_u \) are explained by crossing with the lower states of \( X^1 \Sigma_g^+ \) at about \( J = 50 \), where the \( a^3 \Pi_u \) rovibronic states are lower than the \( X^1 \Sigma_g^+ \) rovibronic states. Up to \( J = 48 \) the lowest state in each \( J \)-manifold

Table 6. Fitting parameters used to represent the partition functions of C₂ (see equation 13). Fits are valid for temperatures up to 10 000K.

| Parameter | \( ^{12}\text{C}^{12}\text{C} \) | \( ^{12}\text{C}^{13}\text{C} \) | \( ^{13}\text{C}^{13}\text{C} \) |
|-----------|----------------|----------------|----------------|
| \( a_0 \) | 7.6691867335 | 0.0426980211 | 0.2401679500 |
| \( a_1 \) | -45.6411466388 | 16.5774126902 | 15.5801797784 |
| \( a_2 \) | 91.4980228540 | -66.5674034182 | -65.2114249415 |
| \( a_3 \) | -88.7302064590 | 113.4659696600 | 112.571888350 |
| \( a_5 \) | 48.2113438335 | -102.5476537440 | -102.3357156140 |
| \( a_6 \) | -15.3601370784 | 54.3985236316 | 54.4790813354 |
| \( a_7 \) | 48.2113438335 | -102.5476537440 | -102.3357156140 |
| \( a_8 \) | -15.3601370784 | 54.3985236316 | 54.4790813354 |
| \( a_9 \) | 7.6691867335 | 0.0426980211 | 0.2401679500 |
The line lists cover eight lowest electronic (singlet and triplet) states, are based on high level ab initio (MRCI) calculations and implemented by empirical curves representing different corrections (Born-Oppenheimer-breakdown, A-doubling, spin-spin and spin-rotation). The line lists should be complete up to about 30 000 cm\(^{-1}\) with the energies stretching up to 50 000 cm\(^{-1}\). In order to improve the accuracy of the line positions, where available the electronic energies were replaced by experimentally derived MARVEL values. The line lists were benchmarked against high temperature stellar and plasma spectra. Experimental lifetimes were especially important for assessing our absolute intensities as well as the quality of the underlined ab initio dipole moments of C\(_2\) used. The line lists, the spectroscopic models and the partition functions are available from the CDS (http://cdsarc.u-strasbg.fr) and ExoMol (www.exomol.com) data bases.

### Acknowledgements

We thank Andrey Stolyarov, Timothy W. Schmidt, and George B. Bacskay for help at different stages of the project. This work was supported by the UK Science and Technology Research Council (STFC) No. ST/M001334/1 and the COST action MOLIM No. CM1405. This work made extensive use of UCL’s Legion high-performance computing facility. A part of the calculations were performed using DARWIN, high-performance computing facilities provided by DiRAC for particle physics, astrophysics, and cosmology and supported by BIS National E-infrastructure capital grant ST/J005673/1 and STFC grants ST/H008586/1, ST/K00333X/1.

### References

Abrams M., Sherrill C., 2004, J. Chem. Phys., 121, 9211
Al-Shboul K. F., Harilal S. S., Hassanein A., 2013, J. Appl. Phys., 113, 163305
Amiot C., 1983, ApJS, 52, 329
Amiot C., Chauville J., Mailllard J.-P., 1979, J. Mol. Spectrosc., 75, 19

---

**Table 7.** Experimental and calculated lifetimes of C\(_2\) vibronic states: note the different time-scales used to represent the lifetimes associated with different electronic states. Previous calculations have only considered limited decay routes for each state; these are noted in the footnote. The results suggest that these assumptions were justified.

| State | Source | 0  | 1  | 2  | 3  | 4  | 5  |
|-------|--------|----|----|----|----|----|----|
| \(A^1\Pi_u\) Calc. | 13 | 10.4 | 8.77 | 7.65 | 6.84 | 6.22 Schmidt & Bacskay (2007) |
| Exp. | 16.6 | 13.1 | 11.0 | 9.55 | 8.50 | 7.71 Kokkin et al. (2007) |
| Exp. | 13.4 ± 2.5 | 15.4 ± 4.0 | 14.4 ± 2.0 | 12.0 ± 2.0 | 10.7 ± 2.0 | 7.9 ± 2.0 Bauer et al. (1985) |
| Exp. | 18.5 ± 3 | – | 11.4 ± 2 | – | – | – Bauer et al. (1986) |
| Exp. | 13.13 | 10.62 | 8.95 | 7.77 | 7.63 | 6.91 This work |
| d\(^1\Pi_e\) Calc. | 95.1 | 96.7 | 99.1 | 102 | 107 | 113 Schmidt & Bacskay (2007) |
| Calc. | 98 | 99.8 | 102.4 | 106 | 110.9 | 118.2 Brooke et al. (2013) |
| Calc. | 103.20 | 104.97 | 107.86 | 111.66 | 117.77 | 123.23 Kokkin et al. (2007) |
| Exp. | 101.8 ± 4. | 96.7 ± 5.2 | 104 ± 17 | – | – | – Naulin et al. (1988) |
| Exp. | 106.15 | 105.15 | – | – | – | – Bauer et al. (1986) |
| Exp. | 123 ± 6 | 124 ± 6 | 130 ± 6 | 128 ± 6 | 131 ± 6 | 137 ± 10 Curtis et al. (1976) |
| Calc. | 99.37 | 101.62 | 104.71 | 108.69 | 115.18 | 119.3 This work |
| Calc. | 17.83 | 14.59 | 12.47 | 11.09 | 9.88 | 9.38 Schmidt & Bacskay (2007) |
| Calc. | 95.1 | 96.7 | 99.1 | 102 | 107 | 113 Schmidt & Bacskay (2007) |
| Calc. | 17.2 | – | – | – | – | – Cooper & Nicholls (1975) |
| Calc. | 17.00 | 14.46 | 12.68 | 11.46 | 10.39 | 9.612 This work |

**Note:**

- \(D^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+\), \(B^1\Pi_g\), and \(C^1\Pi_g\) only considered.
- \(A^1\Pi_u \rightarrow X^1\Sigma_g^+\) only considered.
- \(d^3\Pi_f \rightarrow a^3\Pi_u\) only considered.
- \(b^3\Sigma_g^+ \rightarrow a^3\Pi_u\) only considered.
- \(\Sigma\) Average value for a range of vibrational states.
Rousselot P., Jehin E., Manfroid J., Hutsemékers D., 2012, A&A, 545, A24
Roux F., Wannous G., Michaud F., Verges J., 1985, J. Mol. Spectrosc., 109, 334
Sauval A. J., Tatum J. B., 1984, ApJS, 56, 193
Schmidt T. W., Bacskay G. B., 2007, J. Chem. Phys., 127, 234310
Schmidt M. R., Začs L., Pulecka M., Szczera B., 2013, A&A, 556, A46
Sherrill C., Piecuch P., 2005, J. Chem. Phys., 122, 124104
Smith W. H., 1969, ApJ, 156, 791
Snow T. P., McCall B. J., 2006, ARA&A, 44, 367
Sonnentrucker P., Welty D. E., Thorburn J. A., York D. G., 2007, ApJS, 168, 58
Sorkhabi O., Blunt V. M., Lin H., Xu D., Wrobel J., Price R., Jackson W. M., 1997, J. Chem. Phys., 107, 9842
Souza S. P., Lutz B. L., 1977, ApJ, 216, L49
Stawikowski A., Greenstein J. L., 1964, ApJ, 140, 1280
Tanabashi A., Amano T., 2002, J. Mol. Spectrosc., 215, 285
Tanabashi A., Hirao T., Amano T., Bernath P. F., 2007, ApJS, 169, 472
Tennyson J., Yurchenko S. N., 2012, MNRAS, 425, 21
Tennyson J., Lodi L., McKemmish L. K., Yurchenko S. N., 2016a, J. Phys. B, 49, 102001
Urdahl R. S., et al., 2016b, J. Mol. Spectrosc., 327, 73
Varandas A. J. C., 2008, J. Chem. Phys., 129, 234103
Varandas A. J. C., 2009, Chem. Phys. Lett., 471, 315
Vartya M. S., 1970, ARA&A, 8, 87
Vidier M., Tennyson J., 2000, J. Chem. Phys., 113, 9766
Watson J. K. G., 2003, J. Mol. Spectrosc., 219, 326
Wehres N., Romanzin C., Limmart H., Van Winckel H., Tielens A. G. G. M., 2010, A&A, 518, A36
Werner H.-J., Knowles P. J., 1985, J. Chem. Phys., 82, 5053
Werner H.-J., Knowles P. J., 1988, J. Chem. Phys., 89, 5803
Werner H.-J., Knowles P. J., Kinzla G., Manby F. R., Schütz M., 2012, WIRES Comput. Mol. Sci., 2, 242
Wong A., Yurchenko S. N., Bernath P., Mueller H. S. P., McConkey S., Tennyson J., 2017, MNRAS, 470, 882
Woon D. E., Dunning T. H., 1993, J. Chem. Phys., 98, 1358
Yan W.-B., Curl R., Merer A. J., Carrick P. G., 1985, J. Mol. Spectrosc., 112, 436
Yeung S.-H., Chan M.-C., Wang N., Cheung A. S.-C., 2013, Chem. Phys. Lett., 557, 31
Yurchenko S. N., Carvajal M., Jensen P., Herregodts F., Huet T. R., 2003, Chem. Phys., 290, 59
Yurchenko S. N., Lodi L., Tennyson J., Stolyarov A. V., 2016a, Comput. Phys. Commun., 202, 262
Yurchenko S. N., Blissett A., Asari U., Vasilios M., Hill C., Tennyson J., 2016b, MNRAS, 456, 4524
Yurchenko S. N., Bond W., Gorman M. N., Lodi L., McKemmish L. K., Nunn W., Shah R., Tennyson J., 2018a, MNRAS, 478, 270
Yurchenko S. N., Williams H., Leyland P. C., Lodi L., Tennyson J., 2018b, MNRAS, 479, 1401
Yurchenko S. N., Sinden F., Lodi L., Hill C., Gorman M. N., Tennyson J., 2018c, MNRAS, 473, 5324
Yurchenko S. N., Al-Refaie A. F., Tennyson J., 2018d, A&A, 614, A131
Zamora O., Abia C., Plez B., Dominguez I., Cristallo S., 2009, A&A, 508, 909
Zhang X.-N., Shi D.-H., Sun J.-F., Zhu Z.-L., 2011, Chin. Phys. B, 20, 043105

SUPPORTING INFORMATION

Supplementary data are available at MNRAS online.

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 TeX/LaTeX file prepared by the author.