ExoMol molecular line lists – XXVII. Spectra of C₂H₄

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ABSTRACT
A new line list for ethylene, ¹²C₂¹H₄, is presented. The line list is based on high-level ab initio potential energy and dipole moment surfaces. The potential energy surface is refined by fitting to experimental energies. The line list covers the range up to 7000 cm⁻¹ (1.43 μm) with all ro-vibrational transitions (50 billion) with the lower state below 5000 cm⁻¹ included and thus should be applicable for temperatures up to 700 K. A technique for computing molecular opacities from vibrational band intensities is proposed and used to provide temperature-dependent cross-sections of ethylene for shorter wavelength and higher temperatures. When combined with realistic band profiles (such as the proposed three-band model), the vibrational intensity technique offers a cheap but reasonably accurate alternative to the full ro-vibrational calculations at high temperatures and should be reliable for representing molecular opacities. The C₂H₄ line list, which is called MaYT, is made available in electronic form from the CDS (http://cdsarc.u-strasbg.fr) and ExoMol (www.exomol.com) databases.

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

1 INTRODUCTION
Hydrocarbons are an important class of molecules for planetary atmospheres. Methane in particular has been detected in many places in the solar system including: the atmospheres of Jupiter (Gladstone, Allen & Yung 1996; Atreya et al. 2003), Saturn (Guerlet et al. 2009), Mars (Atreya, Mahaffy & Wong 2007), Uranus and Neptune (Lunine 1993) as well as in exoplanetary atmospheres (Swain, Vasisht & Tinetti 2008; Beaulieu et al. 2011). Methane is thought to be a key biosignature (Sagan et al. 1993). In atmospheres with an abundance of methane, chemical reactions initiated by photolysis of C–H bonds leads to the formation of larger hydrocarbons (Gladstone et al. 1996; Guerlet et al. 2009; Hu & Seager 2014). Particularly important are the C₂H₆ hydrocarbons: acetylene, ethylene and ethane. These molecules have been detected (along with propane, C₃H₈) in the atmospheres of the solar system gas giants (Lunine 1993; Gladstone et al. 1996; Atreya et al. 2003; Guerlet et al. 2009). They have also been observed in the atmosphere of Saturn’s largest moon Titan (Niemann et al. 2005) which has lakes of liquid hydrocarbons (Stofan et al. 2007). Hydrocarbons were even detected by the Cassini probe in plumes from Enceladus (Waite et al. 2006). Ethylene, the focus of this work, is well-known in the circumstellar envelope of IRC+10216 (Betz 1981; Fonfria et al. 2017) and is thought to be important in the atmospheres of exoplanets (Tinetti, Encrenaz & Coustenis 2013).

The ro-vibrational energy levels of ethylene have been the focus of multiple theoretical works in this decade. This is due to both its importance and because it is one of the few six-atom molecules which is relatively rigid: the barrier to rotation of the CH₂ groups is 23 000 cm⁻¹ and involves breaking the π bond (Krylov et al. 1998). This makes ethylene an ideal candidate to develop theoretical methods for medium-sized molecules. Avila & Carrington (2011) calculated vibrational energies of C₂H₄ up to 4100 cm⁻¹ using a basis pruning scheme and the Lanczos algorithm for obtaining the eigenvalues. This was carried out using the quartic force field potential energy surface (PES) of Martin et al. (1995). Carter, Sharma & Bowman (2012) then built upon this work by calculating the ro-vibrational energies up to J = 40 and transition intensities using a dipole moment surface (DMS) computed at the MP2/aug-cc-pVTZ level of theory. The ethylene molecule was also used as a test system to develop a new pruning approach by the same group (Wang, Carter & Bowman 2015). New C₂H₄ PES (Delahaye et al. 2014) and DMS (Delahaye et al. 2015) were recently constructed which gives even more accurate energies and intensities. A high temperature line list was subsequently constructed using these surfaces by Rey et al. (2016).

In this work we present new ab initio potential energy and dipole moment surfaces for ethylene and use them to compute a line list for elevated temperatures as part of the ExoMol database project.
2 METHODS

2.1 Potential energy surface and refinement

An initial PES was constructed from ab initio quantum chemistry calculations. The explicitly correlated coupled cluster method CCSD(T)-F12b (Adler, Knizia & Werner 2007) was used with the F12-optimized correlation consistent polarized valence cc-pVTZ-F12 basis set (Peterson, Adler & Werner 2008) in the frozen core approximation. A Slater’s semiparametric form of the valence electrons was used (Hill et al. 2009). For the resolution-of-the-identity approximation to many-electron integrals we utilized the OptrI (Yousaf & Peterson 2008) basis set, specifically matched to the cc-pVTZ-F12. The additional many-electron integrals arising in the explicitly correlated methods are calculated using the density fitting approach, for which we employed cc-pV5Z/JKFIT (Weigend 2002) and aug-cc-pwV5Z/Mp2FIT (Hättig 2005) auxiliary basis sets. All calculations were carried out using MOLPRO2012 (Werner et al. 2012).

Electronic energies were calculated on a grid of 120 000 molecular geometries for energies of up to 4h·c·cm⁻¹ above the equilibrium geometry value. Up to 12 of the internal coordinates were varied at once. The 12 coordinates used to represent the PES are: \(\xi_1 = r_0 - r_0^\text{eq}\) for the C–C bond stretching coordinate; \(\xi_j = r_j - r_j^\text{eq}\) for each of the C–H bond stretching coordinates; \(\xi_j = \theta_i - \theta_i^\text{eq}\) for each of the C–H bending coordinates; \(\xi_{10} = \tau - \beta_1\) and \(\xi_{11} = \beta_2 - \tau\) where \(\beta_1\) and \(\beta_2\) are the two H–C–H type dihedral angles; and \(\xi_{12} = 2\tau - \beta_1 + \beta_2\) where \(\tau\) is the dihedral angle between the two cis hydrogens. For clarity, the angular internal coordinates are shown in Fig. 1.

Values of \(r_0^\text{eq} = 1.331\) Å, \(r_1^\text{eq} = 1.081\) Å and \(\theta_1^\text{eq} = 121.45^\circ\) have been used.

Figure 1. Definition of angular internal coordinates in ethylene.

The \textit{ab initio} energies were least-squares fit to an analytical form consisting of long- and short-range parts as

\[
f = V_{\text{short}} \times f_\text{damp} + V_{\text{long}}
\]

where \(f_\text{damp}\) is a damping function to remove the contribution of the short range component at geometries where the internal coordinates are far from their equilibrium values and has the form

\[
f_{\text{damp}} = \exp\left(-\delta_1 (\xi_1^2 + 2\xi_2^2)\right) \times \exp\left(-\delta_2 \sum_{i=2}^{5} (\xi_i^2 + 2\xi_i^2)\right)
\]

\[
\times \exp\left(-\delta_3 \sum_{i=6}^{9} (\xi_i^2 + 2\xi_i^2)\right) \times \exp\left(-\delta_4 \sum_{i=10}^{12} (\xi_i^2 + 2\xi_i^2)\right)
\]

\[
\times \exp\left(-\delta_5 (\xi_{12}^2 + 2\xi_{12}^2)\right).
\]

The damping constants \(\delta_i\) were kept fixed in the fitting at the values \(\delta_1 = 0.3\), \(\delta_2 = 0.05\), \(\delta_3 = 0.01\), \(\delta_4 = 0.005\), \(\delta_5 = 0.005\). The long range function has the form

\[
V_\text{long} = \sum_{i=1}^{5} D_i^{(2)} \xi_i^2 + D_i^{(4)} \xi_i^4 + \exp\left(-\gamma_1 \xi_i^2 - \gamma_2 \sum_{i=2}^{5} \xi_i^2\right)
\]

\[
\times \sum_{i=6}^{12} \left(D_i^{(2)} \xi_i^2 + D_i^{(4)} \xi_i^4\right),
\]

where \(\gamma_1 = 0.1\) and \(\gamma_2 = 0.1\) and the values for other parameters \(D_i^{(2)}\) and \(D_i^{(4)}\) were obtained in the least-squares fit to \(ab initio\) data points. The short range function is a sum of symmetrized products of form

\[
V_{\text{short}} = \sum_{i,j,k} \left(\xi_i^\text{eq} \xi_j^\text{eq} \xi_k^\text{eq}\right) C_{ijk} \Gamma
\]

where \(\Gamma \equiv A_x\) produces symmetrized combinations of different permutations of the coordinates in the \(D_{2h}\) (Molecular symmetry group, \(C_{ijk}\) are expansion parameters, and Morse oscillator functions describe the stretching coordinates \(\xi_i^\text{eq} = 1 - \exp(-a_i\xi_i)\) with \(a_1 = 1.881\) 39 Å⁻¹ and \(a_2 = 1.798\) 90 Å⁻¹. The product was limited to a maximum of eight coordinates coupled at the same time with the sum of powers \(i + j + k \leq 4\). A total of 1269 terms were used in the sum.

The constants of the long range function in equation (5) and the expansion parameters of the short range potential in equation (6) were found by least-squares fitting to the \textit{ab initio} energies. Weight
factors for energies were used as proposed by Partridge & Schwenke (1997)

\[ w_i = \left( \frac{\tanh[-0.0006 \times (E_i - V_{\text{top}})] + 1.002002002}{2.002002002} \right) \times \frac{1}{N_i \max(E_i, V_{\text{lim}})}, \tag{7} \]

where \( hcE_i \) is the electronic energy at the \( i \)th geometry, \( V_{\text{top}} = 30000 \text{ cm}^{-1}, V_{\text{lim}} = 15000 \text{ cm}^{-1} \) and \( N_i \) is the normalization constant. A weighted root-mean-square (rms) error of 3.2 cm\(^{-1}\) was obtained for energies up to \( hc \cdot 40000 \text{ cm}^{-1} \). Expansion parameters and the explicit forms of the symmetrized products in equation (6) are given in a Fortran 90 subroutine in the supplementary information.

To improve the accuracy of nuclear motion calculations, the PES was refined using experimental data. Refinement was carried out using a least-squares fitting procedure as implemented in TROVE (Yurchenko et al. 2011a) with the pruned basis set (see below) in a very similar manner to that described in a recent paper from our group (Owens et al. 2017). Due to the large number of parameters used for the analytical representation of the PES and the size of the eigenfunctions for ethylene, only parameters in equation (6) with exponents summing to 2 were allowed to vary. This includes linear \((\xi_i)\), harmonic \((\xi_i^2)\) and mixed terms \((\xi_i \xi_j)\) for a total of 21 parameters. Refinement was carried out in two stages. First, 109 experimental vibrational \( J = 0 \) band centres taken from Georges, Bach & Herman (1999) were used. This gave an initial refinement. Then, 21 rotational-vibrational \( J = 1 \) energies from the HITRAN database (Gordon et al. 2017) were added and the refinement restarted. Pure rotational energies were obtained as the largest weights in the refinement of the order of \( 10^4 \) followed by \( J = 1 \) rotational-vibrational levels of the order of \( 10^3 \) and finally vibrational energies of the order of \( 0-10^3 \) depending on the reported accuracy of these levels. Weights are normalized during the refinement and so only relative values are important (Yurchenko et al. 2011a).

The refined PES was found to give accurate values for a further 155 \( J = 2, 3 \) and 4 energy levels which were included, but further iterations of refinement did not give improved values. This is due to both the size of the least-squares fitting problem and that added rotational-vibrational levels were from the same vibrational bands as the \( J = 1 \) energies. The differences between all observed energy levels used and the values given by our refined PES are shown in Fig. 2. The vibrational energies with observed—calculated errors of \( >4 \text{ cm}^{-1} \) were retained in the refinement to still provide some constraint to these states but were given relative weightings of a thousand times less than the HITRAN vibrational energies.

For the refined surface we obtained an rms error of 2.73 cm\(^{-1}\) for the vibrational energies (reduced to 1.95 cm\(^{-1}\) when bands which were given weights of zero in the refinement were excluded) compared to the values quoted in Georges et al. (1999). This is a large error but many of the bands included also gave large errors for the global effective Hamiltonian model used by Georges et al. and are of low accuracy. Bands with the largest errors were given a weighing of zero in our fit. For the \( J = 1 \) data we obtain an rms error of 0.45 cm\(^{-1}\) and 0.50 cm\(^{-1}\) when all \( J = 1 - 4 \) is included, respectively. When combined with the vibrational levels we obtain an overall rms of 1.75 cm\(^{-1}\), which is reduced to 1.27 cm\(^{-1}\) when bands which were given weights of zero in the refinement were excluded.

Table 1 compares empirical fundamental vibrational band origins with values obtained using both our \textit{ab initio} and refined PES. The energies were computed variationally using the basis set described in Section 2.3.

As is usual for a refined PES used with TROVE (Yurchenko & Tennyson 2014; Al-Refaie et al. 2015b; Sousa-Silva et al. 2015; Al-Refaie et al. 2016; Underwood et al. 2016a; Owens et al. 2017), the accuracy is only guaranteed with the computational setup employed in this work.

2.2 Dipole moment surface

\textit{Ab initio} calculations for the DMS were carried out at the CCSD(T)-F12b/aug-cc-pVTZ level of theory using the finite field method. The frozen core approximation with a Slater geminal exponent \( \beta = 1.0 \) \( \alpha_0^{-1} \) was employed using the same ansatz and auxiliary basis sets as the explicitly correlated PES calculations. For each of the \( x, y \) and \( z \) Cartesian components, an electric field of strength \( \pm 0.001 \) au was applied and the dipole moment projections \( \mu_x, \mu_y \) and \( \mu_z \) computed as derivatives of the electronic energy with respect to the field strength using central finite differences. Calculations were carried out at about 93 000 different molecular geometries with energies up to \( hc \cdot 40000 \text{ cm}^{-1} \), with up to six of the 12 internal coordinates varied at once.

The DMS was fitted to an analytical form as follows. The origin of the molecule-fixed \( xyz \) coordinate system \( r_0 \) was taken to be the centre of the \( C_1-C_2 \) bond. The \( z \)-axis is chosen to be along the \( C_1-C_2 \) bond:

\[ e_z = \frac{r_{C_1} - r_0}{||r_{C_1} - r_0||}, \]

where \( r_{C_1} \) denotes Cartesian coordinates of carbon atom \( C_1 \). The \( x \)-axis is a symmetric combination average of the four normals to the four planes \( C_1C_2H_i \) (\( i = 1, 2, 3, 4 \)) as given by

\[ e_x = \frac{e_{1} + e_{2} + e_{3} + e_{4}}{||e_{1} + e_{2} + e_{3} + e_{4}||}, \]

and the \( y \)-axis is chosen as in the right-handed system. Here the normals are defined using the cross-products of the unit vector \( e_z \) with the corresponding \textit{C–H} bond vectors \( e_{H_i} = (r_{H_i} - r_{0}) / ||r_{H_i} - r_{0}|| \).
where $\mu$ is the dipole moment vector. The dipole moment vector can be expressed as

$$
\mathbf{m} = \mu_x \mathbf{e}_x + \mu_y \mathbf{e}_y + \mu_z \mathbf{e}_z,
$$

where $\mu_x$, $\mu_y$, and $\mu_z$ are functions of the internal coordinates of the form

$$
\mu_{\alpha} = \sum_{i,j,k} \left( \xi_i^{\alpha} \xi_j^{\alpha} \xi_k^{\alpha} \cdots \xi_{12}^{\alpha} \right)^{\Gamma} F_{ijk}^{(\alpha)}
$$

where $\Gamma$ produces symmetrized combinations of different permutations of the coordinates in the $B_{1u}$, $B_{2u}$, and $B_{1u}$ irreps for $\alpha = x, y, z$, respectively, and $F_{ijk}^{(\alpha)}$ is the expansion parameter. The symmetry-adapted analytical expressions in equation (9) have been obtained using the SYMPy PYTHON library for symbolic mathematics (Meurer et al. 2017). The PYTHON program is freely available from the authors upon request. The coordinates $\xi_1, \xi_2, \ldots, \xi_{12}$ chosen for analytical representation of the DMS in equation (9) are the same as those used for the PES.

For each component of the dipole we used a sixth-order expansion consisting of 1881, 1861 and 1399 terms for the $B_{1u}$, $B_{2u}$ and $B_{1u}$ symmetries, respectively. The expansion parameters $F_{ijk}^{(\alpha)}$ were determined by least-squares fitting to the $ab\text{ initio}$ data giving rms errors of $7 \times 10^{-4}$, $7 \times 10^{-4}$ and $6 \times 10^{-4}$ D, respectively. The expansion parameters $F_{ijk}^{(\alpha)}$ and Fortran 90 subroutines to compute $\mu_{\alpha}$ are provided as part of the supplementary information.

### 2.3 Variational calculations

Variational ro-vibrational calculations were carried out using the TROVE program. The TROVE methodology is well documented (Yurchenko, Thiel & Jensen 2007; Yurchenko et al. 2009; Yachmenev & Yurchenko 2015; Tennyson & Yurchenko 2017; Yurchenko, Yachmenev & Ovsyannikov 2017a) and has been applied to a variety of molecules as part of the ExoMol project (Yurchenko et al. 2009; Yurchenko, Barber & Tennyson 2011b; Polyanovsky et al. 2013; Sousa-Silva, Yurchenko & Tennyson 2013; Underwood, Tennyson & Yurchenko 2013; Yurchenko & Tennyson 2014; Sousa-Silva et al. 2015; Al-Refaie et al. 2015a,b; Owens et al. 2015; Underwood et al. 2016b; Owens et al. 2017). Only the specific details used in this work on ethylene will be discussed here.

The ro-vibrational Hamiltonian was constructed numerically via an automatic differentiation method (Yachmenev & Yurchenko 2015). The Hamiltonian was expanded using a power series in curvilinear coordinates around the equilibrium geometry of the molecule. The coordinates used were the same as those used to fit the PES.

The kinetic energy operator was expanded to sixth order and the potential energy operator to eighth order. The same Morse coordinates as used in equation (6) were used for the potential expansion for the stretching coordinates ($\nu_1 \leq \nu_2 \leq \nu_3 \leq \nu_4 \leq \nu_5$) with the other bending coordinates expanded as $\xi_i$ themselves. Atomic masses were used throughout.

A multistep contraction scheme was used to build the vibrational basis set. For each coordinate a one-dimensional Schrödinger equation was solved using the Numerov–Cooley approach (Nummerov 1924; Cooley 1961; Yurchenko et al. 2007) to generate basis functions $\phi_n(\xi_i)$ with vibrational quantum number $n_i$. The vibrational basis set functions $|v\rangle$ are formed as products of the 1D basis functions

$$
|v\rangle = \prod_{i=1}^{12} \phi_{n_i}(\xi_1) \phi_{n_2}(\xi_2) \cdots \phi_{n_{12}}(\xi_{12}).
$$

The basis set is truncated by the polyad number $P$ via

$$
P = n_1 + 2(n_2 + n_3 + n_4 + n_5) + 6n_6 + 7n_7 + 8n_8 + 9n_9 + 10n_10 + 11n_11 + 12n_{12} \leq P_{\text{max}}.
$$

A value of $P_{\text{max}} = 10$ was used. This is a smaller value than used for previous ExoMol line lists (Yurchenko & Tennyson 2014; Al-Refaie et al. 2015b, 2016; Sousa-Silva et al. 2015; Underwood et al. 2016a; Owens et al. 2017) but with 12 degrees-of-freedom the basis set rapidly increases with increasing $P$. To estimate the convergence of vibrational energies with this basis set we used a complete vibrational basis set (CVBS) extrapolation procedure similar to that described by Owens et al. (2015). Variational calculations were carried out with $P_{\text{max}} = 6, 8$ and 10, respectively. From this we estimate that above 4000 cm$^{-1}$ there are some vibrational levels (typically those with multiple bending modes excited) which are only converged to around 4 cm$^{-1}$ with a $P_{\text{max}} = 10$ basis. The average convergence error for 0–5000 cm$^{-1}$ is estimated to
be only 1.5 cm\(^{-1}\) however. It should be noted that these estimates do not account for the fact that the PES refinement procedure described above tends to compensate partly or fully for the basis set convergence errors, even when extrapolating to higher vibrational excitations. Strictly speaking, in order to get a sensible convergence error, one would need to produce a refined PES for all three values of \(P_{\text{max}}=6, 8\) and 10. These estimates do, however, indicate the possible error of our effective \((P=10)\) PES if used with larger basis sets or other nuclear motion methods. To extend the vibrational basis, further 1D and 2D functions were added with \(|\xi_{n}|\) \(\leq 14\) and \(\phi_{n}\) \((1 \leq i \leq 14)\). A contracted basis set was then formed by reducing the 12-dimensional problem into five subspaces: \((\xi_{1})\), \((\xi_{2}, \xi_{3}, \xi_{4}, \xi_{5})\), \((\xi_{6}, \xi_{7}, \xi_{8}, \xi_{9})\), \((\xi_{10}, \xi_{11})\) and \((\xi_{12})\). A Hamiltonian matrix is constructed and diagonalized for each of these subspaces to give symmetrized contracted vibrational basis functions. The details of this step have been discussed in a recent publication (Yurchenko et al. 2017a). Products of these eigenfunctions are formed which are also truncated via equation \((11)\).

To increase the computational efficiency of this step, a new algorithm for sorting and calculating matrix elements of the PES between primitive basis functions was implemented. This procedure also sets these elements to zero for potential expansion coefficients with values smaller than a tolerance factor. Here we take this as 0.01 (in the units of cm\(^{-1}\), Angstrom and radian). This procedure led to around a 70-fold speed up for smaller basis test calculations whilst only affecting the accuracy of vibrational states by 0.01 cm\(^{-1}\), far lower than the error of the \textit{ab initio} PES. This new ‘fast-ci’ method will be described fully in a subsequent publication.

Following this procedure, 145240 vibrational eigenfunctions \(|\Phi_{\text{vib}}^{(i)}\rangle\) of C\(_{2}\)H\(_{4}\) were obtained with term energies \(E_{i}^{(J=0)}\) up to 21 000 cm\(^{-1}\) above the ground state (our post-refinement zero-point-energy is 11 022.5 cm\(^{-1}\)). According to the \(J=0\)-contraction scheme TROVE uses these \(J=0\) eigenfunctions as the vibrational basis set. However using a basis set of this size for high rotationally excited levels is currently impractical and it was necessary to reduce the number of basis functions. The basis set was further truncated using the same approach based on the vibrational band intensity as described in a recent paper for the silane (SiH\(_{4}\)) line list (Owens et al. 2017), which will be referenced to as intensity basis set pruning (IBSP). According to this approach, the vibrational basis functions \(|\Phi_{\text{vib}}^{(i)}\rangle\) above some energy threshold, \(E_{\text{max}}^{(J=0)}\), should be truncated with the exception of functions responsible for significant contribution to the absorption opacity (larger than some intensity threshold \(I_{\text{max}}\)). In turn, the absorption contribution is estimated from the intensities of the corresponding bands using these functions as the upper or lower states.

We define the vibrational absorption intensity (cm/molecule) for the band \(j \leftrightarrow i\) as

\[
I_{ji}^{(J=0)} = \frac{A_{j}^{(J=0)} \exp(-c_{E_{i}^{(J=0)}}/T)}{8\pi c} q^{(J=0)} \left(E_{i}^{(J=0)} / \nu_{ji}^{(J=0)} \right)^{2},
\]

where \(A_{j}^{(J=0)}\) is the transition dipole moment, \(c_{E_{i}^{(J=0)}}\) is the average vibrational energy, and \(q^{(J=0)}\) is the line shape parameter.
The vibrational Einstein coefficient (s⁻¹) is given by

\[
A_{f_i}^{(J=0)} = \frac{8 \times 10^{-36} \pi^4}{3h} \mu_{f_i}^2 J_i^{(0)} \ ,
\]

where the vibrational transition moment \(\mu_{f_i}(D)\) is

\[
\mu_{f_i} = \sum_{\alpha=x,y,z} |\Phi_{vib}^{(f_i)}(\alpha)|^2 \ ,
\]

Here \(h\) is Planck’s constant, \(Q^{(J=0)}\) is the vibrational (\(J=0\)) partition function, \(E_i^{(J=0)}\) and \(\Omega_i^{(J=0)}\) are the vibrational lower state term value and band centres, respectively, and \(c_2\) is the second radiation constant. Here, \(\Phi_{vib}^{(i)}\) and \(\Phi_{vib}^{(f)}\) are the initial and final state vibrational eigenfunctions, respectively, and \(\mu_{\alpha}\) is the electronically averaged dipole moment along the molecular fixed axis \(\alpha = x,y,z\).

The vibrational absorption intensities were computed between each state at an elevated temperature of 800 K. For each vibrational state, the largest intensity to or from that state was then associated with that state. The \(J = 0\) basis set was then pruned based on this.

The pruning procedure based on the \(J=0\)-contraction has the advantages that the accuracy of the vibrational energy levels and eigenfunctions computed using the unpruned basis is retained. The errors introduced in pruning the basis for the \(r\)-vibrational levels are compensated for by refining the PES with the pruned basis. The pruning procedure based on the \(J=0\)-contraction has the advantages that the accuracy of the vibrational energy levels and eigenfunctions computed using the unpruned basis is retained.

Fig. 3 shows vibrational intensities of \(\text{C}_2\text{H}_4\) computed using \(Yurchenko et al. 2009, 2017a\). This basis was then used for \(J>0\) calculations by combining it with symmetrized rigid-rotor functions as described previously (Yurchenko et al. 2009, 2017a).

All states up to \(hc \cdot 8000 \text{ cm}^{-1}\) were retained. States with energy above this were discarded if their largest intensity was less than some value \(I_{\text{max}}\). Here, a value of \(I_{\text{max}} = 1 \times 10^{-22} \text{ cm/molecule}^{-1}\) was used. This value was chosen to retain as many states as possible (which support intense transitions) whilst making the calculations for high \(J\) practical. The resulting pruned vibrational basis contained 13 572 functions corresponding to energies up to \(hc \cdot 12000 \text{ cm}^{-1}\). This basis was then used for \(J>0\) calculations by combining it with symmetrized rigid-rotor functions as described previously (Yurchenko et al. 2009, 2017a).

The vibrational intensities of \(\text{C}_2\text{H}_4\) computed using equation (12) for \(T=500 \text{ K}\) as cross-sections. Here we compare the total cross-sections (no pruning) and the contribution missing due to the intensity-based pruning. The effect of the pruning on the intensities is negligible for the range below 7000 \text{ cm}^{-1} (~0.01 per cent). This is especially important for hot spectra applications, where the

**Figure 4.** Partition functions of \(\text{C}_2\text{H}_4\): Convergence of partition function \(Q(T)\) at different temperatures with respect to the rotational quantum number \(J\) (left) and \(Q_{\text{total}}/Q\) as a function of temperature (right).
2.4 Line intensities

The eigenvectors from the variational calculation along with the DMS were used to compute Einstein-A coefficients of transitions. These satisfy the rotational selection rules (Bunker & Jensen 1998)

\[ J - J'' = 0, \pm 1, \text{ and } J' + J'' \neq 0, \]

where \( J \) and \( J' \) are the upper and lower values of the total angular quantum number \( J \) and symmetry selection rules

\[ A_{i\nu} \leftrightarrow A_{i\nu}, B_{i\nu} \leftrightarrow B_{i\nu}, B_{2\nu} \leftrightarrow B_{2\nu}, B_{3\nu} \leftrightarrow B_{3\nu}. \]  

The absolute absorption intensities are then given by (Bunker & Jensen 1998)

\[
I(f \leftarrow i) = \frac{A_{i\nu}}{8\pi c} \frac{g_{\text{m}}(2J_i + 1)}{Q(T)\gamma^2_{\text{m}}} \times \left[ 1 - \exp \left( -\frac{\gamma^2_{\text{m}}}{T} \right) \right],
\]

where \( J_i \) is the rotation quantum number for the final state, \( \gamma_{\text{m}} \) is the transition frequency \( (\nu_i = E_i - E_f) \), \( E_i \) and \( E_f \) are the initial and upper state term values, respectively, and \( Q(T) \) is the partition function (Section 3.1). The Einstein-A coefficients \( A_{i\nu} \) between the ro-vibrational states \( i \) and \( f \) are defined in Yurchenko et al. (2005). The nuclear spin statistical weights \( g_{\text{m}} \) for ethylene are (7,7,3,3,3,3,3) for states of symmetry \( A_1g, A_1u, B_1g, B_1u, B_2g, B_2u, B_3g, B_3u \), respectively (Bunker & Jensen 1998), within the HITRAN convention, adopted by ExoMol, of including the full nuclear spin of each species.

The temperature-independent Einstein-A coefficients were computed using the gain-MPI program (Al-Refaie, Tennyson & Yurchenko 2017). With this program we were able to calculate up to 93 000 transitions per second using NVIDIA Tesla P100 GPUs on the Wilkes2 cluster.

Intensities were computed using a lower energy range of 0–5000 cm\(^{-1}\) taking into account up to \( J = 78 \) for transitions frequencies between 0 and 7000 cm\(^{-1}\). An intensity cut-off of 10\(^{-50}\) cm molecule\(^{-1}\) at \( T = 298 \) K was used, ensuring that essentially all transitions are taken into account for up to around 700 K (see Section 3.1).

3 RESULTS

3.1 Partition function

The temperature-dependent partition function \( Q(T) \) is defined as

\[
Q(T) = \sum_i g_i \exp \left( -\frac{E_i}{T} \right),
\]

where \( g_i = g_{\text{m}}(2J_i + 1) \) is the degeneracy of the state \( i \) with energy \( E_i \) and rotational quantum number \( J_i \).

Fig. 4 shows the convergence of \( Q(T) \) as a function of \( J \) at different temperatures. At 700 K the partition function is converged to 0.02 per cent. In Table 2 we compare the partition function calculated at various temperatures with those of literature values. In general, agreement between the various sources is good. Our value which increases slightly faster with temperature than those of Rey et al. (2016) is probably due to our more complete treatment of the energy levels. In the supplementary information we provide the partition function between 0 and 1500 K at 1 K intervals.

The current line list was computed with a lower energy threshold of \( hc \cdot 5000 \) cm\(^{-1}\). To assess the completeness of our line list we compute a reduced partition function, \( Q_{\text{limit}} \), which only takes into account transitions
Figure 6. Detailed comparison of the MaYTY line list with those from HITRAN and TheoReTS at 296 K. The strongest bands are labelled in each plot.

Table 5. Extract from vibrational .trans file.

<table>
<thead>
<tr>
<th>f</th>
<th>i</th>
<th>( \mu_{fi} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 040</td>
<td>1</td>
<td>5.441 012 47E-07</td>
</tr>
<tr>
<td>1040</td>
<td>1</td>
<td>3.355 560 08E-16</td>
</tr>
<tr>
<td>85 543</td>
<td>1</td>
<td>1.815 801 11E-16</td>
</tr>
<tr>
<td>127 077</td>
<td>1</td>
<td>7.884 023 51E-16</td>
</tr>
<tr>
<td>63 744</td>
<td>1</td>
<td>1.925 786 61E-07</td>
</tr>
<tr>
<td>8779</td>
<td>1</td>
<td>1.454 187 20E-16</td>
</tr>
<tr>
<td>43 097</td>
<td>1</td>
<td>1.237 338 15E-20</td>
</tr>
</tbody>
</table>

\( f \): Upper state ID; 
\( i \): Lower state ID; 
\( \mu_{fi} \): Vibrational transition moment (in D).

account energies up to \( \frac{hc}{\nu} \cdot 5000 \text{ cm}^{-1} \) in equation (18). Fig. 4 also shows a plot of the ratio of \( Q_{\text{ratio}}/Q \). At 700 K the ratio is 0.98 and this temperature can be taken as a soft limit. At higher temperatures opacity will progressively be underestimated (see Section 4).

3.2 Line list format

A complete description of the ExoMol data structure along with examples was reported by Tennyson et al. (2016). The .states file contains all computed ro-vibrational energies (in \( \text{cm}^{-1} \)) relative to the ground state. Each energy level is assigned a unique state ID with symmetry and quantum number labelling as shown in Table 4. The .trans files, which are split into frequency windows for ease of use, contain all computed transitions with upper and lower state ID labels, and Einstein A coefficients. An example from a .trans file for the line list is given in Table 4.

3.3 Validation

The MaYTY line list contains nearly 50 billion (49 841 085 051) transitions between over 45 million (45 446 267) states.

Figs 5 and 6 compare the MaYTY line list to empirical intensities from the HITRAN database at 296 K. To take into account the abundance of the \(^{12}\text{C}_2\text{H}_4\) isotopologue we divide the HITRAN intensities by 0.977 29 to obtain the value for pure \(^{12}\text{C}_2\text{H}_4\). Fig. 5 gives an overview of our line list compared to HITRAN. HITRAN is currently missing data for the 1600–2750cm\(^{-1}\) region which contains the relatively intense \( \nu_7 + \nu_8 \) band amongst others. For this region Fig. 6 compares our line list to that of Rey et al. (2016) from the TheoReTS database. HITRAN also currently does not have any data above 3500 cm\(^{-1}\).

As a further comparison of the MaYTY line list to experiment we compare cross-sections to those in the PNNL database (Sharpe et al. 2004) in Fig. 7. The PNNL spectrum is a composite recorded at 298 K and re-normalized for 296 K. The ethylene used was 99.5 per cent pure. For comparison with our line list PNNL cross-sections were multiplied by \( 9.286\times 10^{-16}/0.977\times 29 \) to convert to \( \text{cm}^2\text{ molecule}^{-1} \) units and account for the \(^{12}\text{C}_2\text{H}_4\) isotopologue. We simulated the spectrum using a resolution of 0.1 cm\(^{-1}\) using a Voigt profile with a half-width half-maximum (HWHM) value of
0.1 cm$^{-1}$. The PNNL spectrum allows a comparison to our calculated line list up to around 6200 cm$^{-1}$.

Fig. 8 shows the temperature dependence of the absorption cross-sections for the MaYTY line list simulated using a resolution of 5 cm$^{-1}$ where again a Voigt profile with an HWHM of 0.1 cm$^{-1}$ was used. While regions of weak absorption at 296 K increase by an order of magnitude or more as the temperature is increased, the overall band structure of the absorption does not change greatly with temperature. This behaviour contrasts with other molecules, such as methane (Yurchenko & Tennyson 2014), whose band shapes show a strong temperature dependence.

### 4 Vibrational Cross-Sections: Realistic Band Shapes

Our final ro-vibrational line list for C$_2$H$_4$ is limited to the frequency range of 0–7000 cm$^{-1}$ and the temperatures up to about 700 K. On the other hand, our vibrational line list, which we used to assist the basis set pruning, has much larger coverage, in terms of both frequency and temperature ranges. Here we show how to use this more complete vibrational line list to (i) top-up the ro-vibrational line list with missing opacities and (ii) directly simulate realistic spectra at high temperatures for large polyatomic molecules.
bands of C$_2$H$_4$. We select the three strongest fundamental bands, one for each type: $v_{12} (B_{1u}, B_{2u})$, $v_9 (B_{2a})$ and $v_7 (B_{3u})$, and use the corresponding ro-vibrational cross-sections at different temperatures to construct three temperature-dependent, normalized band profiles as follows. For each temperature and band in question the corresponding cross-sections on a grid of 1 cm$^{-1}$ are normalized and shifted to have the centre at $\bar{v} = 0$. Three profile templates for $T = 500$ K and $T = 1500$ K are shown in Fig. 9. The $T = 500$ K profiles were generated using the MaYTY line list in conjunction with the Voigt line profile with HWHM = 0.1 cm$^{-1}$. For the 1500 K temperature case our line list is rotationally incomplete ($J_{\text{max}} = 78$); therefore we used the effective Hamiltonian approach to generate the corresponding band profiles with significantly higher $J_{\text{max}} = 120$. Towards this we employed PGOPHER together with the $v_7$, $v_9$ and $v_{12}$ spectroscopic constants from Bach et al. (1998) and Rusinek et al. (1998), and a Voigt line profile with HWHM = 0.1 cm$^{-1}$.

These profiles are then applied for the vibrational cross-sections at the temperature in question by using the symmetry multiplication rule: if $\Gamma_i$ and $\Gamma_f$ are, respectively, the symmetries of the initial and upper states and $\Gamma_u$ is the symmetry of the dipole moment component $\bar{\mu}_u$, for an IR active band $\Gamma^{(J=0)}_u$ the following relation holds (Bunker & Jensen 1998):

$$\Gamma_u = \Gamma_i \otimes \Gamma_f.$$ 

Note that the equal sign here (not $\in$) is due to D$_{2h}$(M) being an Abelian symmetry group. We thus use this rule to choose between the $B_{1u}$, $B_{2a}$ or $B_{3u}$ templates when generating cross-sections for specific bands $\Gamma^{(J=0)}_u$.

This rule, however, does not always hold: a large number of forbidden (and weak) bands have non-zero intensities due to interactions between vibrational states. In such cases we use a simple Lorentzian band profile with HWHM of 60 cm$^{-1}$.

An example of vibrational cross-sections of C$_2$H$_4$ at $T = 500$ K and $T = 1500$ K generated using this methodology is shown in Fig. 10, where they are also compared to the ro-vibrational cross-sections. The vibrational cross-sections are more complete and also provide larger coverage (here shown up to 10 000 cm$^{-1}$). For example, the lower display in Fig. 10 shows the predicted opacity of C$_2$H$_4$ at $T = 1500$ K by using our vibrational cross-section technique compared to the MaYTY intensities, which are incomplete at $T = 1500$ K.

The methodology of combining realistic band profiles with vibrational intensities can be especially useful for larger polyatomic molecules, where the size of the calculations becomes prohibitive. This requires knowing the ro-vibrational spectra of the three fundamental bands to generate the realistic band profiles, for which we took advantage of having the complete, ro-vibrational line list. In practical applications when this is not accessible, these profiles could be modelled using effective rotational methods, using for example PGOPHER (Western 2017) as we demonstrated, which only requires the corresponding spectroscopic constants of these (up to) three fundamental bands.

The temperature-dependent vibrational cross-sections can be useful for evaluating opacities of molecules (especially at higher temperatures) when completeness is more important than high accuracy. The approximations used for vibrational intensities are: (i) the rotational and vibrational degrees of freedom are independent and (ii) lower resolution is assumed.

Due to the missing interaction between the rotational and vibrational degrees of freedom, this vibrational methodology is not capable of reconstructing some forbidden bands, which are caused by this interaction. This is evident in Fig. 10, where some weaker parts are missing. It is important to note that the vibrational band...
Figure 9. Normalized $\nu_{12}$, $\nu_9$ and $\nu_7$ band profiles with a HWHM = 0.1 cm$^{-1}$. Left: the $T = 500$ K profiles were generated using the MaYTY line list with the Voigt profile. Right: the $T = 1500$ K profile was generated using PGOPHER with the Lorentzian line broadening and spectroscopic constants from Bach et al. (1998) and Rusinek et al. (1998).

Figure 10. Comparing the ro-vibrational and vibrational intensities of C$_2$H$_4$ at $T = 500$ K and $T = 1500$ K. The ‘ro-vibrational’ cross-sections of C$_2$H$_4$ were computed using the MaYTY line list and the Gaussian line profile with HWHM = 1 cm$^{-1}$. The ‘vibrational’ cross-sections were computed using the vibrational line list with the normalized band profiles scheme (see text).

The intensity of a given vibrational band computed using equation (12) is the same as the corresponding integrated ro-vibrational intensities from equation (17), at least if the interaction with other vibrational bands is ignored. Thus although the vibrational intensity treatment is highly approximate, it should be better for preserving the opacity in simulations.

In line with our ‘hybrid’-methodology (Yurchenko et al. 2017b), the generated vibrational cross-sections can be now divided into the strong and weak parts, with the latter representing the absorption, missing from our line list due to the vibrational basis set pruning. These ‘weak’ vibrational bands form absorption ‘continuum’ cross-sections and can be used to compensate for missing absorption when higher temperatures or larger spectroscopic coverage is required.

5 CONCLUSIONS

We have produced a new line list for $^{12}$C$_2$H$_4$ called MaYTY. Energy levels were calculated variationally using the TROVE program on a refined PES and transition intensities calculated with a new ab initio DMS. The MaYTY line list includes transitions between ro-vibrational states with $J \leq 78$ and covers the frequency region up to 7000 cm$^{-1}$. Based on analysis of the partition function the variational line list is applicable up to 700 K beyond which opacity will be underestimated. Our line list is in good agreement with experimental intensities from the HITRAN database and experimental cross-sections from the PNNL database. The MaYTY line list is available from the CDS (http://cdsarc.u-strasbg.fr) and ExoMol (www.exomol.com) data bases.
To extend the temperature range of applicability of the line list we have implemented a new approximate method of producing absorption cross-sections from vibrational (J = 0) energies and transition moments. The vibrational line list of C2H4 is also provided as part of the MaTYT data set. Using this approach we have also generated vibrational cross-sections of C2H4 covering the wavenumber range up to 12 000 cm⁻¹ and covering temperatures up to T = 1500 K. The vibrational cross-sections based on the three-band model can be also generated using a vibrational version of EXOCROSS. This program, vibrational cross-sections and vibrational line list for ethylene are available from the CDS and ExoMol data bases. The J = 0 method proposed should be useful for calculating opacities of larger molecules where high J variational calculations are extremely challenging.

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SUPPORTING INFORMATION

Supplementary data are available at MNRAS online.

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