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ExoMol molecular line lists – XII. Line lists for eight isotopologues of CS

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ABSTRACT

Comprehensive vibration–rotation line lists for eight isotopologues of carbon monosulphide (CS; $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, $^{12}C^{36}S$, $^{13}C^{32}S$, $^{13}C^{33}S$, $^{13}C^{34}S$, $^{13}C^{36}S$) in their ground electronic states are calculated. These line lists are suitable for temperatures up to 3000 K. A spectroscopically-determined potential energy curve (PEC) and dipole moment curve (DMC) are taken from literature. This PEC is adapted to suit our method prior to the computation of ro-vibrational energies. The calculated energies are then substituted by experimental energies, where available, to improve the accuracy of the line lists. The ab initio DMC is used without refinement to generate Einstein *A* coefficients. Full line lists of vibration–rotation transitions and partition functions are made available in an electronic form as Supporting Information to this paper and at www.exomol.com.

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

1 INTRODUCTION

It was the development of radio astronomy that led to the realization that the majority of our galaxy, and hence the universe, is dominated by molecular processes. More than 150 molecules have been detected so far in the interstellar medium by direct observation of their spectra. Carbon monosulphide (CS) is one of these molecules (Penzias et al. 1971) and is a diatomic of both atmospheric as well as astrophysical interest. In the Earth's atmosphere, CS plays a role in the formation of aerosols, in particular carbonyl sulphide (OCS) in the troposphere (Li et al. 2013).

In the Solar system, CS has been observed in comets (Canaves et al. 2007) and the collision of comet Shoemaker–Levy 9 (Orton et al. 1995) led to its detection in the atmosphere of Jupiter (Moreno et al. 2003). Astronomically the molecule has been observed in a variety of objects such as carbon-rich stars (Bregman, Goebel & Strecker 1978; Botschwina & Sebald 1985; Agundez & Cernicharo 2006), star-forming regions (Davis et al. 2013) and dense interstellar clouds (Nilsson, Bergman & Hjalmarson 2000; McQuinn et al. 2002; Scoville et al. 2015). In fact CS is one of the most abundant sulphur-containing species in interstellar clouds (Shi et al. 2011; Bilalbegovic & Baranovic 2015) with several isotopologues long detected outside the Milky Way (Henkel & Bally 1985; Mauersberger et al. 1989a,b; Henkel et al. 1993).

The numerous astronomical detections of CS and the importance of the molecule in our own atmosphere have motivated copious laboratory studies. Experimentally the CS spectrum has been studied in wavelength regions ranging from the microwave to the ultraviolet (UV). A pioneering study was carried out by Crawford & Shurcliff (1934) who discovered the main $A\,^1\Pi - X\,^1\Sigma^+$ transition in the visible. Additional electronic transitions in the visible to near UV have been investigated by, for example, Bell, Ng & Suggitt (1972), Cossart, Horani & Rostas (1977) and Stark, Yoshino & Smith (1987).

Mockler & Bird (1955) made the first measurements of rotational lines for the $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$ and $^{13}C^{32}S$ isotopomers in the microwave region. Transitions in this region have also been observed by, for example, Lovas & Krupenie (1974). Early work in the millimetre wave region began with measurements of rotational $^{12}C^{32}S$ and $^{12}C^{34}S$ lines by Kewley et al. (1963), later extended by Bogey, Demuynck & Destombes (1982) who additionally observed $^{13}C^{32}S$. Bogey, Demuynck & Destombes (1981) also presented a study of the millimetre spectrum of rarer isotopologues $^{12}C^{33}S$,$^{12}C^{36}S$, $^{13}C^{33}S$ and $^{13}C^{34}S$. More recent work in the region has been carried out by Ahrens & Winnewisser (1999, $^{12}C^{32}S$, $^{12}C^{34}S$, $^{12}C^{33}S$, $^{13}C^{32}S$, $^{12}C^{36}S$, $^{13}C^{33}S$, $^{13}C^{34}S$), Kim & Yamamoto (2003, $^{12}C^{32}S$, $^{12}C^{34}S$) and Gottlieb, Myers & Thaddeus (2003, $^{12}C^{32}S$, $^{12}C^{34}S$, $^{12}C^{33}S$, $^{13}C^{32}S$).

The first study in the infrared region was performed by Todd (1977) who measured the $v = 2$–0 vibrational band of the main isotope while Todd & Olson (1979) and Yamada & Hirota (1979) measured several $\Delta v = 1$ bands of $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$ and $^{13}C^{32}S$. The resulting molecular parameters were later refined by Winkel et al. (1984) and Burkholder et al. (1987). Winkel et al. (1984) measured many $\Delta v = 2$ bands for vibrational levels up to $v = 8$ while Burkholder et al. (1987) obtained high-resolution measurements of the 1–0 band, and 2–1 band for the main isotope of $^{12}C^{33}S$, $^{12}C^{34}S$ and $^{13}C^{32}S$ for *J* up to 41, 28, 32 and 28, respectively. $\Delta v = 1$ bands up to $v = 9$–8 for the main isotope were later measured by Ram, Bernath & Davis (1995). The most recent research on CS

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infrared spectra has been performed by Uehara, Horiai & Sakamoto (2015), who reported $\Delta v = 1$ transitions of $^{13}C^{32}S$ up to $v = 5$–4. Additionally they measured $\Delta v = 1$ transitions of $^{12}C^{32}S$ up to $v =$ 7–6 to a higher accuracy than Ram et al. (1995).

Using the vibration–rotation and pure rotation data on this molecule available to them, Coxon & Hajigeorgiou (1992) derived a spectroscopic potential energy curve (PEC) that reproduced all the input experimental data within experimental error. This PEC is the starting point for the current work.

Transition probabilities or Einstein *A* coefficients have been provided by Botschwina & Sebald (1985) and Pineiro, Tipping & Chackerian (1987). The latter produced transition lists for rotational quantum numbers $J' - J'' = \pm 1$ for $J \leq 200$, and vibrational $v \leq 20$, though only for the four most abundant isotopes ($^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$ and $^{13}C^{32}S$). Line lists for all isotopologues of CS, including some rotation–vibration transitions, are available from CDMS (Müller et al. 2005). These were constructed from experimental data obtained by Bogey et al. (1981, 1982), Ahrens & Winnewisser (1999), Kim & Yamamoto (2003), Gottlieb et al. (2003), Burkholder et al. (1987), Ram et al. (1995) and Winkel et al. (1984) and the only available experimental measurements of the dipole moment (Winnewisser & Cook 1968). The line lists are very accurate and recommended for use in radio astronomy, though are limited to $v \leq 4$ and $J \leq 99$ and hence temperatures, *T* below about 500 K. The aim of this work is to produce comprehensive line lists for all stable isotopologues of CS suitable for modelling hot environments, such as carbon stars ($T \sim 3000$ K).

The ExoMol project aims to provide line lists on all the molecular transitions of importance in the atmospheres of planets (Tennyson & Yurchenko 2012). The ExoMol methodology has already been applied to a number of diatomic molecules: BeH, MgH and CaH (Yadin et al. 2012), SiO (Barton, Yurchenko & Tennyson 2013), NaCl and KCl (Barton et al. 2014), PN (Yorke et al. 2014), AlO (Patrascu, Tennyson & Yurchenko 2015) and NaH (Rivlin et al. 2015). In this paper, we present ro-vibrational transition lists and associated spectra for all stable isotopologues of CS.

2 METHOD

The line lists for all eight isotopologues of CS, which we have named JnK, were obtained by solving the Schrödinger equation allowing for Born–Oppenheimer Breakdown (BOB) effects using the program LEVEL8.0 (Le Roy 2007). In principle the calculations were initiated using the spectroscopic PEC of Coxon & Hajigeorgiou (1992). In practice, as described below, the PEC was first expressed in a form compatible with LEVEL. The PEC was then adapted to improve the results of calculations performed using LEVEL. After computation the line lists are improved by replacing calculated energies with experimentally derived energies, where available, and shifting the remaining energies to maintain LEVEL predicted energy level separations. A theoretical dipole moment curve (DMC) from Pineiro et al. (1987) was also employed.

2.1 Potential energy curve

We did not generate a new PEC for CS. A full set of potential parameters representing a very accurate PEC is already available from Coxon & Hajigeorgiou (1992). The authors employed data for four isotopomers ($^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$ and $^{13}C^{32}S$) in a least-squares fit to a potential function in the Born–Oppenheimer approximation and BOB functions to determine a PEC valid for all isotopologues. They set the dissociation energy D_e to 59 300.0 cm^{-1} and expressed their fitted potential $U_{CS}^{BO}(R)$ as a Morse potential with a variable β:

$$U_{CS}^{BO}(R) = D_e \left(1 - \exp\left[-\beta(R)(R - R_e)\right]\right)^2, \quad (1)$$

where

$$\beta(R) = \beta_0 + \beta_1(R - R_e) + \beta_2(R - R_e)^2 + \cdots. \quad (2)$$

The isotopically invariant breakdown functions were modelled as

$$U_C(R) = \Sigma_{i=1} u_i^C (R - R_e)^i, \quad (3)$$

and

$$U_S(R) = \Sigma_{i=1} u_i^S (R - R_e)^i, \quad (4)$$

while the *J*-dependent non-adiabatic breakdown function was modelled as

$$q_{CS}(R) = q^C(R)/M_C + q^S(R)/M_S, \quad (5)$$

where

$$q^{(k)}(R) = \Sigma_{i=1} \rho_i^{(k)} (R - R_e)^i, \quad (6)$$

such that $q^{(k)}(R_e) = 0$. These were applied in the effective radial Hamiltonian according to

$$H_{CS}(R) = -\beta_{at}^2 \nabla_R^2 + U_{CS}^{eff}(R) + (\beta_{at}^2/R^2) J(J+1)[1 + q_{CS}(R)], \quad (7)$$

where $\beta_{at}^2 = \hbar^2/2\mu_{at}$, defined with the atomic masses and

$$U_{CS}^{eff}(R) = U_{CS}^{BO}(R) + U_C(R)/M_C + U_S(R)/M_S. \quad (8)$$

The variable β Morse is not implemented in LEVEL8.0. The coefficients from Coxon & Hajigeorgiou (1992), given in Column II of Table 1, were hence used to generate turning points for a range of internuclear distances. The turning points were used directly in LEVEL.

Employing the potential parameters of Coxon & Hajigeorgiou (1992) in this way we could not reproduce the vibrational energies to the spectroscopic accuracy achieved by Coxon & Hajigeorgiou (1992). By applying small 'corrections' to potential parameters u_1^C, u_1^S, ρ_1^S and ρ_2^S, we were able to predict the ro-vibrational energies up to $v = 9$ and experimental frequencies for $^{12}C^{32}S$ and $^{13}C^{32}S$ to within 0.02 and 0.04 cm^{-1}, respectively (see JnK columns in

Table 1. Coefficients of the Born–Oppenheimer potential and radial functions for the $X^1\Sigma^+$ state of CS.

Parameter	Coxon & Hajigeorgiou (1992)[a]	This work
R_e Å	1.534 8175 (27)	1.534 8175
β_0	1.898 309 10 (907)	1.898 309 10
β_1	0.017 3292 (2255)	0.017 3292
β_2	0.122 0304 (5245)	0.122 0304
β_3	0.031 7616 (6808)	0.031 7616
β_4	0.043 7801 (7351)	0.043 7801
β_5	0.028 153 (1245)	0.028 153
u_1^C	−473.55 (11.10)	−474
u_2^C	1631.08 (21.83)	1631.08
u_3^C	−1380.3 (640.8)	−1380.3
u_4^C	−13714.9 (730.8)	−13714.9
u_1^S	−448.24 (18.61)	−448
u_2^S	1124.90 (52.07)	1124.90
u_3^S	−1245.2 (116.2)	−1245.2
ρ_1^S	−0.004 1274 (3021)	−0.003 8353
ρ_2^S	−0.000 8036 (4672)	−0.000 3364

Note. [a]Uncertainties are given in parentheses in units of the last digit.

Table 2. A comparison of theoretically and experimentally derived vibrational term values for $^{12}C^{32}S$ and $^{13}C^{32}S$ in cm^{-1}.

T_v	Experiment (JnK–Exp)	Calculated This work (JnK)	Obs−Calc This work (JnK)	Coxon & Hajigeorgiou (1992) (JnK–Cox)	(JnK–Cox)
		$^{12}C^{32}S$			
Uehara et al. (2015)					
T_1	1272.162 085	1272.1690	−0.0069	1272.162 14	−0.000 06
T_2	2531.353 715	2531.3486	0.0051	2531.353 84	−0.000 13
T_3	3777.597 715	3777.5899	0.0078	3777.598 00	−0.000 29
T_4	5010.916 850	5010.9087	0.0082	5010.917 39	−0.000 54
T_5	6231.333 760	6231.3229	0.0109	6231.334 56	−0.000 80
T_6	7438.870 820	7438.8584	0.0124	7438.871 83	−0.001 01
T_7	8633.550 080	8633.5338	0.0163	8633.551 25	−0.001 17
Ram et al. (1995)					
T_8	9815.392 54	9815.3752	0.0173	9815.394 57	−0.0020
T_9	10984.420 06	10984.4025	0.0176	10984.422 97	−0.0029
		$^{13}C^{32}S$			
Uehara et al. (2015)					
T_1	1236.315 929	1236.3524	−0.0364	1236.315 91	0.000 02
T_2	2460.388 235	2460.3782	0.0100	2460.390 43	−0.002 20
T_3	3672.237 852	3672.2234	0.0145	3672.244 79	−0.006 94
T_4	4871.885 67	4871.8831	0.0026	–	–
T_5	6059.352 46	6059.3547	−0.0021	–	–

Tables 2 and 3). To give an example, the residual (obs−calc) for $^{12}C^{32}S$ T_1 without the 'corrections' was 0.027 and 0.007 cm^{-1} after correction. The term 'correction' is used tentatively in this context as, although the modification of the potential parameters improved the present results, this is not an improvement on the variable β Morse presented by Coxon & Hajigeorgiou (1992). The potential parameters used in this work are given as Column III of Table 1.

To further improve our results we took advantage of the ExoMol format used to store the line list, see Section 3. Put simply, this is a states file containing level energies and a transitions file detailing allowed energy level couplings. The advantage of the format is it gives the option of replacing calculated energies with more refined or experimental energies such that, when the files are unpacked to produce the line list, more accurate line frequencies are computed, see Barber et al. 2014 for example.

First we attempted to refine our ro-vibrational energies ($E^{\rm JnK}_{v,J}$) for all isotopologues using the vibrational ($J = 0$, $v \leq 20$) energies given in Coxon & Hajigeorgiou (1992, $E^{\rm Cox}_{v,0}$) and the formula:

$$E^{\rm JnK-Cox}_{v,J} = \left(E^{\rm JnK}_{v,J} - E^{\rm JnK}_{v,0}\right) + E^{\rm Cox}_{v,0}. \quad (9)$$

Ro-vibrational energies for $v > 20$ were shifted to maintain the energy level separations predicted by LEVEL according to

$$E^{\rm JnK-Cox}_{v,J} = \left(E^{\rm JnK}_{v,J} - E^{\rm JnK}_{v-1,J}\right) + E^{\rm Cox}_{v-1,J}. \quad (10)$$

We could then reproduce the vibrational energies to the same spectroscopic accuracy achieved by Coxon & Hajigeorgiou (1992); however, not all the line frequency predictions improved (see JnK–Cox columns in Table 3).

This is likely due to the fact experimental data available to Coxon & Hajigeorgiou (1992) was limited to $J \leq 41$ and $J \leq 28$ while Ram et al. (1995) and Uehara et al. (2015) assigned lines for J up to 113 and 86 for $^{12}C^{32}S$ and $^{13}C^{32}S$, respectively.

Therefore we decided to determine experimental energies directly from frequencies measured by Ram et al. (1995) and Uehara et al. (2015) using the measured active rotation–vibration energy levels (MARVEL) technique (Furtenbacher, Császár & Tennyson 2007) which involves inverting transition frequencies to extract experimental level energies. Uehara et al. (2015) is the more accurate experimental study and thence energies extracted from these frequencies were used preferentially over those extracted from Ram et al. (1995) frequencies where possible. We extracted 733 energies in total for the main isotopologue and 341 energies for $^{13}C^{32}S$, see Table 5.

$^{12}C^{32}S$ and $^{13}C^{32}S$ energies for the experimental ranges were replaced with experimentally derived energies. Ro-vibrational energies for (v, J) outside the experimental ranges were shifted to maintain the energy level separations predicted by LEVEL according to the following equations. For $v < v^{\rm Exp}_{\rm max}$ and $J > J^{\rm Exp}_{\rm max}$:

$$E^{\rm JnK-Exp}_{v,J} = \left(E^{\rm JnK}_{v,J} - E^{\rm JnK}_{v,0}\right) + E^{\rm Exp}_{v,0}. \quad (11)$$

For $v > v^{\rm Exp}_{\rm max}$:

$$E^{\rm JnK-Exp}_{v,J} = \left(E^{\rm JnK}_{v,J} - E^{\rm JnK}_{v-1,J}\right) + E^{\rm JnK-Exp}_{v-1,J}. \quad (12)$$

The experimental frequencies for $^{12}C^{32}S$ and $^{13}C^{32}S$, by default, were reproduced almost exactly using this method. The largest residual is < 0.001 cm^{-1}. Hence the accuracy of these line lists should be equal to the experimental accuracies, which are expected to be 0.012 and 0.01 cm^{-1} for Ram et al. (1995) and Uehara et al. (2015), respectively.

For $^{12}C^{33}S$ and $^{12}C^{34}S$ Burkholder et al. (1987) measured infrared $v = 1 - 0$ absorption frequencies at 0.004 cm^{-1} unapodized resolution. The Coxon refined energies, see equations (9) and (10), reproduce these frequencies to very high precision (see Table 4), as would be expected considering they fitted to these frequencies. The Coxon refined energies also represent an improvement on the unrefined JnK energies (see Table 4), therefore we chose to employ them in our final line lists for these two isotopologues.

For the remaining isotopologues, with the exception of $^{13}C^{36}S$ which has not been observed experimentally, we have only measurements of rotational frequencies from Ahrens & Winnewisser

Table 3. Comparison of predicted ro-vibrational frequencies, in cm^{-1}, with experimental line positions measured by Ram et al. (1995) and Uehara et al. (2015) for $^{12}C^{32}S$ and $^{13}C^{32}S$.

J'	J''	v'	v''	Experimental JnK–Exp	Calculated JnK	Obs−Calc JnK	Calculated JnK–Cox	Obs−Calc JnK–Cox
$^{12}C^{32}S$								
				Uehara et al. (2015)				
10	9	1	0	1287.847 083	1287.8541	−0.0070	1287.8472	−0.0001
10	11	1	0	1253.542 068	1253.5490	−0.0070	1253.5421	−0.0000
9	10	2	1	1242.440 398	1242.4286	0.0118	1242.4407	−0.0003
11	10	2	1	1276.248 067	1276.2363	0.0118	1276.2484	−0.0003
100	101	2	1	1040.852 470	1040.8485	0.0039	1040.8606	−0.0082
20	21	6	5	1172.020 927	1172.0201	0.0008	1172.0219	−0.0010
21	20	6	5	1237.819 388	1237.8182	0.0012	1237.8200	−0.0006
78	79	6	5	1049.137 636	1049.1376	0.0000	1049.1394	−0.0018
10	11	7	6	1176.836 843	1176.8360	0.0008	1176.8400	−0.0032
15	14	7	6	1216.680 436	1216.6786	0.0018	1216.6827	−0.0022
63	64	7	6	1072.087 367	1072.0888	−0.0010	1072.0928	−0.0054
				Ram et al. (1995)				
102	103	1	0	1047.2868	1047.2910	−0.0040	1047.2841	0.0027
107	106	1	0	1371.8550	1371.8529	0.0021	1371.8459	0.0090
107	106	2	1	1357.5752	1357.5763	−0.0011	1357.5884	−0.0132
89	88	6	5	1296.2749	1296.2749	0.0000	1296.2767	−0.0018
89	88	7	6	1282.3246	1282.3263	−0.0017	1282.3303	−0.0057
25	26	8	7	1137.7464	1137.7446	0.0018	1137.7465	−0.0001
30	31	8	7	1128.3927	1128.3910	0.0017	1128.3928	−0.0001
52	53	8	7	1084.0478	1084.0496	−0.0018	1084.0514	−0.0036
59	58	8	7	1251.2061	1251.2079	−0.0018	1251.2098	−0.0037
25	26	9	8	1125.2391	1125.2367	0.0024	1125.2379	0.0012
28	27	9	8	1207.1842	1207.1833	0.0009	1207.1844	−0.0002
52	53	9	8	1071.8531	1071.8548	−0.0017	1071.8559	−0.0028
59	58	9	8	1237.6787	1237.6766	0.0021	1237.6778	0.0009
$^{13}C^{32}S$								
				Uehara et al. (2015)				
2	1	1	0	1239.369 011	1239.4051	−0.0360	1239.3686	0.0004
79	80	1	0	1080.972 174	1080.9775	−0.0053	1080.9411	0.0311
12	13	2	1	1203.322 346	1203.2753	0.0470	1203.3239	−0.0015
70	71	2	1	1089.992 782	1089.9459	0.0469	1089.9944	−0.0016
7	8	3	2	1199.383 201	1199.3761	0.0071	1199.3855	−0.0023
53	52	3	2	1276.188 741	1276.1977	−0.0089	1276.2070	−0.0182
6	7	4	3	1188.850 787	1188.8625	−0.0117	1188.8411	0.0097
64	65	4	3	1080.169 544	1080.1756	−0.0061	1080.1542	0.0154
14	13	5	4	1207.300 671	1207.3057	−0.0051	1207.3057	−0.0051
45	46	5	4	1107.707 636	1107.7159	−0.0083	1107.7159	−0.0083

Table 4. Comparison of predicted ro-vibrational frequencies, in cm^{-1}, with experimental line positions measured by Burkholder et al. (1987) for $^{12}C^{33}S$ and $^{12}C^{34}S$.

J'	J''	v'	v''	Experimental	Calculated JnK	Obs−Calc JnK	Calculated JnK–Cox	Obs−Calc JnK–Cox
$^{12}C^{33}S$								
3	2	1	0	1271.735 37	1271.736 018	−0.000 648	1271.735 366	0.000 004
4	5	1	0	1258.723 86	1258.724 631	−0.000 771	1258.723 979	−0.000 119
29	28	1	0	1308.726 99	1308.728 068	−0.001 078	1308.727 416	−0.000 426
25	26	1	0	1221.097 17	1221.098 153	−0.000 983	1221.097 501	−0.000 331
$^{12}C^{34}S$								
3	2	1	0	1266.780 54	1266.775 300	0.005 240	1266.780 744	−0.000 204
4	5	1	0	1253.871 37	1253.865 751	0.005 619	1253.871 195	0.000 175
35	34	1	0	1310.802 36	1310.797 693	0.004 667	1310.803 137	−0.000 777
35	36	1	0	1197.096 19	1197.091 827	0.004 363	1197.097 271	−0.001 081

Table 5. Summary of energies extracted from experimental frequencies.

v	Jmax	Total extracted	Using Uehara et al. (2015)	Using Ram et al. (1995)
$^{12}C^{32}S$				
0	106	107	87	20
1	106	107	102	5
2	101	102	94	8
3	93	94	86	8
4	89	90	89	1
5	89	80	62	18
6	76	55	41	14
7	70	46	24	22
8	59	32	0	32
9	59	32	0	32
$^{13}C^{32}S$				
0	80	78	78	0
1	71	70	70	0
2	70	69	69	0
3	65	64	64	0
4	46	30	30	0
5	46	30	30	0

Table 6. Comparison of predicted rotational frequencies, in cm^{-1}, with experimental line positions measured by Ahrens & Winnewisser (1999) for $^{12}C^{36}S$, $^{13}C^{33}S$ and $^{13}C^{34}S$.

J'	J''	v'	v''	Experimental	Calculated JnK JnK–Cox	Obs−Calc JnK JnK–Cox
$^{12}C^{36}S$						
6	5	0	0	9.507 279	9.507 297	−0.000 018
22	21	1	1	34.561 685	34.561 709	−0.000 024
$^{13}C^{33}S$						
6	5	0	0	9.173 973	9.173 971	0.000 002
20	19	0	0	30.545 844	30.545 846	−0.000 002
$^{13}C^{34}S$						
20	19	0	0	30.293 201	30.293 299	−0.000 098
13	12	2	2	19.429 173	19.429 154	0.000 019

(1999) to compare with. These are expected to have an accuracy of at least 0.000 02 cm^{-1}. As can been seen in Table 6 the agreement is excellent. Due to our methods, unrefined JnK and Coxon refined energies predict the same rotational frequencies. However, since the Coxon refined energies improved ro-vibrational frequency predictions for other isotopologues, these are employed in our final line lists for the remaining four isotopologues.

An overview of the energy-level content of our final 'hybrid' line lists is given in Table 7. Although we have used terms JnK, JnK–Cox and JnK–Exp in the text to refer to unrefined, Coxon refined and experimentally substituted energies, respectively, the final line lists as provided in supplementary data and on www.exomol.com are simply named JnK.

We note that the behaviour of the potential curve for longer internuclear distances than 3 Å was found to be divergent and non-physical resulting in the molecule not dissociating properly. This is consistent with the findings of Coxon & Colin (1997), that the model employed by Coxon & Hajigeorgiou (1992) does not account for the inverse-power behaviour of the PEC at long range. For this reason we only generated turning-points for internuclear distances between $R_{min} = 1.00$ Å and $R_{max} = 3.00$ Å with a grid spacing of 0.0007 Å. This has consequences for the temperature range considered. Based on our partition sum, see Section 2.3, this range now extends to 3000 K.

One approach proposed by Hajigeorgiou & Le Roy (2000) to overcome the problem is to employ a Modified Lennard–Jones (MLJ) potential function in place of the Morse variable β (Coxon & Colin 1997). As it is possible to produce a high temperature line list without this treatment, it is beyond the scope of this work.

2.2 Dipole moment curve

The only experimental dipole moment data for CS in the literature are Stark measurements of the $J = 1 \leftarrow 0$ matrix elements for $v = 0$ and $v = 1$ (Winnewisser & Cook 1968). This motivated Botschwina & Sebald (1985) to perform *ab initio* calculations of the dipole moment for CS over a range of internuclear separations ($2.5\ a_0 < R < 3.3a_0$). The resulting DMC yielded results that were in good agreement with the Stark values and so it was extended to longer and shorter internuclear distances by Pineiro et al. (1987) using a Padé approximant

$$M(x) = \frac{N_0 + N_1 x}{1 + D_1 x + D_2 x^2 + D_3 x^3 + D_4 x^4 + D_5 x^5}, \quad (13)$$

Table 7. Overview of sources of energy levels used in the JnK 'hybrid' line lists.

Isotopologue	Experimental energies	Coxon energies	Shifted energies
$^{12}C^{32}S$	$v \leq 9, J \leq 106$	None	$v > 9, J > 106$ using equation (11) and equation (12)
$^{12}C^{33}S$	None	$v \leq 7$ using equation (9)	$v > 7$ using equation (10)
$^{12}C^{34}S$	None	$v \leq 7$ using equation (9)	$v > 7$ using equation (10)
$^{12}C^{36}S$	None	$v \leq 7$ using equation (9)	$v > 7$ using equation (10)
$^{13}C^{32}S$	$v \leq 5, J \leq 80$	None	$v > 5, J > 80$ using equation (11) and equation (12)
$^{13}C^{33}S$	None	$v \leq 3$ using equation (9)	$v > 3$ using equation (10)
$^{13}C^{34}S$	None	$v \leq 3$ using equation (9)	$v > 3$ using equation (10)
$^{13}C^{36}S$	None	$v \leq 3$ using equation (9)	$v > 3$ using equation (10)

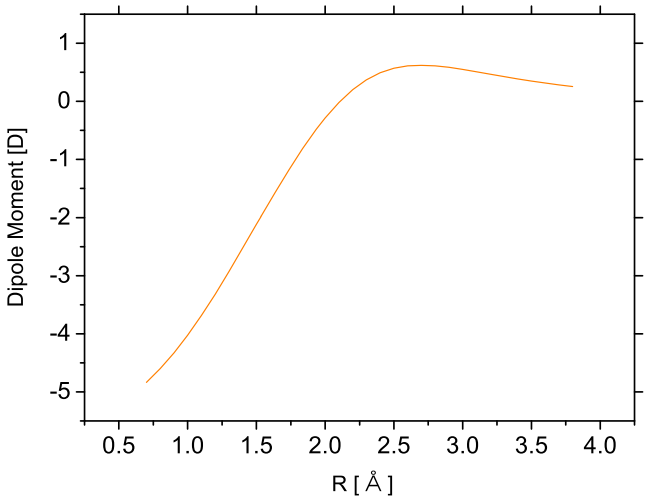

Figure 1. Dipole moment curve for CS obtained from the Padé expansion parameters of Pineiro et al. (1987).

Table 8. Comparison of $^{12}C^{32}S$ partition functions.

T(K)	This work	CDMS	HITRAN
150	127.9828	127.9818	128.1770
300	256.3156	256.3136	257.0819
500	437.5903	437.5868	439.6790
1000	1018.57	–	1026.38
2000	2880.03	–	2910.73
3000	5705.80	–	5803.37

where $x = (R - R_e)/R_e$, see Fig. 1. This function and coefficients N_i, D_i were used to generate turning points for input to LEVEL. The results of Pineiro et al. (1987) were reproduced to the precision quoted in their paper by this approach.

2.3 Partition functions

Partition function values for all eight isotopologues of CS were calculated by a direct sum of all calculated energies for a range of temperatures. We determined that our partition function is at least 95 per cent converged at 3000 K and much better than this at lower temperatures. Therefore, temperatures up to 3000 K were considered. Partition function values for the parent isotopologue from CDMS and HITRAN (Laraia et al. 2011) are compared to this work in Table 8.

At lower temperatures the CDMS partition function values are expected to be the most accurate and our values compare very well in this case. At higher temperatures only partition function values from HITRAN are available and our values are noticeably lower in this case. As the HITRAN partition function values are derived from using analytical approximations rather than a direct sum over energy levels, and do not agree as well with the CDMS values at lower temperatures, the results from this work are expected to be more accurate.

For ease of use, we fitted our partition functions, Q, to a series expansion of the form used by Vidler & Tennyson (2000):

$$\log_{10} Q(T) = \sum_{n=0}^{6} a_n [\log_{10} T]^n \qquad (14)$$

with the a_n values given in Table 9.

2.4 Line-list calculations

Line lists were calculated for all stable isotopologues of CS ($^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, $^{12}C^{36}S$, $^{13}C^{32}S$, $^{13}C^{33}S$, $^{13}C^{34}S$ and $^{13}C^{36}S$). These line lists span frequencies of up to 11 000 cm^{-1}. A summary of each line list is given in Table 10. All rotation–vibration states up to $v = 49$ and $J = 258$, and all transitions between these states satisfying the dipole selection rule $\Delta J = \pm 1$, were considered. Only changes in v up to 9 were retained in the final line list because of numerical issues with high transitions, see Medvedev et al. (2015).

Table 9. Fitting parameters used to fit the partition functions. Fits are valid for temperatures between 500 and 3000 K.

	$^{12}C^{32}S$	$^{12}C^{33}S$	$^{12}C^{34}S$	$^{12}C^{36}S$	$^{13}C^{32}S$	$^{13}C^{33}S$	$^{13}C^{34}S$	$^{13}C^{36}S$
a_0	−80.005 915	−76.155 662	−80.005 983	−80.004 802	−79.895 945	−79.450 814	−79.753 470	−72.151 123
a_1	135.900 176	130.515 908	135.900 484	135.901 969	136.196 073	136.926 482	136.119 795	132.718 091
a_2	−92.069 670	−88.464 147	−92.068 939	−92.067 292	−92.226 365	−92.982 691	−92.125 142	−99.251 755
a_3	32.390 529	31.162 671	32.390 765	32.392 690	32.426 480	32.752 272	32.286 797	39.931 597
a_4	−6.167 993	−5.950 792	−6.168 046	−6.170 901	−6.170 418	−6.233 068	−6.095 478	−9.136 353
a_5	0.599 177	0.581 747	0.599 173	0.600 214	0.599 063	0.603 143	0.582 017	1.139 224
a_6	−0.022 766	−0.022 418	−0.022 766	−0.022 885	−0.022 771	−0.022 683	−0.021 361	−0.060 799

Table 10. Summary of our line lists.

	$^{12}C^{32}S$	$^{12}C^{33}S$	$^{12}C^{34}S$	$^{12}C^{36}S$	$^{13}C^{32}S$	$^{13}C^{33}S$	$^{13}C^{34}S$	$^{13}C^{36}S$
Maximum v	49	49	49	49	49	49	49	49
Maximum J	258	258	258	258	258	258	258	258
Number of lines	199 045	199 917	200 599	201 944	205 826	206 622	207 322	209 071

Table 11. Extract from start of states file for $^{12}C^{32}S$. The full file can be downloaded from http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/MNRAS/ or www.exomol.com. n: state counting number; $\tilde{E}$: state energy in cm^{-1}; g: state degeneracy; J: state rotational quantum number; v: state vibrational quantum number.

n	$\tilde{E}$	g	J	v
1	0.000 000	1	0	0
2	1.634 164	3	1	0
3	4.902 459	5	2	0
4	9.804 822	7	3	0
5	16.341 155	9	4	0
6	24.511 332	11	5	0

Table 12. Extracts from the transitions file for $^{12}C^{32}S$. The full file can be downloaded from http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/MNRAS/ or www.exomol.com. F: upper state counting number; I: lower state counting number; A_{FI}: Einstein A coefficient in s^{-1}.

F	I	A_{FI}
2	1	1.7471E−06
3	2	1.6771E−05
4	3	6.0640E−05
5	4	1.4904E−04
6	5	2.9766E−04
7	6	5.2215E−04

3 RESULTS

The line lists contain around 200 000 transitions each. For compactness and ease of use they are separated into energy state and transitions files using the standard ExoMol format (Tennyson, Hill & Yurchenko 2013), which is based on a method originally developed for the BT2 line list (Barber et al. 2006). Extracts from the start of the $^{12}C^{32}S$ files are given in Tables 11 and 12. The full line lists for all isotopologues considered can be downloaded from CDS, via ftp://cdsarc.u-strasbg.fr/pub/cats/J/MNRAS/, or http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/MNRAS/ or can be obtained from www.exomol.com.

Table 13 compares our CS line lists with the previous ones from Pineiro et al. (1987) and CDMS; note that the 2078 CS transitions given in HITRAN-2012 (Rothman et al. 2013) are reproduced from CDMS. Although this is an assessment of the quantity of the data, not its quality, it demonstrates the reason for computing the new line lists, to provide a more comprehensive coverage of the problem.

Fig. 2 provides an overview of CS absorption at infrared wavelengths as function of temperature. At 300 K, and below, the spectrum is dominated by a series of vibrational bands starting with the fundamental band at about 8 μm. At higher temperatures the bands become very much broader and their peak absorption is reduced.

Table 13. Comparison of CS rotation–vibration line lists. Given are the number of isotopologues considered, the maximum values for vibrational (v) and rotational (J) states considered, the maximum change in vibrational state (Δv) and whether intensity information and a partition function are provided.

Reference	Pineiro et al. (1987)	CDMS	This work
Isotopes	4	6	6
Maximum v	20	4	49
Maximum J	200	99	258
Maximum Δv	4	2	9
Intensities?	Yes	Yes	Yes
Partition function?	No	Yes	Yes

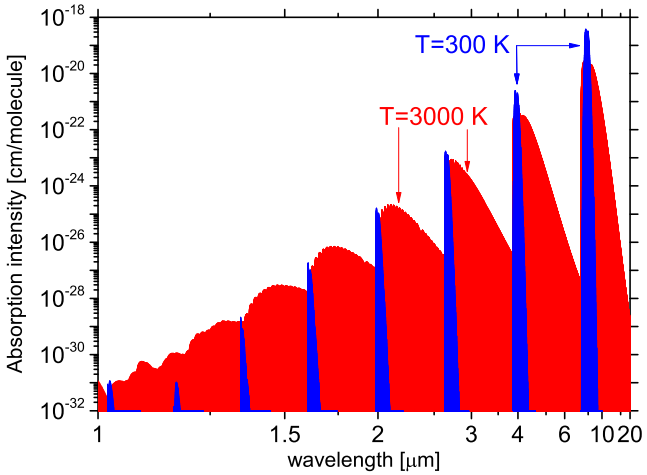

Figure 2. $^{12}C^{32}S$ absorption spectrum at infrared wavelengths as calculated in this work for a temperature of 300 K (narrow features) and 3000 K (broad features).

Comparisons with the CDMS rotational, $v' - v'' = 1 - 0$ and $v' - v'' = 2 - 0$ lines for $^{12}C^{32}S$ are presented in Fig. 3. The agreement is excellent for both frequency and intensity.

Ram et al. (1995) give two figures showing their observed spectrum, a compressed view of the vibration–rotation bands (1000 – 1400 cm^{-1}) and a portion of the R-branch region (1290 – 1310 cm^{-1}). Emission cross-sections for $^{12}C^{32}S$ were simulated using a Gaussian line shape profile with HWHM = 0.01 cm^{-1} as described in Hill, Yurchenko & Tennyson (2013). The resulting synthetic emission spectra are compared to the experimental spectra in Figs 4 and 5. For the former, the band structure and intensity ratio in our calculated spectra are very similar to the experiment. For the latter, there is generally good agreement; however the intensities of five strongest lines are almost 50 per cent larger in the theoretical spectrum which may be due to saturation effects in the measured spectrum.

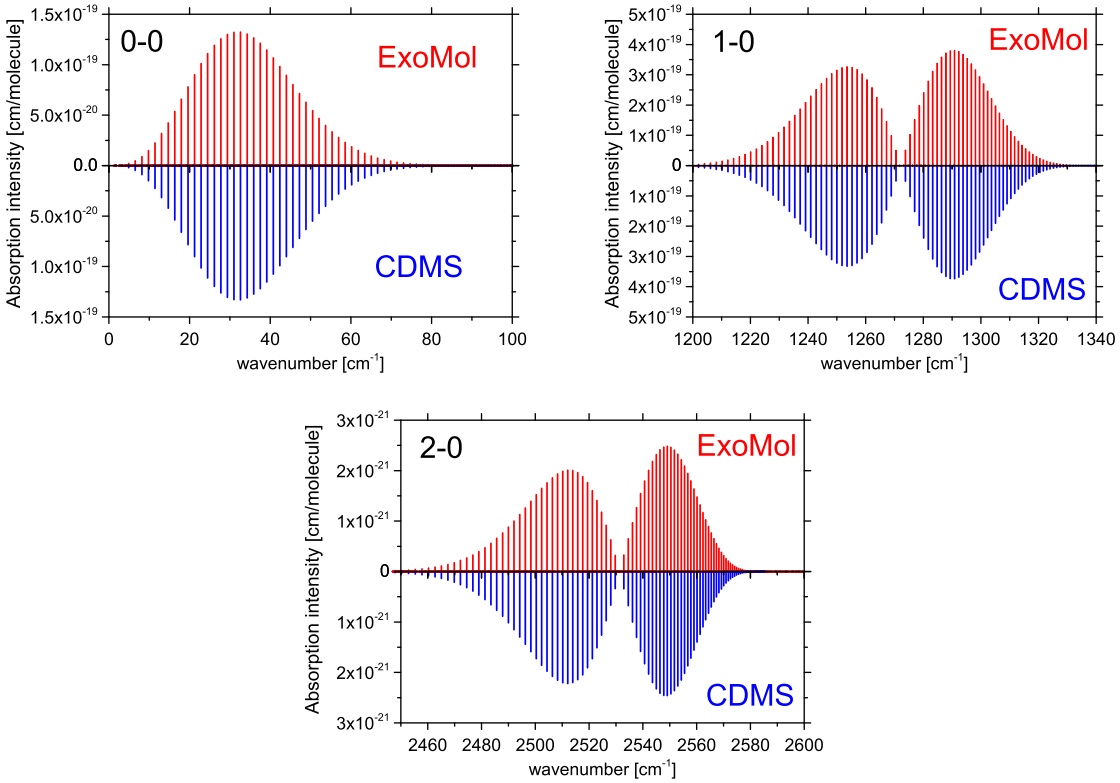

Figure 3. Absorption lines of $^{12}C^{32}S$ at 300 K: ExoMol verses CDMS.

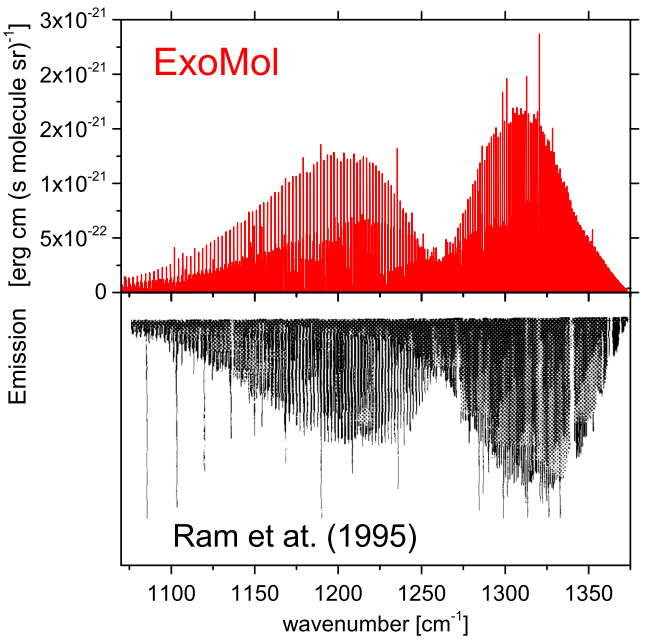

Figure 4. $^{12}C^{32}S$ at 2300 C: emission spectrum upper, Ram et al. (1995); emission lines lower, ExoMol [Reprinted from Ram et al. (1995)].

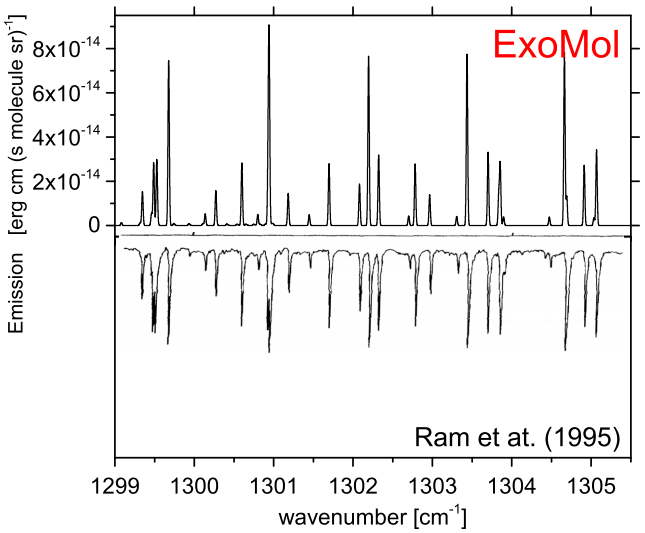

Figure 5. Emission spectrum of $^{12}C^{32}S$ at 2300 C: upper, Ram et al. (1995); lower, ExoMol [Reprinted from Ram et al. (1995)].

4 CONCLUSIONS

In this work, we have computed comprehensive line lists for all stable isotopologues of CS. We determined a PEC using LEVEL and modified potential parameters from the literature. We then substituted calculated energies in the states file with energies derived directly from experimental frequencies to match the experimental accuracy. This accuracy should extend to all predicted transition frequencies up to at least $v = 9$ and $J = 106$ for $^{12}C^{32}S$, and $v = 5$ and $J = 80$ for $^{13}C^{32}S$, the experimental ranges. Based on comparisons with other experiments the frequencies for the remaining isotopologues should be predicted to sub-wavenumber accuracy at least for $v < 3$ and $J < 21$. Einstein A coefficients were computed from a DMC taken from the literature. Comparisons with the semi-empirical CDMS data base suggest that the pure rotational, $v' - v'' = 1$–0 and $v' - v'' = 2$–0 intensities are accurate.

The results are line lists for rotation–vibration transitions within the ground states of $^{12}C^{32}S$, $^{12}C^{33}S$, $^{12}C^{34}S$, $^{12}C^{36}S$, $^{13}C^{32}S$, $^{13}C^{33}S$, $^{13}C^{34}S$ and $^{13}C^{36}S$, which should be accurate for a range of temperatures up to at least 3000 K. The line lists can be downloaded from CDS or from www.exomol.com.

Finally we note that, although our line lists are more comprehensive, for the purposes of high-resolution radio astronomy and far-infrared studies of the low temperature objects, the CDMS line lists are recommended.

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