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CO line intensities: Towards subpercent accuracy of intensities of all bands

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ABSTRACT

Accurate predictions of the carbon monoxide dipole moment as a function of geometry provide a challenge to theory not least because lower-level theories such as Hartree–Fock give dipoles with the wrong sign at equilibrium making reliable calculations of even the intensity of pure rotational transitions difficult. Intensities of CO lines are calculated using higher level theory based on multi-reference configuration interaction (MRCI). Tests using an increased complete active space (CAS) compared to previous high accuracy studies (Balashov et al., 2023), show that while increasing the σ orbital space from 7 to 8 orbitals produces poor (unbalanced) results, increasing the π space from 2 to 3 gives an ab initio model with reproduced CO pure rotational line intensities at the sub-percent level for the first time. This dipole function gives line intensities of all observed vibrational bands of CO from 0–0 to 7–0 with the sub-percent or experimental accuracy (whichever is the larger). Other possible improvement to the model such as use of larger (7 zeta) basis sets and relativistic corrections are considered. The permanent dipole of CO at its equilibrium geometry is estimated to be −0.1236 D with an uncertainty of 0.0003 D.

1. Introduction

The dipole moment of the carbon monoxide molecule has long been a challenge to theory given that self-consistent field (SCF) calculations give an equilibrium dipole with the wrong sign. This means that an accurate representation of the dipole can only be achieved through detailed treatment of electron correlation. There have been several recent high-level theoretical studies [1–7] where the dipole moment curve (DMC) of CO molecule has been calculated and CO line intensities computed using these DMCs. The reason for this activity is the twofold. First, high accuracy line intensities are necessary for a variety of applications, such as the metrology of temperature and pressure measurements, monitoring of the Earth atmosphere, atmospheres of planets, exoplanets and stars. Secondly, the CO molecule provides a uniquely favorable case for accurate experimental studies of transition intensities; very accurate measurements for vibrational bands from the microwave (0–0) to the optical (7–0) are available [2,8–11]. $^{12}C^{16}O$ is a simple, closed shell diatomic with widely-spaced lines with no hyperfine structure which does not condense on the cell walls during measurements; this behavior is unlike water or carbon dioxide for which accurate intensity measurements are often complicated by the adsorption and desorption [12–14]. We note that while direct excitation from the vibrational ground state reaches $v' = 7$, observations of hot CO spectra have led to the characterization of vibrational states of CO up to $v = 41$ [15,16]. Intensities for transitions between high-lying vibrational states are important for studies of hot CO such as in our own Sun and other stars; in general these are best obtained by calculation but require an accurate DMC.

Attempts to improve theoretical treatments of the DMC and hence line intensities are greatly aided by comparison with accurate measurements. In the case of $^{12}C^{16}O$, the accuracy of intensity measurements have reached the unprecedented sub-promille level [1] and are approaching the remarkable level of 10^{-2} % [17] for the (3–0) band. We note that these new levels of accuracy opens the way to new applications such as the remote measurement of pressure [18], temperature [19] and isotopical analysis [20]. Our theoretical efforts have also reached the very high accuracy of about 1‰ [1] for the (3–0) band but we note that up until now we have not been able to produce a DMC which can be considered reliable for all bands. Indeed our most systematic study both highlighted problems with numerical stability in the electronic structure calculations and gave intensities for pure rotational transitions, the (0–0) band, which differed from the best measurements by more than 10% [2]. Similarly, while we were able to provide DMCs which performed very well for the (3–0) band [1]

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and the (6–0) band [2], our (4–0) band line intensities, for example, were calculated with an accuracy about five times worse than that achieved experimentally. This paper aims to solve this problem by providing a DMC which can be used to reliably predict line intensities for all vibration–rotation transition in CO. We note that empirically fitted DMCs has been used successfully to calculate line intensities of CO molecule in several papers [4,5,9]. The fitting of the data has its advantages and disadvantages in comparison with the first principles calculations. The extrapolation power of the fitted DMC to the previously unknown bands is rather limited. However, the characterization of the CO spectrum reached quite a comprehensive level, so that empirically fitted DMC could play its role in the CO spectral studies.

As preparation for *ab initio* studies of high accuracy line intensities, we showed [21] that the variational nuclear-motion program Duo [22] which we use for the solution of the rovibrational Schrödinger equation can compute line intensities with accuracy up to 10^{-5} % for an idealized potential energy curve (PEC) and the dipole moment curve (DMC). The PEC we use [23] is very accurate. Thus we need to improve the level of quantum chemical theory used for the calculation of the DMC in attempt to improve the accuracy of the line intensity calculations of all the CO bands.

To improve the quality of the electronic structure calculation we could (1) increase the levels of correlation used. Within the framework of the Multi Reference Configuration Interaction (MRCI) approach, which we employ here as well as before [1,2] this means increasing the Complete Active Space (CAS) of the CAS-SCF stage of the calculations. (2) Move to higher n in the aug-cc-pCVnZ the basis set. As our previous [1,2] used $n = 6$ for the basis set, the $n = 7$ should be tried. (3) Relativistic corrections as well as adiabatic correction might be tried as well. As CO does not contain hydrogen atoms, the adiabatic Non-Born–Oppenheimer correction is relatively small and is not be considered here. All components of a possible improvement of the level of *ab initio* calculations are considered in the next section.

2. *ab initio* calculations and fits to a functional form

All CO spectral calculations discussed below are performed using program DUO [22]. Input data for the calculations are a potential energy curve (in our case the PEC of Coxon and Hajigeorgiou [23]) and various dipole moment curves. CO dipole moments were calculated for a grid of bondlengths in the range $R = 1.7 - 3.0$ a_0 with a step of $\Delta R = 0.5$ a_0 using MOLPRO. We used the finite field method to compute dipole moments, as in [2]. For small electric fields, ϵ, the change in system energy, ΔE, is proportional to dipole, d, i.e. $\Delta E = \epsilon d$. So the dipole is the derivative of the energy with respect to the electric field. This derivative was calculated numerically with a small external field value and a convergence criterion for the electronic energy in the electric field of 5×10^{-10}. We made test calculations with electric field strengths 0.001, 0.0002 and 0.00004 a.u. at a bondlength of $R = 2.2$ a_0. The dipole values differ from those calculated at $\epsilon = 0.0002$ a.u. by 5×10^{-6} for the five-times stronger ($\epsilon = 0.001$ a.u.) field, and by 2×10^{-7} for 5 times weaker ($\epsilon = 0.0004$ a.u.) field. We conclude that a value in the range $0.0003 < \epsilon < 0.0001$ is optimal and used $\epsilon = 0.0002$ a.u. in this work. To check the dependence of lines intensities on the grid step we halved the step size to $\Delta R = 0.025$ a_0. This led to differences in intensities of about 0.03%, which we deemed to be insignificant. The grid of dipoles computed using an external field of 0.0002 a.u. is provided in the supporting material.

Program DUO takes either *ab initio* points as a grid (CO distance – dipole moment) or as a set of polynomial coefficients. Here we calculated 27 points using the MRCI/aug-cc-pCV6Z level of theory in MOLPRO [27], as in [1]. The major difference here to our previous studies was the choice of CAS. In general, increasing the CAS results in a higher level of correlation, lowering the total energy and, of course, increased computer time, although we note that there is no direct rule about how the dipole moment converges with such an increase.

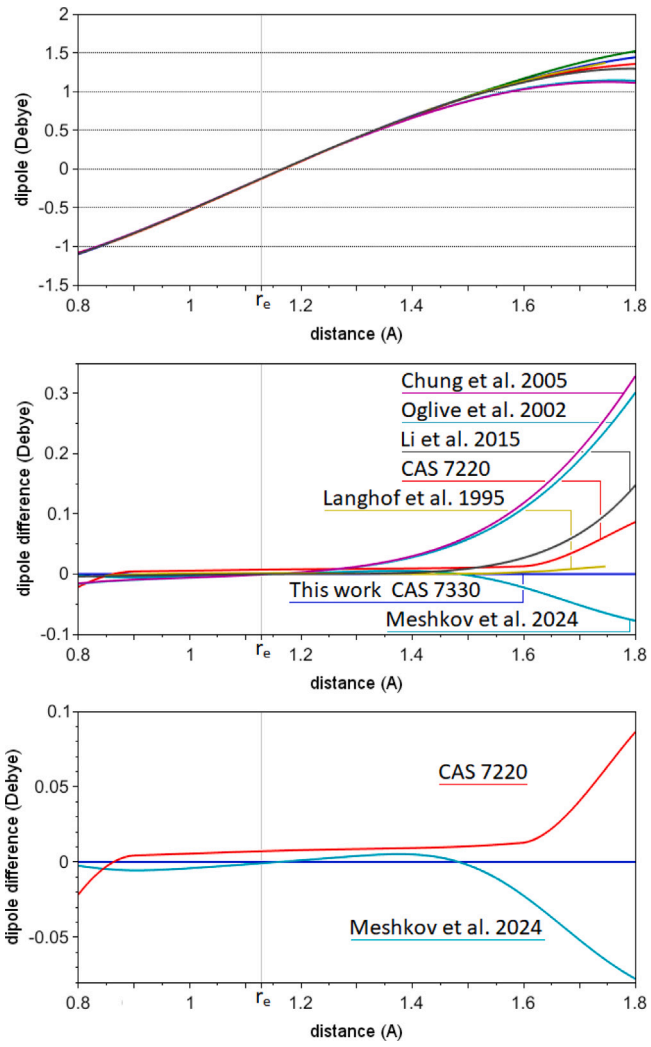

Fig. 1. Top panel: comparison of CO dipole curves computed *ab initio* in this work – CAS 7330 (blue) with CAS 7220 (red) and empirical curves [5] (dark green), [24] (beige), [9] (black), [25] (turquoise), [26] (purple). Bottom panel: offsets of the curve CAS 7330, shown relative to all other presented curves.

Indeed, the variational principle suggests that the energy will always be improved (lowered), this is not necessary true for the dipole as for dipoles it is important to get a balanced treatment between the atoms so that the calculated charge distribution mimics the actual one. For example, we tried first the 8220 CAS, which actually resulted in some deterioration of the intensity calculations in comparison with 7220 CAS used previously [2], where the choice of active orbitals is given in the notation as the number of orbitals with A_1, B_1, A_2 and B_2 symmetry, respectively. This change therefore effectively corresponds to adding another σ orbital to the CAS. We note that the notation used here and in our previous papers counts all orbitals; the notation introduced by Langhoff and Bauschlicher [24] only counts active orbitals meaning that our 8220 and 7220 models would be described as 6220 and 5220, respectively.

Second we tried 7330 CAS, i.e. adding an exta π orbital, as a further attempt to improve the treatment of correlation (the choice of CAS was also discussed in [6]). Table 1 shows the vibrational energy levels of CO calculated using both CAS 7220 and CAS 7330 and compared to the experimentally accurate band origins given by Coxon and Hajigeorgiou [23]. It can be seen that the 7330 levels are about twice as accurate as the 7220 ones. This suggests that the DMF may also be more accurate. Table 1 also presents values for the vibrational

Table 1
Vibrational band origins (VBOs, $J = 0$ energy levels in cm^{-1}), line strengths in D^2 and intensities (cm/molecule) for $^{12}C^{16}O$. The line and intensities are for the R(0) transitions from the ground state to exited vibrational states v. Empirical VBOs are from Coxon and Hajigeorgiou [23], calculated – from the *ab initio* 7330 and 7220 PECs; line strengths and intensities are from the 7330 calculated dipoles using wavefunctions form the empirical PEC of Coxon and Hajigeorgiou [23].

R0	VBOs	Obs.-Calc.		$S(f<-i)$	$I(f<-i)$
v		7220	7330		
0	0.0	0.0	0.0	1.21×10^{-02}	3.35×10^{-24}
1	2143.27	1.53	0.91	1.16×10^{-02}	9.64×10^{-20}
2	4260.06	3.12	1.81	4.36×10^{-05}	7.20×10^{-22}
3	6350.43	4.76	2.71	1.80×10^{-07}	4.44×10^{-24}
4	8414.46	6.45	3.61	4.51×10^{-10}	1.47×10^{-26}
5	10452.22	8.19	4.50	9.80×10^{-13}	3.97×10^{-29}
6	12463.76	9.99	5.40	4.92×10^{-13}	2.37×10^{-29}
7	14449.18	11.85	6.31	4.02×10^{-14}	2.25×10^{-30}

Table 2
Coefficients of the power series expansion from Eq. (1) of the DMC of carbon monoxide (distance in Å, dipole in Debye.).

α_0	4.647172858
α_1	−17.75805061
α_2	44.97475992
α_3	−59.59314304
α_4	39.54373486
α_5	−12.98891499
α_6	1.705980586

band intensities, taken as the values for the CO R0 line for which the Hönl–London factor is one.

Individual line intensities are discussed below. First we summarize the level of theory we used and the results of the fit of the *ab initio* points to a functional form. We used the same basis set aug-cc-pCV6Z for the MRCI calculation with a Davidson fixed correction. As pointed out in [2], the Davidson correction (as well as the Pople correction) can introduce distortions at the certain points. When the DMC *ab initio* points are fitted, this problem is avoided. That is why we fit the DMC *ab initio* points to the functional form described below.

To provide an analytic representation of the DMC we used a simple polynomial with the following functional form

$$D(r) = \sum_{k=0}^{6} \alpha_k (r - r_0)^k, \tag{1}$$

with only seven parameters α_k for the fit to the *ab initio* dipole points. The constants of the fitted DMC are given in the Table 2 with $r_0 = 0.0$. The standard deviation of the fit was 2×10^{-6} D. While this polynomial form gives an excellent fit to the *ab initio* dipoles, we recognize that if we wish to represent the DMC over an extended coordinate range it will be necessary to use a more appropriate functional form such as the one employed by Meshkov et al. [5].

The calculated intensities are practically the same when computed using the grid or the fit for bands (0–0), (1–0), (2–0) and (3–0). For higher frequency bands up to (7–0) the intensities are slightly closer to experiment using the fit than when the dipole is represented by a grid of points taken directly from the MOLPRO calculations.

Fig. 1 compares various *ab initio* and fited dipole moment curves: the *ab initio* DMC of this work which lies somewhat between the empirical DMC of [5] and our previous *ab initio* DMC [2] based on the 7220 CAS. As the empirical DMC is supposed to reproduce the experimental data on all the bands of CO within experimental error, Fig. 1 shows in the present DMC in comparison with the other *ab initio* and empirical ones.

Some further attempts to enhance the level of quantum chemical theory used in this work have been performed. In particular we checked the influence of the use of 7Z basis set as compared to 6Z one used in the previous [1,2] and present work. As MOLPRO cannot handle a 7Z basis, we cannot do this calculation directly and instead we treat it as a correction.

The following procedure was used. We calculated the DMC using MRCI and an aug-cc-pCV5Z basis set and also using CCSD(T) with both aug-cc-pCV5Z and aug-cc-pCV6Z basis sets with MOLPRO. We compared the dipole moments calculated using MRCI aug-cc-pCV6Z DMC with the one obtained using the following formulae with $n = 6$:

$$\mathrm{DMC(MRCI}n\mathrm{Z)}-\mathrm{DMC(MRCI}(n-1)\mathrm{Z)} = \mathrm{DMC(CCSD(T)}n\mathrm{Z)}-\mathrm{DMC(CCSD(T)}(n-1)\mathrm{Z)}, \tag{2}$$

The difference between these two dipoles turned out to be less than 5×10^{-5} Debye. As the relationship Eq. (2) holds, we can extrapolate values for our MRCI DMC using

$$\mathrm{DMC(MRCI}n\mathrm{Z)} = \mathrm{DMC(MRCI}(n-1)\mathrm{Z)}+\mathrm{DMC(CCSD(T)}n\mathrm{Z)}-\mathrm{DMC(CCSD(T)}(n-1)\mathrm{Z)}, \tag{3}$$

to obtain values for $n = 7$. To do this we used the very recent DMC(CCSD(T)7Z) calculations from Koput [3] and used DMC(CCSD(T)6Z) from our test calculations to give an effective DMC(MRCI7Z). Intensities computed using this DMC(MRCI7Z) only differ by only 0.03% for lines in the (3–0) band and by similarly small values for the other CO bands compared to our original DMC(MRCI6Z) calculations. This shows that to obtain calculated intensities with 0.01% accuracy, such 7Z correction would be necessary. However, in passing, we note that if we take the DMC model used to represent the 14 transitions in the (3–0) band measure to high accuracy by Bielska et al. [1] and Huang et al. [10], it reduces the mean differences from 0.05% to 0.025%. This improvement represents another step towards a goal of metrologically important 10^{-3} % uncertainty, which could play a significant role in the creation of tools of the measurements of temperature and pressure of gases with the accuracy, significantly better than the modern existing instruments.

The calculations of Koput [3] can also be used to assess the magnitude of the relativistic correction to the DMC (for previous relativistic dipole calculations see [28]). Koput considered a scalar relativistic correction computed using a CCSD(T)/aug-cc-pV5Z level of theory. However, use of this correction only increases calculated intensities by approximately 0.3%. The inclusion of even higher level theoretical corrections such as higher-order relativistic corrections (which are likely to reduce this figure), adiabatic and non-adiabatic corrections to the Born–Oppenheimer approximation and consideration of further higher-order correlation effects should reduce the computed intensities, bringing them closer to high accuracy measurements.

3. The line intensities of CO. Calculations and comparison with experiment

Table 3 presents the results of the calculation for the line intensities of all CO rotational and rovibrational bands using our CAS (7330) DMC and compares them with the best measurements, the results of our previous calculation using a CAS (7220) DMC [2] and calculations performed with the empirical DMC of Meshkov et al. [5]. The table also includes line intensities from HITRAN [29] which are based on the calculated value of Li et al. [9] who used an empirical DMC. All intensities are for 100% abundance of $^{12}C^{16}O$, which means scaling the HITRAN results by a factor $\frac{1}{0.986544}$ and intensity differences are given as percentages computed as (Obs./Calc.-1)*100.

The most striking result shown in Table 3 is that for the CAS (7330) model the calculated *ab initio* intensities for pure rotational transitions now lie within experimental error when our previous, CAS (7220) DMC calculations give intensities that are systematically more than 11% too strong compared to the recent measurements by Tretyakov et al. [8].

Why is it so hard to reproduce the pure rotational transition intensities? A typical value of the equilibrium dipole moment for most polar

Table 3
Observed $^{12}C^{16}O$ transition intensities compared to those calculated using our (7220) CAS and (7330) CAS models, and the empirical DMC of Meshkov *et al.* [5]. Intensities marked H and all wavenumbers are taken from HITRAN [29]. Observed intensities and uncertainties (unc.) are from Tretyakov *et al.* [8] for (0–0), [1] for (2–0), calculations from Bielska *et al.* [1] for (3–0), Grenoble measurements from [9] for(4–0), Li *et al.* [9] for (6–0) and Balashov *et al.* [2] for (7–0).

Band	Line	Wavenumber (cm^{-1})	S(Obs.) (cm molecule^{-1})	S(Obs) unc. %	Ref.	7220 CAS O−C (%)	7330 CAS O−C (%)	Ref. [5] O−C (%)
0–0	R0	3.8450	3.33×10^{-24}	0.5	[8]	−11.4	−0.74	0.44
	R0	3.8450	3.35×10^{-24}	1.0	H	−11.3	−0.18	1.35
	R1	7.6899	2.60×10^{-23}	0.5	[8]	−11.5	−0.66	1.18
	R1	7.6899	2.59×10^{-23}	1.0	H	−11.5	−0.15	0.79
	R2	11.5345	8.37×10^{-23}	1.0	H	−11.4	−0.16	1.23
	R10	42.2630	1.42×10^{-23}	1.0	H	−11.3	−0.13	1.52
	R15	61.4206	1.20×10^{-23}	1.0	H	−11.8	−0.14	1.13
	R20	76.7053	5.95×10^{-23}	1.0	H	−11.7	−0.15	1.41
1–0	P21	2055.4010	2.54×10^{-20}	5.0	H	−1.3	−2.34	−0.99
	P15	2082.0022	1.45×10^{-19}	5.0	H	−1.3	−2.34	−0.96
	P10	2103.2697	3.29×10^{-19}	5.0	H	−1.3	−2.33	−0.95
	R9	2179.7719	4.17×10^{-19}	5.0	H	−1.4	−2.33	−1.01
	R10	2183.2238	3.78×10^{-19}	5.0	H	−1.4	−2.34	−1.09
2–0	P10	4218.4857	5.44×10^{-21}	1.0	[1]	1.0	−1.49	0.07
	R14	4309.2540	1.64×10^{-21}	1.0	[1]	0.9	−1.08	0.09
	R20	4324.4100	3.37×10^{-22}	1.0	[1]	1.1	−0.89	0.28
	R24	4333.0540	7.70×10^{-23}	1.0	[1]	1.0	−0.97	0.21
3–0	P37	6139.4738	2.18×10^{-28}	0.1	[1]	0.2	−1.92	−0.45
	P27	6210.2458	7.36×10^{-26}	0.1	[1]	0.2	−1.82	−0.37
	P10	6307.2875	1.37×10^{-23}	0.1	[1]	0.4	−1.69	−0.24
	R10	6385.7715	1.95×10^{-23}	0.1	[1]	0.4	−1.56	−0.12
	R27	6414.9301	1.50×10^{-25}	0.1	[1]	0.0	−1.49	−0.04
	R37	6417.3988	5.60×10^{-28}	0.1	[1]	0.3	−1.46	−0.01
4–0	P38	8171.2723	1.27×10^{-31}	2.0	[9]	−10.0	1.27	3.36
	P37	8180.1948	2.61×10^{-31}	2.0	[9]	−9.7	1.32	3.15
	P24	8283.8841	5.17×10^{-28}	2.0	[9]	−9.4	−1.28	−1.33
	P22	8283.8841	1.24×10^{-27}	2.0	[9]	−8.4	−0.63	−0.80
	P10	8369.7429	3.56×10^{-26}	2.0	[9]	−7.0	−0.98	−1.43
5–0	P10	10405.9210	3.18×10^{-28}	20.0	H	18.5	−6.19	158
	P9	10411.3344	3.24×10^{-28}	20.0	H	19.9	−6.32	168
	P5	10431.24990	2.37×10^{-28}	20.0	H	23.0	−7.03	228
	R0	10455.89217	3.62×10^{-29}	20.0	H	24.0	−8.75	493
6–0	R5	12482.42374	9.30×10^{-29}	3.3	[9]	2.9	−2.60	1.84
	R7	12486.95665	9.33×10^{-29}	2.2	[9]	3.3	−1.60	3.08
	R9	12490.64487	7.85×10^{-29}	2.6	[9]	2.0	−3.99	0.79
	R10	12492.17185	7.04×10^{-29}	1.7	[9]	2.1	−2.87	2.09
7–0	P16	14358.36321	3.70×10^{-30}	7.4	[2]	0.6	4.38	−4.14
	P13	14380.14103	6.79×10^{-30}	4.1	[2]	−2.1	5.66	−1.91
	P8	14411.57398	1.11×10^{-29}	3.4	[2]	−5.1	7.53	1.17
	R0	14452.78145	2.49×10^{-30}	12	[2]	7.3	10.78	4.96

molecules is around one Debye, which results in intensities of order of 10^{-17} to 10^{-19} cm/molecule. However, CO is a special case, where two factors, influencing the value of the dipole moment at equilibrium nearly cancel each other and produce a permanent dipole moment of about 0.1 Debye and correspondingly weak intensities. Clearly the *ab initio* reproduction of this value requires much larger number of correct digits in all constituents of the *ab initio* calculation to reproduce the permanent dipole than for the other molecules. It can be seen from Fig. 1 that the shift in the equilibrium dipole between our two *ab initio* models is only about 0.01 D. It is clear that a very high level and well-balanced, sophisticated quantum chemical calculation is necessary to reproduce such small shifts. Looking at Table 3 our pure rotational transition intensities are between about 0.5 and 1% stronger than the current best measurements while the empirical DMC gives intensities between 0.5 and 1% weaker, this suggests that the true value of the equilibrium dipole moment of CO is somewhere between the values predicted by these two models which give values of −0.1240 D (CAS 7330) and −0.1232 D [5]. We therefore conclude that the equilibrium dipole moment of CO is −0.1236 D with an uncertainty of about ±0.0003 D for R_e = 1.12822960 Å taken from [30]. The uncertainty was estimated from difference between the dipoles at r_e of [30] and this work, and the fact that the true value must line between these two points.

Looking at the intensities of lines with the various vibrational bands considered in Table 3, it is clear that using our DMC gives intensities which are close to the observed values for all bands and that the variation of observed minus calculated within each band is generally uniform. Neither of these observations appear to hold for the empirical DMC. In general the intensities given by using the empirical DMC are, as one would expect, very close to the observations; in most cases lying within the uncertainties. However, the results for (5–0) band are an order of magnitude more than already large uncertainties in contrast to both our previous and current results which lie with the experimental uncertainty limits. Somewhat surprisingly, the observed minus calculated variations within a given band are much less smooth for the empirical DMC than found when using our DMC; it is unclear what the cause of this is.

The intensities of transitions within the very strong fundamental band of CO have been measured several times [31–35] and the scatter of the results spans about 4%. In the Table 3 we present the comparison

with the HITRAN lines, designated in the Table 3 by the letter H.

The line intensities for the (2–0) and (3–0) bands presented in the Table 3 show similar results for the CAS (7220) and (7330) models. Two other CO bands should also be particularly mentioned. The (4–0) band line intensities are predicted with significantly less accuracy by Balashov et al. [2] than the results given in the 7330 column of Table 3. However, our CAS (7330) results differ significantly from the CAS (7220) and are within the experimental error of the Grenoble laboratory measurements presented by Li et al. [9]. Conversely, transition intensities within the (5–0) band are yet to be measured with high accuracy. However, accurate measurements for lines in this band should be available soon [36]. CO intensity calculations by Li et al. [9], as used by HITRAN, our previous 7220 calculation [2] and our present 7330 agree within about 30% for all transitions in this band. However, use of the empirical DMC [5] gives intensities that are very significantly weaker than these other predictions. New measurements should reveal whether our predictions are indeed correct. We note that Meshkov et al. [5] already pointed that for the (5–0) band, theoretical transition probabilities proved to be extremely sensitive to any systematic variation in the DMC and PEC [37,38].

4. Conclusion

In this work we study the effect of increasing the level of the quantum chemistry first principles calculations on the DMC of the CO molecule. In particular, we manage for the first time to achieve the experimental accuracy of the anomalous rotational band intensities using a purely *ab initio* DMC. We improve the other *ab initio* band intensities. This represents a step towards the major goal of intensity calculations: *ab initio* calculation of line intensities of all the bands of a molecule within experimental accuracy. Clearly, further work to achieve this goal is necessary. This work will need to consider the significance of any further improvements of the *ab initio* model used to compute the dipole moments and whether changes to the potential energy curve influence the results. In this context we note the CO potential energy curve of Meshkov et al. [39], which is designed to have the correct physical behavior in the limits of small and large inter-atomic separations, may provide subtly different wavefunctions for higher excited states compared to the empirical potential of Coxon and Hajigeorgiou [23] which we use here.

CRediT authorship contribution statement

Nikolay F. Zobov: Writing – review & editing, Investigation, Formal analysis, Data curation. **Roman I. Ovsyannikov:** Formal analysis, Data curation. **Mikhail A. Rogov:** Investigation, Data curation. **Evgenii I. Lebedev:** Investigation. **Jonathan Tennyson:** Writing – review & editing, Funding acquisition, Formal analysis. **Oleg L. Polyansky:** Writing – original draft, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Oleg Polyansky reports financial support was provided by European Partnership on Metrology. Nikolay Zobov reports financial support was provided by Russian Academy of Sciences. The corresponding author is an Associate Editor of the Journal of Quantitative Spectroscopy and Radiative Transfer If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.jqsrt.2025.109510.

Data availability

Data is made available in the supplementary material.

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