Ames-2021 CO_2 Dipole Moment Surface and IR Line Lists: Toward 0.1% Uncertainty for CO_2 IR Intensities

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Abstract

A highly accurate CO_2 *ab initio* dipole moment surface (DMS), Ames-2021, is reported along with $^{12}C^{16}O_2$ Infrared (IR) intensity comparisons approaching 1-4‰ level of agreement and uncertainty. The Ames-2021 DMS was accurately fitted from CCSD(T) finite-field dipoles computed with the aug-cc-pVXZ (X=T,Q,5) basis for C atom and the d-aug-cc-pVXZ (X=T,Q,5) basis for O atoms, and extrapolated to the one particle basis set limit. Fitting σ_{rms} is 3.8E-7 a.u. for 4443 geometries below 15,000 cm^{-1}. The corresponding IR intensity, $S_{Ames\text{-}2021}$, are computed using the Ames-2 potential energy surface (PES), which is the best PES available for CO_2. Compared to high accuracy IR studies for 2001*i*-00001 and 3001*i*-00001 bands, $S_{Ames\text{-}2021}$ matches NIST experiment based intensities [$S_{NIST\text{-}HIT16}$ or S_{HIT20}] to -1.0±1.3‰, or matches DLR experiment based intensities [$S_{DLR\text{-}HIT16/UCL/Ames}$] to 1.9±3.7‰. This indicates the systematic deviations and uncertainties have been significantly reduced in $S_{Ames\text{-}2021}$. The $S_{UCL2015}$ (or $S_{HITRAN2016}$) have larger deviations (vs S_{DLR}) and uncertainties (vs S_{DLR}, S_{NIST}) which are attributed to the less accurate Ames-1 PES adopted in UCL-296 line list calculation. The $S_{Ames\text{-}2021}$ intensity of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ is utilized to derive new absolute $^{13}C/^{12}C$ ratios for Vienna PeeDee Belemnite (VPDB) with uncertainty reduced by 1/3 or 2/3. Further evaluation of $S_{Ames\text{-}2021}$ are carried out on those CO_2 bands discussed in the HITRAN2020 update paper. Consistent improvements and better accuracies are found in band-by-band analysis, except for those bands strongly affected by Coriolis Couplings, or very weak bands measured with relatively larger experimental uncertainties. The Ames-2021 296K IR line lists are generated for 13 CO_2 isotopologues, with 18,000 cm^{-1} and S_{296K} > 1E-31 cm/molecule cutoff, then combined with CDSD line positions (except $^{14}C^{16}O_2$). The Ames-2021 DMS and 296K IR line lists represent a major improvement over previous CO_2 theoretical IR intensity studies, including Ames-2016, UCL-296, and recent UCL DMS 2021 update. A real 1 permille level of agreement and uncertainty will definitely require *both* more accurate PES *and* more accurate DMS.

I. Introduction

Carbon Dioxide, CO_2, has attracted a huge amount of public attention and scientific interests. Its Infrared (IR) absorption capacity at different wavelengths is a key area that has been the focus of many experimental and theoretical studies. From terrestrial environments to solar system objects[1–7] and exoplanetary atmospheres[8–14], scientists want to know the whole picture of CO_2 IR spectroscopy at different temperatures, pressures, and with different atmospheric constituents.[13] The picture needs to be complete and as accurate as possible. For example, the OCO-2 mission[15] aims to estimate the CO_2 concentration with precision better than 0.3%. This means the intensity of target absorption line(s) needs to be determined to a similar or even higher level.

Traditionally, experimental IR scientists measure the spectrum, estimate the CO_2 IR intensities, and fit the observed intensities to effective dipole models. The models should include the most important expansion terms and necessary coupling terms. Then the fitted models are used to derive a new set of IR intensities. The high-resolution Carbon Dioxide Spectroscopic Databank (CDSD) database[16,17] is the most inclusive and updated collection of CO_2 effective dipole models and intensity data published for CO_2 isotopologues. Compared to the directly measured, pre-fitting intensities, the intensities computed from effective dipole models have much less noise, e.g., see Ref.18. The experimental difficulty and the uncertainty of dipole models may significantly increase for weak bands, e.g., see Refs.19,20. On the other hand, theoretical IR line lists include intensity predictions computed using high-quality *ab initio* dipole moment surfaces (DMS) and rovibrational wavefunctions calculated from semi-empirically refined potential energy surfaces (PES).[18,21–26] Given specific energy and intensity cutoffs, theoretical IR line lists such as Ames-2016[18] and UCL-296[27,28] have complete coverage for all allowed IR transitions, including those weak and inaccessible by experiment bands. In general, they are also expected to have higher consistency for the cross-band or cross-isotopologue intensity ratios.[29,30] The theoretical IR intensities computed by the UCL group,[27,28,31] $S_{UCL\text{-}296}$, have been adopted by HITRAN2016[32] and for most CO_2 IR lines below 8000 cm^{-1}. However, to assure the accuracy of theoretical IR intensities, highly accurate experiments for quality control and future improvements are still required. For example, HITRAN2020[33] has further scaled $S_{UCL\text{-}296}$ (or $S_{HITRAN2016}$) to match the experimental measurements of several $^{12}C^{16}O_2$ bands.

Over the last few years, the competition for the most accurate CO_2 IR intensity has entered a new era. The Hodges group (NIST) has reported several highly accurate experimental studies for the 2001*i*-00001[34–36] and 3001*i*-00001 [37,38] band series, and claimed better than 0.1% accuracy. Early 2021, they published a collaborative study[39] with the UCL group presenting a new $^{13}C/^{12}C$ ratio determination for Vienna PeeDee Belemnite (VPDB) with experimentally determined intensities and updated theoretical

($S_{UCL\text{-}2021}$) intensities. In 2021, Birk, Roske and Wagner (the DLR group) also reported their Fourier-Transform IR spectrum measurement between 6000 cm^{-1} and 7000 cm^{-1},[40] where the intensities of the 3001*i*-00001 and 00031-00001 bands were reported with 0.15% uncertainty. The difference on certain vibrational band(s) has raised concerns for part of the NIST group's work. Compared to S_{NIST} measurements, the S_{DLR} intensity for the 30012-00001 band was lower by ~0.5%, which is a few times larger than the estimated experimental uncertainty.

This paper reports our latest – which also should be the most accurate available – *ab initio* dipole moment surface(s) and 296K theoretical IR intensities for $^{12}C^{16}O_2$ and its minor isotopologues. Following the Ames-2016 work[18], the new dipole surface and new 296K IR line lists are all denoted Ames-2021, and the new 296K IR intensities are denoted $S_{Ames2021}$, or $\mathbf{S_{Ames}}$. These high quality *ab initio* IR intensities have provided us an opportunity to participate the discussion about the $^{12}C^{16}O_2$ 3001*i*-00001 intensity, to estimate the power and deficiency in S_{Ames}, and to identify some hidden factors which may have affected the $^{13}C/^{12}C$ ratio determination.[39] Both NIST and DLR studies are taken as highly accurate experimental data sources, and separately compared with S_{Ames}.

It is also necessary to prove the Ames-2021 DMS and S_{Ames} intensity is truly a major advance for CO_2 IR studies, i.e., the sub-percent level agreement for the 2001*i* and 3001*i* bands is not accidental. We have run additional quality checks on other IR bands discussed in the recent HITRAN2020 update[33,41], because they may represent the latest progress and more reliable data for those bands. Many of them were identified as problematic in previous UCL-296 line list study.[31] The analysis in this work involves experiment and model data, and various versions of Ames, UCL, HITRAN, and CDSD line lists.

For unequivocal understanding, the experimentally measured intensities should be separated from the intensities derived from fitted models, and those generated from experiment based scaling. In this paper, S_{NIST} or S_{DLR} refer to the intensity measurement before fitting or scaling. Model or line list intensities are denoted as S_{CDSD} (for CDSD 2015 or 2019), S_{HIT16} (for HITRAN2016), S_{HIT20} (for HITRAN2020), S_{Ames} or $S_{Ames2021}$ (for Ames-2021), $S_{Ames2016}$ (for Ames-2016), S_{UCL} or $S_{UCL2015}$ (for UCL-296), and $S_{UCL2021}$ (for updated UCL intensities). The *scaled* intensities are expressed by the names of experimental group and source line list. For example, $\underline{S_{NIST\text{-}HIT16}}$ means HITRAN2016 intensity was scaled by a ratio (β) calculated from S_{NIST} vs S_{HIT16} analysis, and $\underline{S_{DLR\text{-}Ames}}$ means $S_{Ames2021}$ was scaled by another β computed from S_{DLR} vs S_{Ames} analysis. Details of statistical analysis can be found in next section.

The paper is organized as follows: Section 2 of "Theory and Methods" first reviews the recent theoretical CO_2 IR line list work after 2010 to provide more detailed background, then give simple introduction for rovibrational intensity calculations and weighted averages of intensity ratios. Section 3 of "Results and Discussions" has five subsections: (1) the details of Ames-2021 DMS, S_{Ames} vs. S_{NIST} and

$S_{NIST-HIT16}$, and how it compares to other DMS including the published ones;[18,23,31,34,42]; (2) S_{Ames} vs S_{DLR} and $S_{DLR-HIT16/UCL/Ames}$ comparison for 3001*i* bands and 00031 band; theoretical perspectives about the (dis)agreements and (future) PES/DMS improvements; (3) how the $^{13}C/^{12}C$ VPDB ratio determination[39] may be affected by $S_{Ames2021}$ and scaled NIST and DLR intensities; (4) band-by-band analysis for those bands mentioned in the HITRAN2020 update; (5) briefly introduces the new Ames-2021 296K IR line lists. The final section of "Conclusions" emphasizes the importance of *both* an accurate PES *and* an accurate DMS, and the importance of the interaction between experiment and theory.

The CO_2 isotopologues may be referred by the ones digit of C and O atom mass numbers, e.g., the main isotopologue $^{12}C^{16}O_2$ is "626", and $^{16}O^{12}C^{18}O$ is "628". The CO_2 vibrational states use $\nu_1\nu_2 l_2\nu_3 r$ labeling, where $\nu_2=l_2$ and r is the rank in the polyad series, r=1,2,…ν_1+1.[33,43]

II. Theory and Methods

II.1 A review for recent CO_2 theoretical IR line list calculations

The Ames-1 PES was published in 2012[23]. It was originally a CCSD(T)[44]/cc-pCVQZ[45] based PES augmented by a scaled ACPF[46]/cc-pVTZ[47] correction. The PES was fitted with σ_{RMS} = 0.08-0.20 cm^{-1} for energies up to 40,000 cm^{-1}, then empirically refined with 467 selected purely experimentally determined $^{12}C^{16}O_2$ energy levels, which was the reference dataset. For $^{12}C^{16}O_2$, the Ames-1 PES refinement had root-mean-square (rms) deviations, σ_{rms} = 0.0197 cm^{-1} for the reference dataset, and σ_{rms} = 0.0156 cm^{-1} for 6873 purely experimental levels up to 13,000 cm^{-1} (J=0-117). A CCSD(T)/aug-cc-pVQZ[48] DMS was also published in 2012, denoted DMS-0Z.[23] We adopted a permutation-invariant basis to fit the pseudo-charges on the O atoms. The first Ames-296K line list for $^{12}C^{16}O_2$ was computed using the Ames-1 PES and DMS-0Z, including transitions up to 13,000 cm^{-1} and stronger than 1E-32 cm/molecule. It allowed us to determine that an old effective dipole model in HITRAN2008[49] had underestimated the 5001*i*-00001(*i*=3,4) band intensities by two orders of magnitude.[23,42]

In 2013, the DMS-0Z dipole surface was upgraded to DMS-N2.[42] The DMS-N2 was constructed at the same level of CCSD(T)/aug-cc-pVQZ, but we added more points to the energy range of 0 – 30,000 cm^{-1}. The *ab initio* dipoles were fit to a complete 16th order polynomial of simple bond length and 1+cos(∠OCO), which includes 969 coefficients. The 2531 points in the DMS-N2 fit were sampled from a larger three-dimensional grid of 13,302 geometries below 60,000 cm^{-1} on the Ames-1 PES, with step sizes 0.01Å and 1°. Due to the lack of computing resources, we were not able to compute the whole grid in 2013. The DMS-N2 was chosen because it improved the intensity convergence in the 4000-8000 cm^{-1} range and produced much less noise (or fake intensity) in the range of 11000 – 15000 cm^{-1}.[42] It was adopted for all the Ames 296K-4000K line lists that we computed between 2013 and 2017.[18,24,29,42] Note Huang et al (2013)[42] accidentally misquoted the fitting error of DMS-N2, by reporting |δ%| instead of |δ|. The real σ_{rms} of δ was 1.18E-6 a.u. for *x* components, and 0.77E-6 a.u. for *y* components.

When the Ames-1 PES was published in 2012, we noticed that the band origins computed for CO_2 minor isotopologues had δE deviations as large as -0.15 ~ +0.15 cm^{-1}. See Fig.5 of Ref.23. This should not happen. There also existed sudden δE changes at certain *J*s, see Fig.8 of Ref.23. Thanks to the independent calculations that UCL group carried out in 2014, the source of these problems was finally identified: a parameter controlling the convergence of the C-O stretching basis had not been properly set before and during the refinement. We had to fix this PES defect.

Along with the PES bug fix, we were investigating two options: should we try to get a one-for-all PES refinement using the experimental data of *all* minor isotopologues, or attempt an isotopologue-specific refinement? Without non-adiabatic corrections, it turned out the high *J* accuracy of some CO_2 isotopologues would be reduced from 0.01-0.02 cm^{-1} to 0.10~0.15 cm^{-1}. Taking the main isotopologue $^{12}C^{16}O_2$ as reference, the magnitude of these isotope impacts follows the order: $^{18}O > {}^{17}O >> {}^{13}C$. In the end, an all-isotopologue PES refinement was further refined using only the $^{12}C^{16}O_2$ reference dataset. This is the Ames-2 PES we finalized at the end of 2015. The Ames-2 PES has been used in this study and all the Ames CO_2 line list calculation and benchmark studies[18,29] published ever since. The isotopologue band origins (G_v) computed on the Ames-2 PES were consistently within ±0.02 cm^{-1} of experimental values, as demonstrated in the Fig.2a of the Ames-2016 line list paper.[18] The $S_{\text{Ames-2016}}$ intensities computed using the DMS-N2 can match most CDSD2015[16] model intensities to within ±5% and line positions to within ±0.03 cm^{-1}. In addition to the Ames-2 PES properties and intensity agreement, Ref.18 also discussed many other topics. Some of them may relate to this study. For example, the PES sensitivity of theoretically computed intensities was found to be larger than we had expected on both the Ames-1 PES and a $^{12}C^{18}O_2$ oriented PES refinement. The isotopologue consistency of $S_{\text{Ames-2016}}$ intensities was also found to be much better than that of experimental dipole models, because a high quality DMS should have similar performance for isotopologues within the Born-Oppenheimer approximation. Later our 2019 paper[29] presented a benchmark study for CO_2 (and SO_2) isotopologues. We estimated the isotopologue consistency of $S_{\text{Ames-2016}}$ intensities was "*at least 2 or even 3 orders of magnitude*" better (0.005-0.05%) than that of most experimental data and Effective Dipole Moment (EDM) models (1-10%). It was claimed that "*the isotopologue consistency allows us to make intensity predictions with δ% less than ±0.3% (linear) or ±0.02% (quadratic)*".[29]

Before the Ames-2 PES was refined to its final form, the UCL group had carried out 296K intensity calculations and published the UCL-296 line list for $^{12}C^{16}O_2$, using the Ames-1 PES and a UCL

DMS.[31,34] The UCL DMS (2015) was completely different from the Ames DMS-N2. First, it was based on the finite dipole derivatives of MRCI/aug-cc-pwCVQZ energies computed on ~2000 points up to 15,000 cm^{-1} with a perturbative relativistic correction, while the Ames DMS-N2 was fit from CCSD(T)/aug-cc-pVQZ dipoles computed at 2531 points up to 30,000 cm^{-1}. Secondly, the external electric field strength was 0.0003 a.u. in the UCL DMS, vs. 0.0001 a.u. in the Ames DMS-N2. More importantly, the UCL DMS fit the parallel and perpendicular dipole components separately to two polynomial expansions of symmetry coordinates.

The UCL DMS used just 17 and 19 coefficients to reach σ_{rms}=2.25E-5 a.u. and 1.85E-5 a.u. for 1963 μ_x components and 1433 μ_y components, respectively.[31] Apparently, the UCL fits were much more efficient than the Ames DMS fits. But in our recent test, when the Ames DMS fit was also limited to 0 – 15000 cm^{-1}, the total σ_{rms} for all CCSD(T) μ_x and μ_y components were 7.1E-8 a.u. (969 coeff, 16th order), 5.9E-7 a.u. (84 coeff, 6th order), or 3.0E-5 a.u. (35 coeff, 4th order). Therefore, the two fitting approaches have comparable efficiency at 4th-5th order, while the Ames series chose many more coefficients to achieve higher accuracy in the lower energy range but still maintain fairly good quality in the high energy range.

A description of the UCL DMS (2015) first appeared in the supplementary file of Polyansky et al,[34] which reported a -0.33% relative difference between the UCL theoretical IR intensity and the NIST measured IR intensity for the $^{12}C^{16}O_2$ 30013-00001 band. This study signaled the beginning of the recent race to determine CO_2 IR intensities with sub-percent accuracy aiming for 0.1%. When Zak et al[31] reported the first UCL-296 line list for $^{12}C^{16}O_2$ at 296K, it was stated that the UCL DMS should be able to "*give intensities accurate to better than 0.5% ... for the vast majority of transitions below 8000 cm^{-1}*". The first UCL-296 $^{12}C^{16}O_2$ line list[31] was cut off at 8000 cm^{-1} and S_{296K}>1E-30 cm/molecule. In 2017, Zak et al[27,28] further reported UCL-296 line lists for other symmetric isotopologues[27] and asymmetric isotopologues.[28] These line lists were also computed using the Ames-1 PES and UCL DMS (2015), with the same cutoffs. Later the HITRAN2016 database[32] took the UCL-296 intensity data to replace the effective dipole model based intensity values for the majority of IR transitions below 8000 cm^{-1}. Recent NIST high accuracy CO_2 intensity studies[34–38] also adopted the $S_{UCL-296}$ values as the reference.

To the best of our knowledge, all the CO_2 IR line lists and/or intensity data published by the UCL Exomol group[27,28,31,34,39] are based on the Ames-1 PES,[23] not the Ames-2 PES.[18] The same UCL DMS (2015)[31,34] was used in all UCL CO_2 studies published before 2021. The latest example is in 2020 when Yurchenko et al[50] reported a UCL-4000 IR line list for $^{12}C^{16}O_2$. It covers the 0 – 20,000 cm^{-1} range with cutoffs $E''<16000$ cm^{-1}, $E'<36000$ cm^{-1}, $J\leq 202$, and Einstein coefficients larger than 10^{-14} s^{-1}. In the 2021 $^{13}C/^{12}C$ ratio study,[39] the UCL group reported new R12e and R18e intensities for the 2001*i*-00001 (*i*=1-3) and 3001*i*-00001 (*i*=2-4) bands from an updated DMS. It is denoted as UCL DMS (2021) in this paper.

Compared to the UCL DMS (2015), it was fit with ~50% more points, i.e., ~3000 *ab initio* dipole vectors computed at the level of all-electron MRCI[51,52]/aug-cc-pwCVQZ[53] with a relativistic correction[54–56]. In Fig.S1 of Fleisher et al,[39] the relative standard uncertainty for the new UCL theoretical intensities was estimated to be 0.38% for 12C16O2. This is an improvement when compared to the 0.50% uncertainty of UCL-296[27,31] (or HITRAN2016[32]) intensity. This uncertainty was assumed identical for the $^{13}C^{16}O_2$ intensities used in the VPDB $^{13}C/^{12}C$ ratio determination.[39]

Table 1. List of recent theoretical studies for CO_2 semi-empirically refined PES, *ab initio* DMS, intensity and IR line lists. Cutoffs are for intensity (cm/molecule) and transition wavenumber range, e.g., 8K for 8000 cm^{-1}. Note the UCL DMS 2021 based line list is not publicly available.

Year	PES	DMS	Line List	Cutoff	Iso	Reference
2012	Ames-1	Ames DMS-0Z	Ames-296K	1E-42/13K	626	Huang et al [23]
2013	Ames-1	Ames DMS-N2	Ames-1000K	1E-30/24K	626	Huang et al [42]
2014	Ames-1	Ames DMS-N2	Ames-1000K	1E-30/18K	13 isos	Huang et al [24]
2015	Ames-1	UCL DMS 2015			626	Polyansky et al [34]
2015	Ames-1	UCL DMS 2015	UCL-296	1E-30/8K	626	Zak et al [31]
2016	Ames-2					*Fixed C-O stretch defect*
2017	Ames-1	UCL DMS 2015	UCL-296 (→HITRAN2016)	1E-30/8K	13 isos	Zak et al [27,28]
2017	Ames-2	Ames DMS-N2	Ames-2016 (296*K*) (Ames 4000*K*)	1E-42/24K (1E-30/15K)	13 isos (626)	Huang et al [18]
2020	Ames-1	UCL DMS 2015	UCL-4000 (→ExoMol)	A_{21}>1E-14/20K	626	Yurchenko et al [50]
2021	Ames-1	UCL DMS 2021	*n/a*	*n/a*	626, 636	Fleisher et al [39]
2021	Ames-2	Ames-2021 DMS	Ames-2021 296*K*	1E-31/18K	13 isos	This work

In 2016, the UCL group kindly shared their DMS (2015) with us. We planned to run an apples-to-apples comparison but unfortunately its coordinate system is incompatible with the dipole surface re-expansion in the VTET[57] program. We had to re-fit the UCL DMS (2015) dipoles produced for the Ames set of 2531 geometries to the Ames DMS-N2 style.[18] Re-fitting errors were around 1E-5 a.u.. Unfortunately, the intensities we computed using the refitted DMS were not in good agreement with the original $S_{UCL-296}$ values, either. See Fig.3 in Ref.18. The Ames DMS-N2 was also shared with UCL group.

It should be noted that, in addition to the PES and DMS differences, specific rovibrational computational program or algorithmic implementations may also affect the theoretical IR intensities. For example, the UCL vs Ames intensity difference was 7% for the microwave spectrum of $^{17/18}O^{12}C^{16}O$ (or 627 and 628), which was much larger than we expected.[18] The UCL-4000 list[50] was computed by the TROVE[58] program, while the UCL-296 lists were computed with DVR3D.[59] Their J=0 energy level differences can be as large as ±0.05 cm^{-1} at 10,000 cm^{-1}.[50] Another example is a well-known defect in the old S_{Ames} data for symmetric isotopologues: there exist ~0.3-0.7% intensity gap between the P/R branches of a vibrational band. For example, see Fig.1 in Ref.38 and Figs.3-4 in Ref.18. This issue has been fixed in the latest VTET[57] rovibrational calculations. All the new Ames-2021 intensity values reported in this paper for $^{12/13}C^{16}O_2$ and other isotopologues have been re-computed, so they are free of the intensity gap.

From our perspective, we agreed that the Ames-2016 line list and the UCL-296 line list have reached the ±1% agreement level when compared to the experimentally measured intensities for the 2001*i*-00001 and 3001*i*-00001 bands. Examples are Fig.3 of Ref.18, or Fig.1 of Long et al[38] and Fig.12 of Birk et al.[40] Back in 2017, we were not confident with a general claim of sub-percent accuracy. This was not only due to the discrepancy among experiments,[34,60] the lack of high accuracy experimental data for other vibrational bands in the polyads, but also due to the PES sensitivity and the lack of a DMS convergence study. The Fig.4 of Huang et al.[18] demonstrated that, from the Ames-1 PES to the Ames-2 PES, a 0.02 cm^{-1} line position change was associated with a ~0.7% intensity difference for the 30013-00001 band. This difference was not related to the J=0 gap. Then how to prove a PES and (or) DMS being used are really converged to better than 0.1-0.3%? The answer is to do the best, and to utilize the most reliable experiments for quality control. Therefore, starting from 2018, we built up a series of new DMSs and have evaluated their performance. See more details and how the Ames-2021 DMS was selected in next section.

Table 1 lists the Ames and UCL CO_2 studies published from 2012 to 2021 in chronological order. Ames-2 PES is supplied in supplementary files to this paper, and at http://huang.seti.org/CO2/co2.html.

II.2 Experiments

A partial list of related high-accuracy experimental studies is given in Table 2. Starting from Long et al (2019),[38] the NIST group has taken the *ab initio* UCL DMS (2015) based $S_{\mathrm{HITRAN2016}}$ (or S_{HIT16}, and S_{UCL296} or S_{UCL} for many bands) intensities as reference, and run weighted least-squares fitting to determine a scaling parameter, β, to minimize the difference between measured S_{NIST} and $\beta \cdot S_{\mathrm{HIT16}}$. This parameter is vibrational band dependent, e.g., 1.0069 for 20013-00001,[36] 0.9897 for 30012-00001, 1.0003 for 30013-00001, and 0.9994 for 30014-00001.[38] These four β values indicate the agreement between the $S_{\mathrm{HIT16/UCL296}}$ and S_{NIST} was -0.08 ± 0.71%, i.e., -0.8 ± 7.1‰ for the four bands. Original experimental statistical uncertainty was estimated to be 0.06~0.09%.[36,38] This forms the basis of the "toward 0.1% accuracy" claim in our title. The S_{DLR} data was reported with 0.15% total relative standard uncertainty, so the claim is still valid. The weighted $S_{\mathrm{DLR}}/S_{\mathrm{HIT16}}$ ratios reported in Birk et al[40] were 1.00643, 0.984417, 0.998613, and 1.00229 for 30011 – 30014 bands, respectively. The DLR vs NIST differences are -5.3‰ (30012), -1.7‰ (30013), and 2.9‰ (30014). The discrepancy on 30012 band was beyond the published uncertainty range.

Table 2. Partial list of high accuracy CO_2 IR intensity measurements. Those in bold are used in this work.

Year	Band	Experiment	Uncertainty (u)	Reference

2011	**20012**	**PTB-Berlin**	**0.43%**	**Wübbeler et al** [61]
2015	30013	NIST	≤0.5%	Polyansky et al [34]
2016	30013	JPL/Kitt Peak	0.3-0.9%	Devi et al [60]
2016	20013	JPL/Kitt Peak	0.3%	Benner et al [62]
2017	20012	U.Campania/IAP	0.17-0.23%	Odintsova et al [63]
2018	20012	NIST	0.15-0.46%	Yi et al [35]
2018	30011	USTC	≤0.85%	Kang et al [64]
2019	30012	NIST	0.06%	Fleisher et al [37]
2019	**30012**	**NIST**	**0.06%**	**Long et al** [38]
	30013		**0.07%**	
	30014		**0.09%**	
2020	**20013**	**NIST**	**0.08%**	**Fleurbaey et al** [36]
2021	**3001*i***	**DLR**	**0.15%**	**Birk et al** [40]

II.3 Rovibrational and Intensity calculation (this work)

Rovibrational energy levels, wavefunctions, transition dipole moments of CO_2 isotopologues are computed using VTET program,[57] up to J=150. More details were introduced in Ref.23. Energy cutoffs are set to 0.3 Hartree for one-dimensional stretching basis and final coupled stretch-bending functions, 0.6 Hartree for bending functions at each *K* and 0.15 Hartree for contracted functions. All eigen roots with energies up to 0.1 Hartree above zero-point energy were extracted. For intensity calculations, 24 point optimized quadrature were used for the stretches, and the DMS Legendre expansion has 60 terms determined from a 72 point Gauss–Legendre quadrature.

The intensity gap between *P* and *R* branches was first circumvented by running asymmetric calculations for symmetric isotopologues, e.g., 626. Later a minor defect was identified and fixed in the quadrature points generation. It does not change the energies, but affect IR intensities. For consistency, all 13 isotopologues have been re-computed. As illustrated in next sections, the issue has been solved. The intensity difference between asymmetric "patch" and code improvement is usually 10^{-4} ~ 10^{-6} for *P* and *R* transitions, while it may reach 0.2~5% for some *Q* lines.

II.4 Systematic Investigation on Dipole Moment Surface

New CCSD(T) dipole calculations were run on the full grid of 13,302 geometries up to 60,000 cm^{-1}, with aug-cc-pV*XZ*[45,48], aug-cc-pCV*XZ*[45,48], d-aug-cc-pV*XZ*[65], and aug-cc-pwCV*XZ*[53] bases, *X*=T,Q,5. Extrapolation to the one-particle basis set limit, core-correlation effects (QZ, 5Z or beyond), and scalar relativistic correction[54–56] (TZ) were also part of the *ab initio* calculations, following the procedures we reported in Ref.[66] for highly accurate Quartic Force Field (QFF). These calculations were finished in 2020. For consistency and higher accuracy, the dipoles were still fit to the pseudo nuclei charges on O atoms using a full 16th order polynomial with 969 coefficients.[42] Different geometry sets, energy cutoffs, and fitting bases were included in the DMS series. For example, we have three sets of geometries at 30,000 cm^{-1}: small (S) – 2320 or 2531 points, large (L) – 7667 points, and full (F) – 8590 points. Note the core-correlated CCSD(T)/agu-cc-pwCV5Z dipoles were only computed for the small (S) set. Every DMS fit is used in a line list intensity calculation, all of which use the same set of controlling parameters and an identical set of CO_2 rovibrational wavefunctions generated from the Ames-2 PES, unless specified otherwise. Computed IR intensities are then compared to the $S_{NIST-HIT16}$ data reported in 2019-2020.[36,38] The quality of each DMS was estimated by the unweighted "mean±σ_{rms}" on the weighted averages of relative intensity deviations, $(S_1/S_2-1)\cdot 1000$ in permille, for 4-5 bands. See below.

II.5 Weighted mean±σ_{rms} for intensity, line list, and DMS comparisons

Weighted S_{DLR}/S_{HIT16}, S_{NIST}/S_{HIT16}, and S_{DLR}/S_{NIST} ratios were reported in Table 8 of Birk et al.[40] We follow similar procedure to re-compute the statistical mean±σ_{rms} of S_{NIST} and S_{DLR} related ratios, including $S_{NIST-HIT16}$ and $S_{DLR-HIT16}$. One set of ratios is calculated in the full (or specified) range reported with uncertainties, so that we can compare with published reference ratios. Please note that Ref.40 used same transition set for a given band, to make a consistent comparison between NIST and DLR studies. There will be small differences in the ratios, reasonably resulted from different transition set.

Second set of ratios is computed for the range m=-30~30, where m=-J'' (P) or J'' (Q and R). For the 2001i, 3001i and 00031 bands, this is the range of strongest lines measured with least uncertainty. Thus the S_{DLR}/S_{Ames} or S_{NIST}/S_{Ames} ratios may be more reliable for scaling.

$$weighted\ mean = x_{wgt} = \frac{\sum w_i x_i}{\sum w_i}, \quad \sigma_{wgt} = \sqrt{\left(\frac{\sum w_i x_i^2}{\sum w_i} - x_{wgt}^2\right) \Big/ (n-1)}$$

The statistical weight w_i in ratio estimation was defined as the inverse of the square of relative uncertainty, i.e., $(u_{meas}/S_{meas})^{-2}$. x_i is the intensity value or the ratio for i^{th} transition, and n is the number of intensities, ratios, or transitions included in the analysis with uncertainties. The u_{meas} is the total relative standard uncertainty estimated for the measured intensity S_{meas}. Additional 0.05% systematic uncertainty was included for S_{NIST}/S_{HIT16} and S_{NIST}/S_{Ames} calculations, after the multiple measurements for a transition have been averaged using weights $w_i = u_{NIST} / S_{NIST}$.

In this study, S_{Ames} is reported with 7 significant digits and up to 10^{-4}~10^{-6} changes were confirmed for the P and R lines in Ames line list upgrades, including the fixes for intensity gap. The statistical uncertainty estimated for S_{Ames} is less than 0.01%-0.001%, compared to 0.02% estimate for S_{UCL296} (or S_{HIT16}), because the S_{UCL} and $S_{HIT16/HIT20}$ data have 4 significant figures (or only 3 figures for symmetric minor isotopologues) in HITRAN2016 and HITRAN2020. Both are much smaller than the systematic uncertainty for S_{NIST} or S_{DLR}, so they are not included in the uncertainty estimate for ratios. The systematic uncertainty of S_{Ames} or S_{UCL} itself is a focus of this paper.

The overall quality of line lists or dipole moment surfaces is appraised by unweighted mean ± σ_{rms} computed from the weighted intensity ratios, x_{wgt}, for 4-5 bands reported in NIST or DLR studies, where $x = (S_{\mathrm{NIST\ or\ DLR}} / S_{\mathrm{Ames\ or\ HIT16}} - 1)\cdot 1000$. In other words, the experimental bands are treated equally and their x_{wgt} ratios are assumed to carry uniform relative uncertainty, i.e., irrelevant to the band intensity. This is also because the uncertainty of scaled HITRAN intensity is different from that of S_{Expt}. The uncertainty on certain bands (e.g., 30012) is also part of the disagreement between NIST and DLR studies.

III. Results and Discussions

III.1 Ames-2021 Intensity and NIST Experiment

Most contents in this section are either reference independent, or valid in both NIST and DLR based analysis. Exceptions are the shift of "mean" differences and the increases of "σ" uncertainty of Ames and UCL intensity agreement with experiment. Patterns in Ames DMS series are not significantly altered. General "agreement" over multiple bands should include both 'mean' differences and 'σ' uncertainty.

III.1.1 Fitting Details

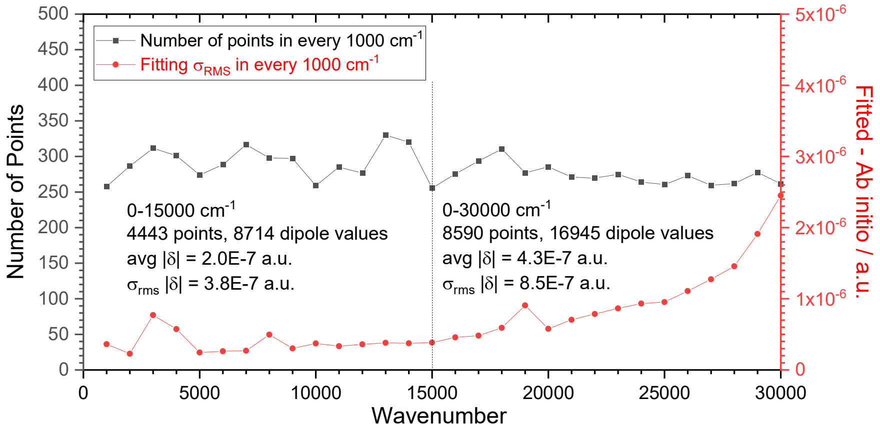

Figure 1. Grid point distribution and fitting deviations of the Ames-2021 DMS, along the increasing energy.

After all the line lists had been computed and compared, the Ames-2021 DMS was selected *before* the DLR study was published. It was fit from 8590 dipole vectors computed on our largest grid (F) up to 30,000 cm^{-1} above the PES minimum. At each grid point, the CCSD(T)/(d-)aug-cc-pVXZ(O) (X=T,Q,5) dipoles were computed with an external electric field of 0.0001 a.u., then extrapolated to one-particle basis set limit using a three-point formula.[67] The "(d-)" and "(O)" mean the O atoms use the doubly augmented basis, d-aug-cc-pVXZ (X=T,Q,5). The first diffuse function is to describe the O^- character because the original Dunning's basis sets[47] was optimized only for the neutral. The 2nd diffuse function is to describe better the molecular orbital polarization.[68]

Statistics for the *ab initio* data points and fitting errors for Ames-2021 DMS are presented in Fig.1. The numbers of geometries for every 1000 cm^{-1} (black squares) are stable up to 30,000 cm^{-1}, i.e., 250-300 points every 1000 cm^{-1}. That was how the original large set of 13,302 geometries were randomly sampled from both the lower energy region and higher energy region. From 0 to 15,000 cm^{-1}, our σ_{RMS} is 3.8E-7 a.u. for the 8714 non-zero dipole components of 4443 geometries. Compared to the UCL DMSs (2015)[34] and (2021)[39], our Ames-2021 DMS has at least 50% more points and 50 times better fitting accuracy for this range. This is a substantial improvement. The total σ_{rms} for the whole 0 – 30,000 cm^{-1} range is 8.5E-7 a.u. for the 16945 non-zero dipole components of 8590 geometries. Actually, the σ_{rms} is less than 1E-6 a.u. for most ranges below 25,000 cm^{-1}.

The Ames-2021 DMS choice was primarily based on three aspects: 1) the dipoles in this DMS fit were computed at *one* of the highest levels that we trust with more confidence; 2) accurately fitted from the most complete grid, it should have reached a better balance between the lower energy (from PES minimum to 15,000 cm^{-1}) accuracy and higher energy coverage; 3) in the list of top candidates, this DMS *luckily* provides *one* of the best agreements with $S_{NIST\text{-}HIT16}$. Overall, the choice is largely based on #1 and #2. See more details in next subsection. Some observations are also shared by NIST and DLR data comparisons. Section III.2 will further explain why it is still our top choice with relatively larger uncertainty (~4‰) found in DLR data comparisons.

Table 3. Comparison of the Ames-2021 DMS with the Ames DMS-N2, the UCL DMS 2015 and the 2021 update.

	Ames DNS-N2	Ames-2021 DMS (best in series)	UCL DMS 2015 (and 2021 update)
ab initio	CCSD(T)/aug-cc-PVQZ	Extrapolated CCSD(T) (d-)aug-cc-pV(T,Q,5)Z for C(O)	MRCI/aug-cc-pwCVQZ, all electron + relativistic correction
external field	0.0001 a.u.	0.0001 a.u.	0.0003 a.u.
Grid	2531 pts < 30,000 cm^{-1}	8590 pts < 30,000 cm^{-1}	1963 (~3000) pts < 15,000 cm^{-1}
Fitting to	Pseudo charge on O Permutation invariant	Pseudo charge on O Permutation invariant	Dipole components Symmetry internal coordinates
Fitting σ_{RMS}	1.0E-6 a.u. (Relative σ_{rms}=8E-4%)	8.5E-7 a.u. (0 – 30,000 cm^{-1}) or 3.8E-7 a.u. up to 15,000 cm^{-1}	2.25E-5 a.u. (m_x) and 1.83E-5 a.u. (m_y)
# coeff	969	969	36

Table 3 gives a quick summary showing how the Ames-2021 DMS compares to the published Ames DMS-N2,[42] the UCL DMS 2015,[34] and its latest 2021 update.[39] Note that the other Ames dipole surfaces fit from the same geometry set also have similar fitting accuracies, indicating the quality of our *ab initio* dipole data and least squares fitting is consistent and stable. The higher fitting accuracy should lead to less noise in DMS fits and less contaminations in the computed intensities, hence reducing the σ_{rms} and the uncertainty when they are compared to experiments.

III.1.2 $S_{Ames2021}$ vs $S_{NIST\text{-}HIT16}$: -1 ± 1‰

In Fig.2a, the relative difference between $S_{Ames2021}$ and $S_{NIST\text{-}HIT16}$ are plotted in permille, for four $^{12}C^{16}O_2$ bands: 20013, and 3001i, i=2-4. For m = -30 ~ +30, or from P30 to R30, the 4 means are in the range -2.5 ~ +0.5‰, and σ_{rms} are all less than 0.6‰. The overall "mean ± σ_{rms}" for the four unweighted "means" is -0.83 ± 0.99‰, or -1 ± 1‰. Fig.2b compares the measured S_{NIST} to S_{Ames}. The weighted means look like those in Fig.2a, but have opposite signs, with 0.1~0.5‰ absolute value differences. The weighted σ_{rms} are larger on 3 bands, but still less than 1‰. The overall "mean ± σ_{rms}" for the four weighted "means" is 0.99 ± 1.28‰, repeating the "-1 ± 1‰" agreement in Fig.2a. Recall that the "mean ± σ_{rms}" for $S_{UCL}/S_{NIST\text{-}HIT16}$ is -1 ± 7‰ for the same bands (see Table 3 of Long et al[38] and Table 4 of Fleurbaey et al[36]). This is a more than 80% reduction on the σ_{rms}. Such improvement should not be purely accidental, and probably have benefitted from the advantages of a more accurate PES and a more reliably fitted DMS.

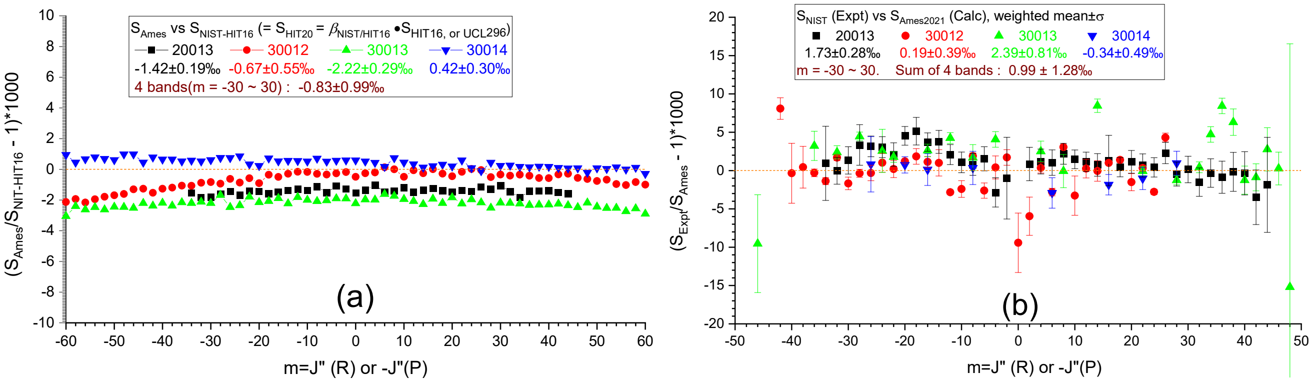

Figure. 2 (a) $S_{Ames2021}$ vs. $S_{NIST\text{-}HIT16}$ intensity comparison for 4 CO_2 IR bands, with unweighted mean±σ_{rms} of $(S_{Ames}/S_{NIST\text{-}HIT16}-1)\cdot 1000$. Note $S_{NIST\text{-}HIT16}$ (or S_{HIT20}) was the S_{HIT16} intensity scaled with the β values reported in Long et al (2019)[38] and Fleubaey et al (2020)[36]. Part of the fluctuations in this plot are because UCL-296 and HITRAN provide only 4 significant figures for the intensities. (b) measured S_{NIST} vs $S_{Ames2021}$ intensity comparison for 4 CO_2 IR bands, with weighted mean±σ_{rms} of $(S_{NIST}/S_{Ames}-1)\cdot 1000$. The S_{NIST} and relative uncertainty associated with a specific transition was the weighted average from multiple measurements. See text for more details about weights and uncertainties.

In Fig.2a, the blue line for the 30014 band (triangles downward) shows a small dependence on m, i.e., almost linearly decreasing by ~0.5‰ from m = -60 to m = 60. The red dotted line for 30012 band has a quadratic local maximum around m = 10, or R10. Because the scaling parameter β was fitted to minimize the difference between S_{NIST} and $\beta\cdot S_{HIT16}$, the defects or impurities in S_{HIT16} or S_{UCL} may transfer into $S_{NIST\text{-}HIT16}$, or S_{HIT20}. On the other hand, this also means that the scaled $S_{NIST\text{-}HIT16}$ intensity results can be further improved by fitting to more reliable *ab initio* intensities when they become available, e.g., $S_{Ames\text{-}2021}$. We cannot rule out the possibility yet that $S_{Ames2021}$ might still contain some linear or quadratic residuals, but they are probably smaller by half or one order of magnitude. The $S_{Ames\text{-}2021}$ should be considered more reliable and more self-consistent. More examples are given in next subsections.

III.1.3 Ames DMS series and other line lists

In addition to the 4 bands in Fig.2, Fleisher et al[39] also adopted the intensity of the 20012-00001 band. The intensity reported in Yi et al (2018)[35] contained systematic oscillations along *m*, not suitable for high accuracy comparison or scaling. Instead, the 20012-00001 *R*12 line intensity from Wübbler et al (2011)[61] was cited as the best experimental value, with 0.43% uncertainty reported. Note the S_{UCL} and $S_{Ames2021}$ agree on the 20012 band to within 1‰.

Following Fleisher et al[39], the $S_{NIST\text{-}HIT16}$ intensity of two transitions, *R*12 and *R*18 in each band, were used in statistics and comparisons. Consequently, the "mean±σ_{rms}" over 4-5 bands will be slightly different from those in Fig.2 for the range *m*=-30~30, but they are very close. The *R*12/*R*18 based analysis does not affect related discussion or the choice of Ames-2021 DMS. The 4-band statistics (in red) is the primary indicator, while the impact of 20012 band is monitored by 5-band statistics (in black).

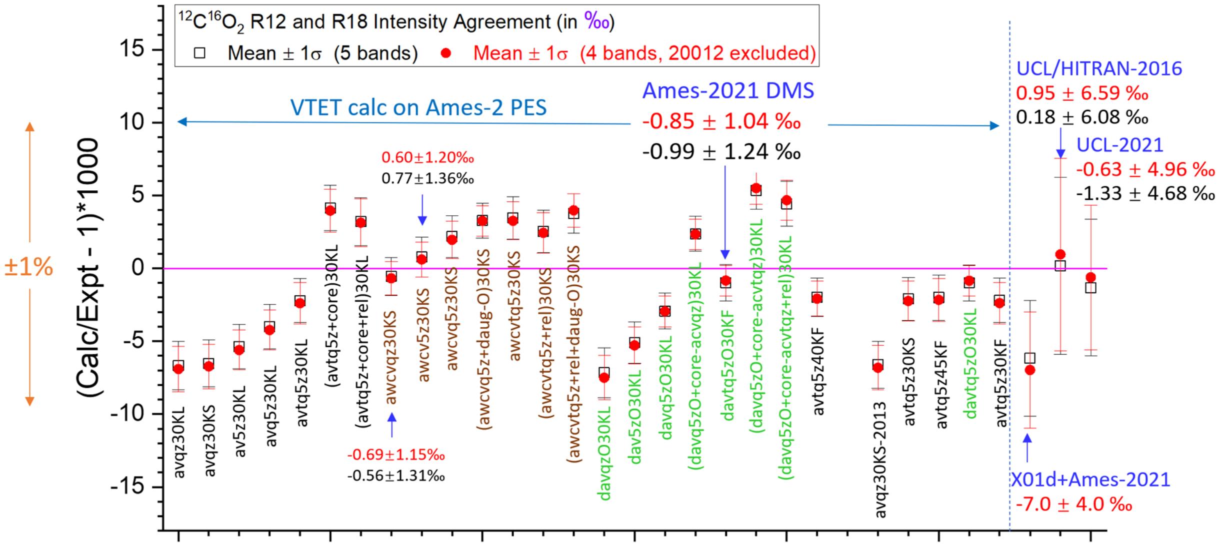

Figure 3. Calc vs Expt ($S_{NIST\text{-}HIT16}$) intensity agreement for selected Ames DMS fits, including Ames-2021. The number of points in the geometry sets at corresponding energy cutoffs are: 30KS – 2320 or 2531 pts; 30KL – 7667 pts; 30KF – 8590 pts; 40KF – 11155 pts; 45KF – 12096 pts, where "30K" = 30,000 cm^{-1} above PES minimum and so on. Notations: "a(w)vxz" – aug-cc-p(w)CVXZ, "davxzO" – d-aug-cc-pVXZ basis on O atoms and aug-cc-pVXZ basis on C atom, *X*=T,Q,5; "2013" – the published surface DMS-N2; "rel" – relativistic correction at CCSD(T)/cc-pVTZ-DK level; "daug-O" – 2nd diffuse function effect on O atoms computed as the differences between the extrapolated (d-)aug-cc-pVXZ(O) dipoles and aug-cc-pVXZ dipoles, *X*=T,Q,5; "core" – all-electron correlation effects computed with specified basis or 2-point extrapolated aug-cc-pCV(T,Q)Z.

Fig.3 summarizes the S_{Calc} *vs* $S_{NIST\text{-}HIT16}$ agreements, for the S_{Calc} intensities computed using a selected series of Ames DMS fits and a fixed set of Ames-2 PES based rovibrational wavefunctions. To the left of the short-dashed line, every point represents one set of intensities computed on a different dipole surface. The 28 DMS fits are selected to evaluate the impact of various *ab initio* calculations, corrections, and controlling parameters. From left to right, all their σ_{rms} are between 1‰ and 2‰, consistent with Fig.2. This suggests that the $\sigma = \pm 1‰$ we found on the Ames-2021 DMS is *not* solely a coincidence.

In Fig.3, we use the color black for the aug-cc-pVXZ series, the color magenta for the aug-cc-pwCVXZ series, and the color green for the (d-)aug-cc-pVXZ(O) series, where *X*=T,Q,5. Obviously, the $S_{Calc}/S_{NIST\text{-}HIT16}$ ratios monotonically increases in the order T → Q → 5 → Q5Z → TQ5Z, for all three series. For the aug-cc-pVXZ and (d-)aug-cc-pVXZ(O) series, the core-correlation corrections raise their S_{Calc} by 0.6%. The relativistic correction reduces the S_{Calc} by ~0.1%. These patterns and effects are consistent through the DMS series, providing systematic support for the reliability and convergence of the Ames-2021 DMS. The energy cutoff and geometry set effects are tested for the extrapolated aug-cc-pV*X*Z and (d-)aug-cc-pVXZ(O) DMS fits, see the data between the green (d-)aug-cc-pVXZ(O) series and short-dashed line. The Ames-2021 DMS, or the “davtq5zO30KF” fit, has the “mean ± σ” very similar to that of the "davtq5zO30KL" fit. It is interesting to observe that the S_{Calc} of the extrapolated aug-cc-pVXZ dipole surfaces is not really impacted by the 30K, 40K, or 45K cutoffs, or the geometry set change from 30KL to 30KS. This further supports the convergence of the least-squares fits, and the stable accuracy for the lower energy range. Remember only 4-5 vibrational bands are included in this analysis.

To the right side of the short-dashed line, there are three extra points. Two of them are based on the published UCL-296 line lists[27,31] and the new UCL DMS 2021[39] intensities. Please note the σ in Fig.3 is not the “standard uncertainty” as defined in Fleisher et al,[39] they should not compare to each other. But the quarter improvement from the UCL DMS 2015 to UCL DMS 2021 is consistent on both sides: 0.66% → 0.50% (4 bands) or 0.61% → 0.47% (5 bands) in Fig.3 vs. 0.50% → 0.38% in Fleisher et al[39].

An interesting observation is the “awcvqz30KS” and “awcv5z30KS” DMS fits. Their “mean” are 0.60‰ and -0.69‰, comparable to or better than the “mean” of the $S_{Ames2021}$ (-0.85‰), $S_{UCL2015}$ (0.95‰) and $S_{UCL2021}$ (-0.63‰). Their σ are 1.15-1.20‰, consistent with Ames-2021 DMS. Note that the Ames CCSD(T) and UCL MRCI calculations are intrinsically different, so the “mean” similarity at aug-cc-pwCVQZ level could be either a coincidence, or resulted from their respective error cancellations. The “awcvqz30KS” or “awcv5z30KS” fits were not chosen for two reasons. Firstly, its geometry set was too small. The 30KF grid (8590 points) probably provides a more complete and balanced description for the dipole spaces, which consequently reduces intensity noise and outliers. Secondly, and more importantly, the (d-)aug-cc-pVXZ(O) DMS series have earned much more confidence for the higher energy region. The 2nd diffuse function on the O atoms helps describe the molecular orbital responses to an external field.[68] In previous SO_2 DMS studies,[69] the d-aug-cc-pVQZ based dipoles show improvement over the aug-cc-pVQZ dipoles, and the aug-cc-pwCVQZ dipoles were also slightly better than the aug-cc-pCVQZ dipoles. In addition, the core-correlation effects overestimate the vibrational effective dipoles, too. These findings in the lower energy range are consistent with the findings in Fig.3.

In short, the complete-basis-set-limit extrapolation, extra d- function, and the 8590-pts grid at 30,000 cm^{-1} are the main strengths of Ames-2021 DMS.

III.1.4. The PES and DMS behind σ_{rms}(UCL)

Compared to the Ames DMS series, the much larger σ_{rms} uncertainty in the UCL intensities can be primarily attributed to the defects in the Ames-1 PES[23] adopted in the UCL calculations,[31,39] which is less accurate than the Ames-2 PES,[18] as was mentioned previously. Regarding this claim, the 3rd point to the right side of the short-dashed line, denoted as "X01d+Ames-2021", provides a convincing evidence. The "X01d" is our new semi-empirical CO_2 PES refinement. It sacrifices the accuracy at lower energy region for the higher energy region which becomes more important for CO_2 spectra calculations beyond 2000K. The X01d PES and related new line list will be reported in a future paper. The J=0 band origins on the X01d PES can be off by ~0.10 cm^{-1} in the range of the 3001*i* polyad, similar to or slightly worse than those on the Ames-1 PES. Using the same Ames-2021 DMS, the Ames-2 → X01d PES change leads to a 300% larger σ_{rms} for the intensity comparison, yielding "mean±σ" = -7.0±4.0‰. This is close to the σ_{rms} = 5.0‰ for the $S_{UCL2021}$. Clearly, the less accurate PES is associated with a larger uncertainty in the computed intensities. Even the best DMS will require a highly accurate PES (and vice versa). To achieve 0.1% uncertainty, further enhancements or refinements must be made upon *both* the PES and DMS.

The UCL DMS fitting accuracy (~2E-5 a.u.) might be a minor contributing factor. But its impact on the 3001*i* and 2001*i* band intensities has not been quantitatively evaluated through systematic studies, so it is largely unknown. A crosscheck with an Ames-2 + UCL DMS 2021 calculation could shed some light, but it cannot be done using our rovibrational program due to the dipole re-expansion incompatibility. On the other hand, *if* similar σ_{rms} = 5~7‰ uncertainties are still found with the UCL intensities computed with the Ames-2 PES, it would suggest most of the uncertainty originate from the UCL DMS 2015 or 2021, because no one would doubt the consistency of their DVR3D[59] calculations. In that case, we can run 4th – 8th order DMS fits over the 0 – 15,000 cm^{-1} range and track the "mean±σ" changes. This could provide some insights or quick answers.

To the right side of "Ames-2021 DMS" in Fig.3, one may notice a data point is missing between the "avtq5z40KF" and "avqz30KS-2013". That data point was the UCL DMS 2015 refit in the Ames style, with 8590 points from the 30KF grid: mean±σ_{rms} = 6.8±7.9‰ (4 bands) and 7.9±8.6‰ (5 bands). It is excluded because it does not belong to the Ames *ab initio* DMS series. Since 2016, it was already known that the UCL DMS refit is not the same UCL 2015 DMS, here it was just verified again. However, there is one thing worth reporting. During the refits, no matter how many points or coefficients or what energy cutoffs were used, it always ended up with a fitting error σ_{rms} ~1E-5 a.u.. This abnormal behavior of σ_{rms} has triggered a search for its root cause. In the end, this traced back to a constant "thetae_rad=3.141592d0" being used as π in the Fortran subroutine "CO2.Qz.DMS.f90" of UCL DMS 2015, which we received in 2016. After changing it from 3.141592 to *dacos*(-1.d0), the DMS refits yielded fitting σ_{rms} = 0.2E-8 a.u. up to 30,000 cm^{-1}, or 0.5E-8 a.u. up to 60,000 cm^{-1}. They are smaller than the last digit in the dipole data for the fit, which was only printed with 1E-8 precision. Such "perfect" fitting σ_{RMS} finally match the nature of refits: to re-expand a 4th-5th order polynomial fit with a 16th order polynomial. All the UCL line list calculations probably have been using the same thetae_rad value. But it is unclear if or how much it has contributed to the σ_{rms} uncertainties for S_{UCL296} and $S_{UCL2021}$ in Fig.3, not to mention if its impact on the 4 bands of the 3001*i* polyad has any recognizable pattern. However, this definition for π could be related to the noise peaks in the UCL-4000 line list,[50] see Section III.4.3.

III.2 Ames-2021 Intensity and DLR Experiment

III.2.1 S_{DLR}/S_{Ames} for 5 bands

Compared to the DLR Fourier-Transform InfraRed (FTIR) study in Birk et al[40], the Cavity Ring Down Spectroscopy (CRDS) measurements in NIST study for different bands and transitions were not simultaneously recorded. This may introduce additional relative errors among bands and lines. The uncertainty associated with the S_{DLR} intensity ratio between 30012 and 30013 bands was estimated to be on average less than 0.1%, or 1‰. The uncertainty associated with the $S_{DLR\text{-}HIT16}$ ratio between 30011 and 30014 bands was also estimated less than 0.1%. But it is always more appropriate for our analysis to use (weighted) average of ratios as reference, instead of ratios for single lines. It is necessary to investigate if noticeable discrepancies are found in the related intensity ratios.

Solid blue symbols in Fig.4 represent the S_{DLR}/S_{Ames} ratios in permille. S_{NIST}/S_{Ames} ratios are also included as open magenta symbols. DLR data has more distribution in the range of -7‰ ~ -4‰, compared to the NIST data scattered between -2‰ and +5‰. The weighted means (x_{wgt}) at the bottom are computed using available experimental data in the range *m*=-30~30. On average, S_{DLR} is 1.9‰ lower than S_{NIST} for 30013 band, 2.3‰ higher for 30014 band. The largest difference is on 30012 band, for which on average S_{DLR} is 5.2‰ lower than S_{NIST}. The DLR intensity ratio between 30012 and 30013 band is 3.34‰ lower than the ratio in NIST study, and it was consistent with the ratio in Toth et al (2008) FTIR study.[70] Because the FTIR ratio is expected to be more reliable, and the S_{DLR} vs S_{NIST} difference on 30013 band is less than 2‰, the absolute accuracy of S_{NIST}(30012) has been under further investigation.

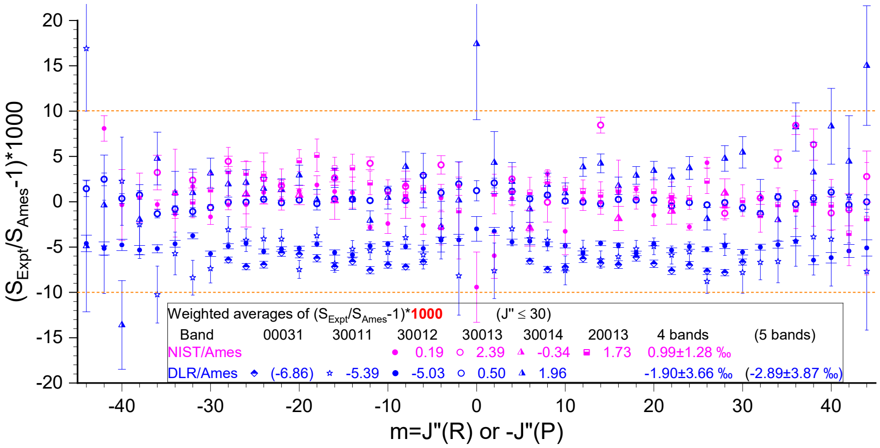

Figure 4. The NIST [Refs.36,38] and DLR (2021) [Ref.40] experiments vs. Ames-2021 theoretical IR intensities [this work] for the $^{12}C^{16}O_2$ 20013, 3001*i* and 00031 bands, with experimental uncertainties. The DLR data was downloaded from https://zenodo.org/record/6573418 on 05/23/2022. The $(S_{NIST}/S_{Ames}-1)\cdot 1000$ value at a specific *m* is averaged from multiple measurements with weights defined as the inversed squares of relative uncertainty. Additional 0.05% system uncertainty was included for the band specific mean±σ statistics of S_{NIST}/S_{Ames}. Please note the Y-scale is in thousandth, or permille.

Replacing 20013 band with 30011 band, the DLR based "mean±σ_{rms}" is -1.90±3.66‰ for the four 3001*i* bands, or -2.89±3.87‰ if 00031 band is also included. Compared to 0.99±1.28‰ in Fig.2b, the mean is doubled or tripled, and the σ_{rms} uncertainty is tripled.

From the perspective of theoretical calculation, both the mean deviations and the σ_{rms} uncertainty need to be minimized as much as possible – assuming the experimental data are correctly understood and appropriately employed. After acknowledging the S_{NIST} (30012) and $S_{NIST\text{-}HIT16}$ (30012) might be not as accurate as 0.1%, it is essential and obligatory to properly re-analyze existing data and Ames-2021 DMS related comparisons, otherwise there is no way to find the right path toward 0.1% uncertainty.

III.2.2 $S_{DLR\text{-}Ames}$ for 00031 band and 30011 band

In principle, the (theoretical) reference intensity to be scaled should have statistical uncertainty much smaller than that of direct measurements. For consistency, it should not have any obvious *J*-dependent deviations, or breaks. The intensity comparison and scaling factor determination for 00031-00001 and 30011-00001 bands have attracted extra attention. See Fig.5 for the differences between S_{Expt} and various line lists.

For 00031 band, the discrepancy between S_{HIT16} and S_{DLR} was already discussed in Birk et al.[40]. The S_{HIT16} data for this band was taken from CDSD database, which intensity model displayed wavenumber and *J* dependent deviations up to 4%. The S_{UCL} intensity[31] published in 2015 was found to match S_{DLR} excellently after multiplied by 1.122, with deviations less than 0.2%. See Fig.13 and Fig.14 of Ref.40. In the published DLR list, intensity of 50 weaker lines (< 3.2E-23 cm/molecule) used the scaled

S_{UCL} values. The HITRAN2020 update further adopted 1.122·S_{UCL} for the whole band, i.e., S_{HIT20} = 1.122·S_{UCL}. This is a good example for the reliability of intra-band relative intensity from high quality *ab initio* calculations.

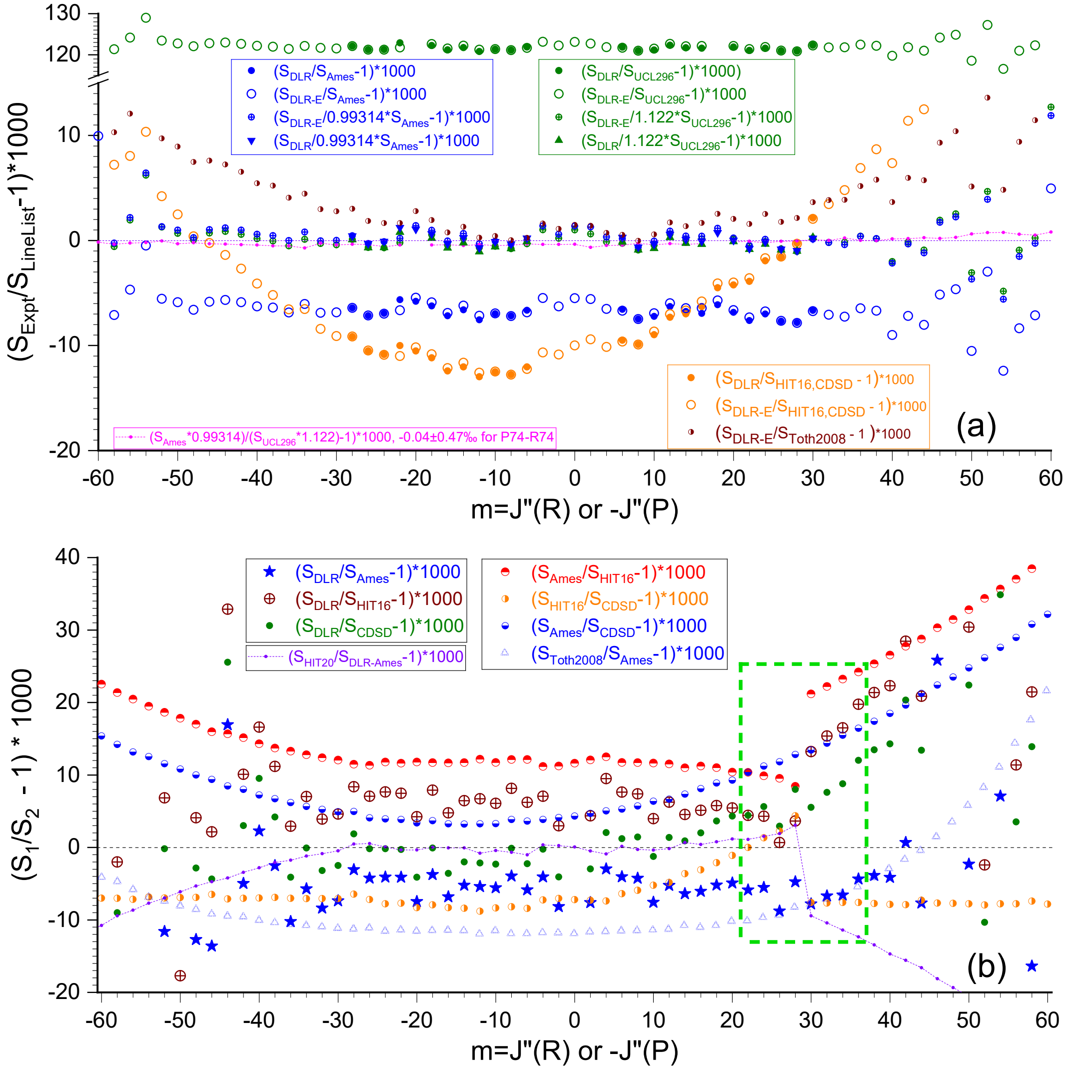

Figure 5. a) 00031 band (left) intensity comparison between S_{DLR}, S_{Ames}, S_{UCL}, $S_{DLR-UCL}$, and $S_{DLR-Ames}$; b) 30011 band (right) intensity comparison between S_{DLR}, S_{Ames}, S_{CDSD}, $S_{Toth2008}$, S_{HIT16} and S_{HIT20}.

In Fig.5a, the differences between DLR experiments and line lists are plotted along *m* coordinate. For the 25 stronger lines (Fig.4), there are two sets of S_{DLR} values. One is from DLR final line list (zenodo.org/record/6573418). The other was taken from an early release (zenodo.org/record/4525273), which reported measured intensities for all 75 lines in *P*74 – *R*74. They have very small differences due to an upgrade of line shape modeling. In Fig.5a, both sets are compared and reported for completeness. The second set is denoted S_{DLR-E}, which ratios are represented by open circles.

The S_{Expt}/S_{list} ratios are grouped in colors: blue for S_{Ames}, green for S_{UCL}, and orange for S_{HIT16} (S_{CDSD}). From *m*=-50 to *m*=40, the S_{DLR-E}/S_{Ames} and S_{DLR-E}/S_{UCL} are parallel to each other, suggesting consistency between the two *ab initio* calculations using different PES and DMS. But S_{Ames} can directly match S_{DLR} to better than 1% (i.e., ~7 permille) without scaling. This is a remarkable improvement in the prediction accuracy over both S_{UCL} and S_{Ames2016}. The $S_{\mathrm{DLR}}/S_{\mathrm{Ames2016}}$ ratios are +20‰ for whole range, or +43‰ (*P* branch) and -0.4‰ (*R* branch) before the *P-R* gap was fixed. They are truly beyond the range of Fig.5a. As S_{Toth2008} and S_{DLR} agree on this band to better than 1.5‰, it is reasonable to claim Ames-2021 DMS have successfully reduced nearly 2/3 of the DMS-N2 intensity deviations for 00031 band. Both $S_{\mathrm{Ames\text{-}2016}}$ and S_{Ames} used the Ames-2 PES.

With the weighted mean (x_{wgt}) ready, corresponding scaling factors may be computed as

$$\beta_{\mathrm{Expt\text{-}Ames}} = 1 + x_{\mathrm{wgt}} / 1000,$$

and

$$S_{\mathrm{DLR\text{-}Ames}} = \beta_{\mathrm{DLR\text{-}Ames}} \cdot S_{\mathrm{Ames}}, \text{ or } S_{\mathrm{NIST\text{-}Ames}} = \beta_{\mathrm{NIST\text{-}Ames}} \cdot S_{\mathrm{Ames}}.$$

The x_{wgt} (00031) in Fig.4 is -6.86‰, so $\beta_{\mathrm{DLR\text{-}Ames}} = 0.99314$. The differences between $S_{\mathrm{NIST\text{-}UCL}}$ and $S_{\mathrm{DLR\text{-}Ames}}$ (i.e., $\beta_{\mathrm{DLR\text{-}Ames}} \cdot S_{\mathrm{Ames}}$) have "mean±$\sigma_{\mathrm{rms}}$" = -0.04±0.47‰, as shown by the magenta dots connected through dashed lines. Table 4 summarizes the statistical difference between S_{Ames}, scaled S_{HIT16} (or S_{UCL}), and S_{Toth2008} intensities, including both 'mean' and 'σ_{rms}'. The $S_{\mathrm{Toth2008}}/S_{\mathrm{Ames}}$ column has σ_{rms} as large as 1~2‰. It is mainly resulted from the *J*-dependent deviations of experiment-based models. For example, in Fig.5a, the half-filled brown circles for 00031 band rise by 10-15‰ from *J*=0 to *J*=60.

Table 4. Statistical difference between S_{Toth2008}, scaled $S_{\mathrm{UCL/HIT16}}$, scaled S_{Ames}, and S_{Ames} for 3001*i* and 00031 bands, $|m| \leq 30$.

Band (*m*=-30~30)	Mean ± σ for ($S_{\mathbf{NIST\text{-}HIT16}}$[a]/$S_{\mathrm{Ames}}$-1) ×1000	Mean ± σ for ($S_{\mathbf{DLR\text{-}HIT16}}$[b]/$S_{\mathrm{Ames}}$-1) ×1000	Mean ± σ for ($S_{\mathbf{Toth2008}}$/S_{Ames}-1) ×1000	δE (Ames-Expt) R18 (cm^{-1})
00031-00001		-6.72 ± 0.27 [c]→ **-6.86** [d]	-8.11 ± 0.96	-0.0166
30011-00001		-5.17 ± 1.92 → **-5.39** [e]	-11.11 ± 1.02	-0.0149
30012-00001	0.34 ± 0.28	-5.00 ± 0.28	-9.32 ± 0.43	-0.0201
30013-00001	2.04 ± 0.22	0.36 ± 0.22	-3.89 ± 0.62	-0.0041
30014-00001	-0.46 ± 0.23	2.44 ± 0.23	0.20 ± 2.04	-0.0004

[a] S_{HIT16} scaled by $\beta_{\mathrm{NIST\text{-}HIT16}}$ values reported in Ref.38; [b] S_{HIT16} scaled by $\beta_{\mathrm{DLR\text{-}HIT16}}$ values reported in Table 8 of Ref.40;
[c] $S_{\mathrm{DLR\text{-}UCL}}$ was used for 00031 band, as reported in Ref.40;
[d] Use $S_{\mathrm{DLR\text{-}Ames}}$ instead of $S_{\mathrm{DLR\text{-}UCL}}$, see text for details; [e] Use $S_{\mathrm{DLR\text{-}Ames}}$ instead of $S_{\mathrm{DLR\text{-}HIT16}}$, see text for details.

Ideally, the difference between (scaled) S_{Ames} and (scaled) S_{UCL} intensities should be highly systematic with negligible σ_{rms}. For example, the σ_{rms} = 0.22-0.28‰ of 30012 – 30014 bands reflect the precision loss in S_{UCL} data using 4 significant figures, while S_{Ames} uses 7 figures. In contrast, σ_{rms}= 0.47‰ for 00031 band is 70-100% larger, indicating the systematic difference between S_{UCL} and S_{Ames} has a minor *J*-dependence. It is unclear if there is any connection to the 12% deviation of S_{UCL}. For higher chance of accuracy, this study recommends $S_{\mathrm{DLR\text{-}Ames}}$ (00031) for future updates.

For 30011-00001 band The S_{DLR}/S_{HIT16} analysis in Birk et al[40] reported a weighted average ratio, 1.00643. Later HITRAN2020 update[41] used 1.0061 for the scaling, i.e., $S_{HIT20}=S_{DLR\text{-}HIT16} = 1.0061 \cdot S_{HIT16}$. Unlike 00031-00001 band, its S_{HIT16} data was taken from UCL-296 list,[31] not CDSD-296.[16]

There are 8 sets of intensity differences in Fig.5b. In addition to S_{DLR} experiment data, five line lists are compared: S_{HIT16}, S_{HIT20}, $S_{Toth2008}$, S_{CDSD}, and S_{Ames}. In the range $|m| < 45$, most data are distributed in the range -10 ~ 30‰. But in Table 4, the σ_{rms} ($S_{DLR\text{-}HIT16}/S_{Ames}$) for $|m|\leq30$ is four times as large as that in 00031 band. In the square of green dashed lines, all four ratios of S_{HIT16} and S_{HIT20} have a discontinuity of 1.2% at *R*30. Other ratios do not have such a problem. This means the S_{HIT16} data is the source of anomaly.

In Zak et al (2015),[31] 30011-00011 was a sensitive band with scatter factor $\rho = 2.6$. There were 24 lines belonged to "intermediate" level, while the UCL-296 list still reported *ab initio* intensities. The HITRAN2016 list inherited $S_{HITRAN2012}$ intensity (not CDSD-296 2015) for all 91 lines from *P*90 to *R*90. Note the CDSD databases do not have such discontinuity. The $S_{HITRAN2012}$ discontinuity was first introduced by adopting $S_{Toth2008}$ for *P*6-*P*28 and *R*6-*R*28 lines, and an earlier S_{CDSD} for other lines. Then it transferred into HITRAN2016 and HITRAN2020. It also contaminated the scaling factor calculation for S_{DLR}. In short, the quality of scaling factor and S_{HIT20} data does not match the accuracy of S_{DLR} study. Recommend to re-run the analysis for $\beta_{DLR\text{-}Ames}$ and re-compute the best estimate for HITRAN2020:

new S_{HIT20} (30011) = $S_{DLR\text{-}Ames} = \beta_{DLR\text{-}Ames} \cdot S_{Ames} = 0.99461 \cdot S_{Ames}$

This will fix the S_{HIT20} intensity deviations beyond *m*=-30~12, as illustrated in Fig.5b by purple dots connected through dashed lines.

The ratio between original ab initio UCL-296 intensity and HITRAN2012 was ~1.05, as shown in Fig.9 of Zak et al[31]. It is approximately 4.8% higher than S_{DLR} and $S_{DLR\text{-}Ames}$. The corresponding "mean±σ" of UCL 2015 *ab initio* intensities should be 1.6±2.1%, with respect to $S_{DLR\text{-}HIT16}$ for 30012-30014 bands and $S_{DLR\text{-}Ames}$ for 30011 band. The UCL 2021 DMS update [private communication] has reduced the prediction deviation of 30011 band from 4.8% to 3.1%, and reduced the "mean±σ" of 3001*i* bands to 1.0±1.4%.

In contrast, the DMS-N2 based $S_{Ames\text{-}2016}$ prediction for 30011 band (with *P-R* gap fixed) is lower than $S_{DLR\text{-}Ames}$ by less than half percent, or more precisely, -3.8‰. For four 3001*i* bands, the 'mean±σ' of $S_{Ames\text{-}2016}$ weighted means (x_{wgt}) is -5.3±2.4‰. The Ames-2021 DMS raised the S(30011) prediction by 9.2‰, now it is +5.4‰ higher than $S_{DLR\text{-}Ames}$ (Table 4). The 'mean±σ' of averaged x_{wgt} becomes 1.9±3.7‰, see Fig.4 and Table 5. This +7.2‰ change of 'mean' roughly agrees with the +6.0‰ increment in Fig.3

statistics for 20013 and 30012/3/4 bands, from -6.82‰ to -0.85‰, while the $S_{\mathrm{NIST\text{-}HIT16}}$ may need improvement on 30012 and 30013 bands.

The deviation analysis for 30011 and 00031 bands further supports the claim that the Ames-1 PES deficiency is the primary source of the S_{UCL} uncertainty.

III.2.3 Table and Figure Summary of Agreements

After the statistical mean values in Fig.4 have been explained, it is time to focus on the agreement indicator, mean = 1.9‰, and uncertainty indicator, σ = 3.7‰, for four 3001*i* bands. The σ uncertainty is not only three times larger than the σ = 0.99 in S_{NIST} based statistics (Fig.2), also 50% larger than the DMS-N2 based σ = 2.40‰ for the same group of 3001*i* bands. Table 5 and Fig.6 are prepared to facilitate the analysis coming next. Table 5 summarized the weighted means determined from $S_{\mathrm{Expt}}/S_{\mathrm{HIT16}}$ and $S_{\mathrm{Expt}}/S_{\mathrm{Ames}}$ differences, or x_{wgt}, in permille. These ratios can be used to derive $\beta_{\mathrm{Expt\text{-}Ames}}$ for intensity scaling. If there are two means in a cell, the bottom one should be used.

Table 5. Weighted average, or "mean", of the relative intensity differences $(S_1/S_2-1)\cdot 1000$‰ for 6 bands measured in NIST and DLR studies. In parentheses are the numbers of corresponding transitions. Statistics for a row is given in first column, as 'mean±σ'. All values are in permille (‰).

Band mean for |m|≤30^{a}	**00031**	**30011**	**30012**	**30013**	**30014**	**20013**
$S_{\mathrm{NIST}}/S_{\mathrm{HIT16}}$ -0.76±7.29‰ (4 bands)			-10.44 (35) -10.39 (29)	0.73 (24) 0.67 (12)	-0.58 (8)	6.99 (39) 7.27 (30)
$S_{\mathrm{DLR}}/S_{\mathrm{HIT16}}$ -2.29±9.35‰ (4 bands) -3.08±8.29‰ (5 bands)	-6.27 (75)^{b} -8.21 (25)	6.36^{c} (59) 5.90 (31)	-15.65 (69) -15.61 (31)	-1.34 (70) -1.23 (31)	1.75 (62) 1.77 (31)	
$S_{\mathrm{NIST}}/S_{\mathrm{Ames}}$ 0.99±1.28‰ (4 bands)			0.25 (35) 0.19 (29)	2.51 (24) 2.39 (12)	-0.34 (8)	1.47 (39) 1.73 (30)
$S_{\mathrm{DLR}}/S_{\mathrm{Ames}}$ **-1.90±3.66‰ (4 bands)** **-2.89±3.87‰ (5 bands)**	-6.61 (75)^{b} **-6.86** (25)	-5.42 (59) **-5.39** (31)	-5.01 (69) -5.03 (31)	0.43 (70) 0.50 (31)	1.94 (62) 1.96 (31)	
$S_{\mathrm{Toth2008}}{}^{d}/S_{\mathrm{Ames}}$		-11.11 (31)	-9.32 (31)	-3.89 (31)	0.20 (11)	

[a] weighted averages from 25 or 8 lines of 00031 (DLR) or 30014 (NIST) bands are included in the mean±σ calc.

[b] $S_{\mathrm{DLR\text{-}E}}$ based means for *P*74-*R*74. The mean±σ for $S_{\mathrm{DLR\text{-}E}}/S_{\mathrm{HIT16}}$ = 6.27±7.37‰, so the S_{CDSD} based S_{HIT16} not suitable for scaling. Mean±σ for $S_{\mathrm{DLR\text{-}E}}/S_{\mathrm{Ames}}$ = -6.61±0.11‰. The mean for $S_{\mathrm{DLR}}/S_{\mathrm{UCL}}$ (00031) = 122‰ (see Fig.5a).

[c] HITRAN2016 intensity data for 30011 band has a discontinuity at R30, not suitable for scaling, see text for details.

[d] Toth et al (2008)[70] data were fitted from measured intensities. S_{NIST} and S_{DLR} are pre-fit measurements.

Fig.6 follows the style of Fig.3 to track the progression of mean and σ in Ames DMS series, using R12 and R18 intensity to measure their agreement with the scaled $S_{\mathrm{DLR\text{-}HIT16}}$ for 3001*i* bands (*i*=2-4), and the scaled $S_{\mathrm{DLR\text{-}Ames}}$ for 30011 band. Several DMS are explicitly marked, along with UCL estimates. All the Ames red dots are still within ±10‰, and their distribution look similar with Fig.3.

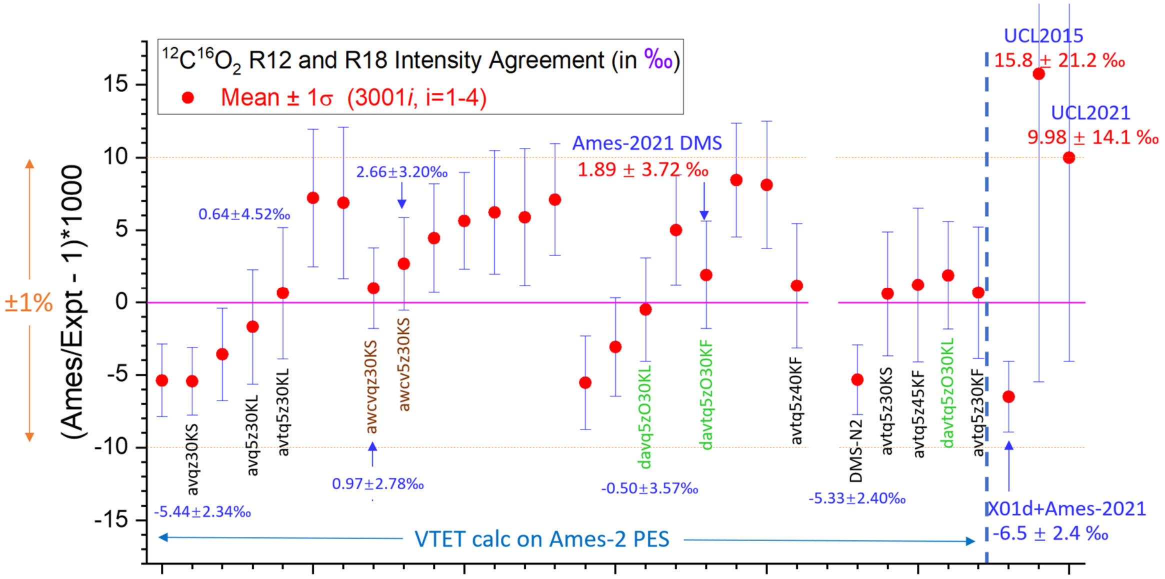

Figure 6. "Calc" vs "Expt" intensity agreement for selected Ames DMS fits, including Ames-2021. $S_{'Expt'}$ uses $S_{DLR\text{-}HIT16}$ for 30012/3/4 bands, and $S_{DLR\text{-}Ames}$ for 30011 band. See Fig.3 for the notation details.

III.2.4 Perspective from Theoretical Calculations

Accurate IR intensity calculations require both accurate PES and accurate DMS. Efforts should be devoted to overall improvements of potential energy surfaces and dipole moment surfaces, not just focusing on those experimental bands that have been measured with high accuracy. They are valuable reference providing constraints and anchors. Whatever approaches are adopted, they should bring in physically meaningful, or at least reasonable and systematic tunning upon hundreds of vibrational band series. In Ames DMS series shown in Fig.3, examples of global improvement trials include using more complete geometry set, extrapolating to complete basis set limit, adding core-correlation corrections, etc.. Systematic changes caused by these improvements have been demonstrated in Fig.3 and Fig.6. Future efforts may include re-fitting DMS with different basis, reducing fitting deviations, extending to higher energies, introducing nonadiabatic and higher order terms, etc. It is not considered worthwhile to do band-specific adjustments.

Rounds of global PES or DMS improvements will gradually reduce the overall deviations, finally reaching consistent and satisfactory agreements for the whole line list including thousands of bands. However, due to different level of error cancellations and vibration dependent accuracy, the claims "better PES ↔ more accurate line position ↔ more accurate intensity" and "better DMS ↔ more accurate intensity" are statistically correct only for overall improvements, not for *every* band(s) or transition(s). The impact on a specific band or transition may be either positive or negative, depending on the vibrational band, the isotopologue, the perturbation, as well as the accuracy of existing line list, etc. This means it also strongly relies on the original PES and DMS used in the calculation. Previous upgrades and tests have demonstrated this is particularly true if existing calculation for a band have reached ~0.01 cm^{-1} accuracy for line position, or within 5-10‰ (0.5-1.0%) of exact line intensity. In those regimes, it is very difficult to predict the *direction* of intensity change associated with more accurate line position for a specific band or transition, and even harder for magnitude.

The Ames and UCL DMS upgrades are good examples. Using $S_{\text{NIST-HIT16}}$ as reference, all the ($S_{\text{calc}}/S_{\text{Expt}}$ – 1) deviations of 30012-30014 and 20012-20013 bands were reduced from (-8,-9,-5,-7,-6)‰ in the corrected Ames-2016 list to (0,2,0,3,-1)‰ in the Ames-2021 list, respectively. From UCL-296 (2015) to UCL 2021 update, corresponding deviations change from (10,0,0,-4,-7)‰ to (6,-2,1,-6,-7)‰, respectively. Only 30012 band deviation were reduced, and #reduced : #increased = 1:3. Using $S_{\text{DLR-HIT16}}$ and $S_{\text{DLR-Ames}}$ as reference, the deviations for 30011-30014 bands changed from (-4,-2,-7,-8)‰ in the corrected Ames-2016 list to (5,5,0,-3)‰ in the Ames-2021 list, with #reduced : #increased = 2:2. From UCL-296 (2015) to UCL 2021 update, corresponding deviations changed from (46,16,2,-2)‰ to (31,11,0,-2)‰, with #reduced : #increased=2:1. These numbers show the UCL DMS 2021 update mainly reduced the intensities of 30011 and 30012 bands by 15‰ and 5‰, while the Ames-2021 DMS update has raised every band intensities by 5-11‰. Note the Ames-2021 reduced 00031 deviations from -20‰ to +7‰, i.e., +27‰ increase of band intensity.

Interested readers can compare these agreement (or disagreement) variations with corresponding band origin or line position deviations, such as those listed in Table 4, then further consider the PES improvement[18] from Ames-1 (UCL-296 and UCL 2021) to Ames-2 (Ames-2016 and Ames-2021). They may better understand why in Ames and UCL lists there does not exist any explicit relations between rovibrational energy accuracy and line intensity agreement. The last 0.5-1.0% will be much more difficult to accomplish than the first 99%, because PES deficiencies and DMS defects are interwoven together in these high quality semi-empirical line lists. They cannot be separated from each other, but can be reduced or minimized through cycles of global PES and DMS enhancements, step by step. After Ames-2021 DMS, next upgrade will be Ames-3 PES refinement. It has been planned to extend the 0.01-0.02 cm^{-1} accuracy to higher energy states and new bands by utilizing recent studies and the CDSD experiment data collection.

Reversely, similar analyses still apply when more reliable or more accurate experimental intensity becomes available. Within the proximity of ±5-10‰, it is not defying expectation for a better dipole surface to have relatively larger deviations, either statistically or for a single band. From Fig.3 to Fig.6, all the red dots of Ames pure *ab initio* DMS series are shifted up by 1.29‰ – 3.75‰, with statistical magnitude 2.62 ± 0.66 ‰ for 27 dipole surfaces. Now in Fig.6, the red dots of 10 out of 27 Ames DMSs fall within ±2‰. Four dots are within ±0.7‰, and three of them are avtq5z30K based: avtq5z30KL (0.64‰), avtq5z30KS (0.59‰), avtq5z30KF (0.67‰), plus davq5zO30KL (-0.50‰). The Ames-2021

DMS (davtq5zO30KF) is at 1.89‰, which is 1.2-1.3‰ higher than avtq5z30K dots, or 2.5‰ higher than the davq5zO dot. However, the doubly augmented basis for O atom is an advantage, not a drawback or weakness. The 'tq5z' three-point extrapolation is also generally considered more reliable than the 'q5z' two-point extrapolation. It is not a wise move to change the Ames-2021 DMS choice based on this 1.2~2.5‰ difference found on the mean deviations. The excluded core-correlation effects are similar in both plots.

Is the σ uncertainty good for DMS screening? Obviously not, either. From Fig.3 to Fig.6, along with the mean shifts, the σ uncertainty of every red dot for Ames DMS series have also increased by 0.82‰ – 3.82‰, with statistical magnitude 2.50 ± 0.80 ‰. In Fig.6, the σ distribution has a much wider range, i.e., 3‰ from 2.34‰ to 5.30‰ vs. 0.61‰ from 1.03‰ to 1.64‰ in Fig.3. In Fig.6, the smallest σ uncertainties are found in avqz based DMS series: avqz30KS (2.33‰), avqz30KL (2.50‰), and DMS-N2 (2.40‰). Obvious, the avqz DMSs are not matches for Ames-2021, as exemplified earlier.

Note that the awcvqz30KS DMS has maintained its ranking in DLR study based Fig.6. With (2,5,-1,-2)‰ deviations for 3001*i* bands, it seems like a better choice, with mean±σ = 0.97±2.78‰, vs 1.89 ± 3.72 ‰ for Ames-2021. As explained in section III.1, such agreement may be attributed to the error cancellation at QZ level, while the Ames-2021 DMS is more complete in coverage, and expected to be more reliable in higher energy region. This DMS will be monitored in future updates.

In section III.1, it was pointed out that a less accurate PES may relate to larger σ uncertainty, where the X01d PES + Ames-2021 DMS had a σ uncertainty as large as 4.0‰, vs $\sigma_{\max}$ = 1.64‰ in other red dots for Ames DMS series. This connection may be statistically correct, but it does not fit all the data in Fig.6. The UCL-296 (2015) and UCL 2021 were based on the less accurate Ames-1 PES, which might be related to the 3-4% deviation for 30011 band intensity. As a result, both UCL uncertainties are more than 10‰, and they are 4-5 times as large as that of Ames-2021. This is consistent with Fig.3. However, the X01d PES + Ames-2021 DMS has (-4,-5,-8,-9)‰ deviations for 3001*i* bands, leading to mean±σ = -6.51±2.44‰. It is one of the smallest σ in Fig.6, resulted from the unique σ reduction vs the σ increments of Ames-2 based tests. Undeniably, the σ outlier of X01d PES is accidental. This is an extreme example of the PES dependence in accuracy comparisons.

The simultaneous measurements over the full spectra range in FTIR studies can provide additional checks for DMS: two ratios, r_{23} = S(30012)/S(30013), and r_{14} = S(30011)/S(30014). They were estimated to be better than 0.1% in DLR study. Using DLR ratios as reference, the r_{23} and r_{14} differences and their average are computed for 27 Ames *ab initio* DMSs, and summarized below.

(in ‰)	δr_{23}	δr_{14}	$(\delta r_{23}+\delta r_{14})/2$
$\delta_{\min}$	4.47	3.34	4.04

δ_{max}	7.63	11.79	9.71
mean±σ	6.03±0.85	7.94±2.22	6.98±1.49
Ames-2021	5.67	7.96	6.82
Toth-2008	*0.08*	*–4.00*	*-1.96*

All the δr_{23} and δr_{14} are positive, and Ames ratios are higher by 3-4‰ at least. These are above the uncertainty range of DLR data, suggesting the existence of unknown systematic deviations in Ames intensity calculations. Accidentally, again, the minimum δr_{23} and δr_{14} differences are found on DMS-N2 and avqz30KS, respectively. The minimum of averaged differences is also found at avqz30KS. The X01d+Ames-2021 intensity has the smallest r_{23} deviation 3.12‰. Therefore, the two intensity ratios are not ready for DMS screening yet. The two sets of UCL intensity suffer from larger deviations on 30011 and 30012, with (δr_{23}, δr_{14}) reduced from (14‰, 48‰) to (11‰, 33‰). It is noted the δr_{23} of $S_{Toth2008}$ is less than 0.1‰, so in nearly perfect agreement with DLR, while it δr_{14} is 0.4% lower because its 30011 band intensity is half percent lower. See the separation between blue stars and open triangles in Fig.5b.

All analysis above supports keeping the Ames-2021 DMS choice on davtq5zO30KF, which was accurately fitted from *ab initio* dipoles computed on the most complete geometry grid up to 30,000 cm^{-1}, including 3-point extrapolation to CBS limit, 2nd diffuse function on O atoms, and excluding core-correlation to avoid intensity overestimation. It is undeniably a major boost for CO_2 semi-empirical line intensity.

Why are the Ames-2021 line list intensities still 2±4‰ different from the DLR experiments? The most probable answer is rather simple: it is the potential energy surface. Analysis in both NIST and DLR sections suggest relation between the less accurate Ames-1 PES and the larger S_{UCL} uncertainty. Although Ames-2 PES is the best available potential for the electronic ground state of CO_2 monomer, it still has a lot of room for improvement. The Ames-2016 paper[18] reported how a 0.02 cm^{-1} difference in the 30013 band was associated with a 0.5% intensity difference. In Table 4, the current $|\delta E|_{Ames-Expt}$ for the 30011 and 30012 bands are in the range of -0.015 ~ -0.021 cm^{-1}, larger than the $|\delta E|$ for the 30013 and 30014 bands, 0.0004~0.004 cm^{-1}. They might partially contributed to the S_{DLR}/S_{Ames} ratio spreading in Fig.4. Therefore, one direction of theoretical efforts is to get a new PES refinement which has consistent δE = 0.000 – 0.005 cm^{-1} for all four 3001*i* bands and three 2001*i* bands, plus their neighboring states and states below. The uniformly positive δr_{23} and δr_{14} suggest the PES deficiency is inclined to slightly overestimate the C-O stretch related band intensity, because the S_{UCL} and S_{Ames} agreements are much better on the other half 3001*i* polyad. If this is the case, S_{Ames} might have similar overestimation for the 20011 band of 2001*i* polyad. Recommend 20011 band for high accuracy CRDS and FTIR studies.

A short-term target of CO_2 PES and DMS improvements is to fully establish the consistencies among isotopologues, intra-polyad bands, and inter-polyad bands, as good as predicted by quantum rovibrational calculation within the Born-Oppenheimer Approximation frame. For example, the intensity deviations of 3001i bands are expected to follow roughly linear relation from 30011 to 30014, unless they are clustered in a narrow range such as the $S_{Ames}/S_{NIST\text{-}HIT16}$ lines in Fig.2a. From Fig.4 to Table 4 and Table 5, both $S_{DLR\text{-}Ames}/S_{Ames}$ and $S_{Toth2008}/S_{Ames}$ differences change monotonically, but their differences on 30011 and 30012 bands are close to each other. This may hint at the intra-polyad consistency has been partially established. Similarly, for an unperturbed band, the intensity deviation of 627 isotopologue should be found between those of 626 and 628 isotopologues. This is the isotopologue consistency investigated by Huang et al (2016)[18] and (2019).[29] Inter-polyad consistency is relatively more difficult to achieve, e.g., estimating the intensity agreement on 20011 band using the differences on 30011 band. One example is the $S_{NIST\text{-}HIT16}/S_{Ames}$ ratio for 20013 band and $S_{DLR\text{-}HIT16}/S_{Ames}$ ratio for 30014 band agree to within 1.5‰. The narrow σ range for different DMS fits in Fig.3 and Fig.6 is another type of such consistency. At this moment, no experimental intensity data signified the need for nonadiabatic or relativistic corrections for CO_2 intensity, but these options are open for future PES and DMS updates.

The averaged 'mean' and uncertainty (or variance) σ of S_{Expt}/S_{UCL} differences increased significantly from -0.63±4.96‰ (NIST) to 9.98±14.1‰ (DLR). It will have negative impact on the S_{UCL} uncertainty estimate for the VPDB $^{13}C/^{12}C$ ratio determination.[39] But the impact will not be too large, because the 30011 band was excluded from related NIST experiment and uncertainty analysis.

III.2.5 Need More High Accuracy Experiments

Thanks to both the NIST and DLR groups for their high-quality work. Combining their studies together, finally it is confident to assert that Ames-2021 intensities have achieved sub-percent accuracy for major bands below 8000 cm^{-1}. The S_{Ames} accuracy for several strong bands has reached sub-half-percent level including both mean and uncertainty, and is moving toward 0.1%, or 1‰.

However, the number of experimental IR studies suitable for such high accuracy analysis and comparison is still very limited. They are only good for sub-percent accuracy check on several strong bands in selected spectra ranges, far from any full-range estimation. Hope more studies can be carried out for other strong to moderate bands below 7000 cm^{-1}, then extended to higher wavenumber range and sensitive bands under 7000 cm^{-1}. Those studies may provide accurate constraints for PES and DMS improvements, and critical anchors for theoretical calculation based conjectures or speculations.

The DLR FTIR study[40] was reported with 1.5‰ uncertainty for the absolute intensity of 3001i and 00031 bands. Accordingly, differences below 1-1.5‰ are not specifically discussed. On the other hand, the scattering in its $^{13}C^{16}O_2$ intensities was too large for a permille level analysis. Even larger scattering was found for even fewer $^{17/18}O^{12}C^{16}O$ isotopologue lines. Therefore, the S_{Ames} vs S_{DLR} comparison has been restricted to $^{12}C^{16}O_2$, but the S_{Ames} data for the 2001i and 3001i bands are provided in supplementary files for the 626, 636, 628 and 627 isotopologues.

A potential upgrade to NIST and DLR studies is to extend the 0.6-1.5‰ accuracy to complete 2001i + 3001i series and the hot band series rising from ν_2 fundamental, e.g., 2111i-01101. Another interesting option is to measure the 2001i, 3001i and 00031 bands for the ^{13}C isotopologue, 636. The isotope effects on resonance polyad intensities follow mass-dependent relations, but they can be surprisingly large.[18,29] For example, the intensity ratio between the 20011 and 20013 bands are reversed upon ^{13}C substitution, i.e., 1:1.5 (626) → 1.5:1 (636). The intensity ratio between the 30012 and 30013 bands also shifts from 1:1 (626) to 1:2.5~3 (636), as shown in Fig.9 of Huang et al.[29] If these 636 bands can be determined with similar accuracy, it may also help elucidate some basic questions on isotopologue consistency, including cross-band and cross-isotopologue consistency. It is one of those factors that may affect the VPDB $^{13}C/^{12}C$ ratio studies[39], to be discussed in the next section.

III.3. New VPDB $^{13}C/^{12}C$ ratio based on S_{NIST}, S_{DLR}, and $S_{Ames\text{-}2021}$

Fleisher et al[39] reported a precise value for the $^{13}C/^{12}C$ ratio, $R(^{13}C/^{12}C)_{VPDB} = 0.011125 \pm 43$. It was derived from high accuracy Cavity Ring-Down spectroscopy. Temperature biases were effectively eliminated by measuring the R18 transitions of $^{13}C^{16}O_2$ (20011 band, 5004.84 cm^{-1}) and $^{12}C^{16}O_2$ (30012 band, 6361.25 cm^{-1}). Their work combined the measured intensities with mole fractions determined by state-of-the-art isotope ratio mass spectroscopy (IRMS), and the theoretical UCL intensity computed on the updated UCL DMS (2021). Our interest is primarily on the impact of the theoretical reference intensity data adopted in the study, and trying to improve it using the latest $S_{Ames\text{-}2021}$, i.e., S_{Ames}.

In Table 1 of Fleisher et al[39], the updated S_{UCL} intensity for $^{13}C^{16}O_2$ had a relative standard uncertainty of 0.38%. It was improved from 0.50% of the old S_{UCL296}[27,31] computed using the UCL DMS 2015.[34] Compared to other uncertainty factors listed in that table, it contributed more than 90% of the combined standard uncertainty u=43×10^{-6}. The 0.38% uncertainty was determined and transferred from the $^{12}C^{16}O_2$ analysis on the R12e of five bands: 20012, 20013, 30012, 30013 and 30014. The 30011 and 00031 bands are not included. The center of the 5 intensity differences, $(S_{NIST\text{-}HIT16}/S_{UCL2021}-1)\times 1000$, was close to 1. Then the half-width of the deviation range was divided by square root of 3 to get the 0.38% uncertainty estimate, assuming a uniform distribution for the errors.[39] In principle, more accurate *ab initio* intensities may help reduce the S_{exp}/S_{theory} differences, and reduce the final combined uncertainty u for the VPDB $^{13}C/^{12}C$ ratio.

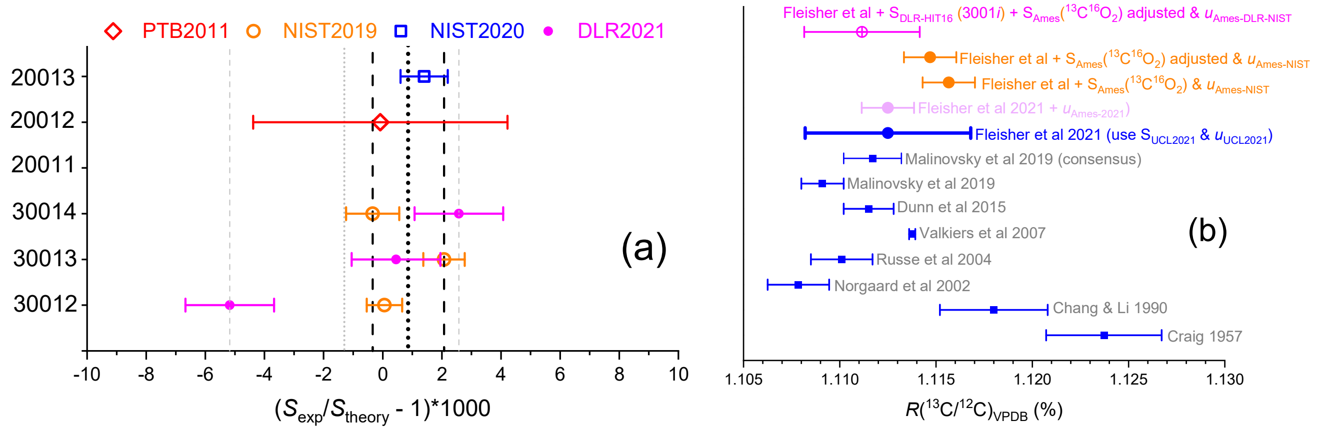

Figure 7. (a) New uncertainty estimate using $S_{Ames2021}$ (theory) with respect to experiment (exp) based intensity data: $S_{DLR-HIT16}$ (DLR 2021)[40] and those cited in Fleisher et al[39], including PTB2011[61] and $S_{NIST-HIT16}$ from NIST2019[38] and NIST2020[36]. Thick black lines are from the $S_{PTB,NIST-HIT16}/S_{Ames2021}$ differences, and light grey lines are from the $S_{PTB,DLR-HIT16,NIST-HIT16}/S_{Ames2021}$ differences. The figure follows the style of Fig.S1 in Fleisher et al.[39] (b) New $^{13}C/^{12}C$ ratios derived with $S_{NIST-HIT16}$, $S_{DLR-HIT16}$ (for $^{12}C^{16}O_2$ 3001i bands) and $S_{Ames-2021}$ (for $^{13/12}C^{16}O_2$), compared to Fleisher et al value and other reference values cited in Fleisher et al. The figure follows the style of Fig.3c in Fleisher et al.[39] See text for details.

Fig.2 and Fig.3 reported the -1±1‰ agreement between $S_{NIST-HIT16}$ and S_{Ames}. Applying the uncertainty procedure in Fig.7a, the S_{exp}/S_{Ames} differences are centered at +0.87‰. The S_{Ames} uncertainty is estimated to be 0.84‰. The new combined standard uncertainty $u = 1.22‰ \times 0.0111 = 14\times10^{-6}$. This is a 2/3 reduction from the published uncertainty, $u = 43\times10^{-6}$.[39] See the light magenta point in Fig.7b.

A reason for Fleisher et al[39] to utilize the UCL theoretical intensity was: the experimental IR intensity of $^{\mathbf{13}}CO_2$ 20011 R18e has not been determined with similar uncertainty, i.e., ~1‰. In Table S1 of Fleisher et al,[39] $S_{NIST-HIT16} = 1.7497\times10^{-23}$ for $^{12}C^{16}O_2$ 30012 R18e, and $S_{UCL2021} = 7.012\times10^{-22}$ for $^{13}C^{16}O_2$ 20011 R18e. The ratio of these two values was directly used to compute the VPDB $^{13}C/^{12}C$ ratio. Because the "Ames-2 PES + Ames-2021 DMS" based S_{Ames} is a significant improvement for $^{12}C^{16}O_2$ over the $S_{Ames2016}$, S_{UCL296}, and recent $S_{UCL2021}$ update, the S_{Ames} value for the $^{13}C^{16}O_2$ R18e transition is expected more accurate and should lead to a more reliable $^{13}C/^{12}C$ ratio.

The Ames-2021 list for $^{13}C^{16}O_2$ has the 20011 R18e transition at 5004.8589 cm^{-1}, which is +0.0164 cm^{-1} higher than the experimental line position at 5004.8425 cm^{-1}. At 296K, $S_{Ames} = 6.99214\times10^{-22}$ cm/molecule, which is less than $S_{UCL2021}$ by 2.83‰. Accordingly, the $^{13}C/^{12}C$ ratio would be shifted to the higher side by 2.84‰, i.e., from $R = 0.011125\pm14$ to $R = 0.011157\pm14$. Because the u is reduced by 2/3, the uncertainty range of the shifted $^{13}C/^{12}C$ ratio is still within the range of Fleisher et al.[39] See the lower orange point in Fig.7b. Assume the S_{Ames} for $^{13}C^{16}O_2$ should be adjusted by +0.87‰ first – which was the center of errors in Fig.7a, the ratio will rise by 1.97‰ to 0.011147±14. See the other orange point in Fig.7b. Use the R12e intensity differences for analysis, the results are similar: +0.0171 cm^{-1}, 6.83898E-22 vs 6.859E-22, +2.93‰ or +2.06‰ (with +0.87‰ correction), and $R(^{13}C/^{12}C)$= 0.011148±14.

Since the FTIR band intensity ratios are considered more accurate than CRDS measurements, it is necessary to evaluate the impact of $S_{DLR2021}$ data on the $^{13}C/^{12}C$ ratio determination. For 30012/3/4 bands, the $S_{DLR\text{-}HIT16}/S_{Ames2021}$ differences of R12e and R18e are averaged to get the relative "mean" deviations. In Fig.7a, the five ($S_{Expt}/S_{Ames2021}$-1) × 1000 differences become: 1.40 (20013), -0.08 (20012), 2.57 (30014), 0.45 (30013), and -5.17 (30012). Note only the PTB2011[61] based R12 ratio was used for 20012 band, because the R18 related experimental intensity of Yi et al[35] contained too large oscillations. These differences are centered at -1.30‰, and the relative standard uncertainty is estimated to be 2.24‰. Accordingly, our $^{13}C^{16}O_2$ intensity for 20011 R18e needs to be adjusted by -1.30‰ to 6.98305×10^{-22} cm/molecule, which is 4.13‰ less than that of $S_{UCL2021}$. Additionally, the $^{12}C^{16}O_2$ 30012 reference intensity is reduced by ~5.34‰ from $S_{NIST\text{-}HIT16}$ to $S_{DLR\text{-}HIT16}$. In the analysis above, the two effects largely (>70%) cancel with each other. As a result, the $^{13}C/^{12}C$ ratio will drop by 1.21‰, from 0.011125 to 0.0111115. Apparently, this value matches closer with Malinovsky et al (2019)[71] and Dunn et al (2015).[72]

With the 2.24‰ uncertainty estimated on the S_{Ames} intensity for $^{13}C^{16}O_2$, and the 1.5‰ uncertainty reported for $^{12}C^{16}O_2$ S_{DLR} intensity,[40] the combined standard uncertainty for $R(^{13}C/^{12}C)$ would become 30×10^{-6}, if other uncertainty factors stay the same. It is still about 1/3 less than the u reported in Fleisher et al.[39] In short, with $S_{NIST\text{-}HIT16}$, $S_{DLR\text{-}HIT16}$, and S_{Ames} intensities, a new VPDB $^{13}C/^{12}C$ ratio is estimated at 0.011112±30. See the magenta point at the top of Fig.7b.

Sub-percent isotopologue consistency is still a brand-new playing field for both experiment and theory. In the benchmark systematic investigations carried out for CO_2 and SO_2 line lists,[29] only the same-band consistency was checked on different isotopologues. The intensity consistency for different bands of different isotopologues has not been investigated before. Need high accuracy experiments to verify the claims about the accuracy and consistency of Ames-2021 IR line lists for 13 isotopologues. The CO_2 2001i and 3001i bands could be a good start, for ^{13}C, ^{17}O, and ^{18}O isotopologues. The related S_{Ames} values are provided in the supplementary file for the four most abundant isotopologues: 626, 636, 628 and 627.

III.4. $S_{Ames\text{-}2021}$ for other bands highlighted in HITRAN2020 update

The HITRAN2016[32] CO_2 intensity for the majority of the lines below 8000 cm^{-1} was taken from the UCL-296 line lists,[27,28,31] which were computed using the UCL DMS 2015[34] + Ames-1 PES.[23] It was agreed that S_{UCL296} and $S_{Ames2016}$ were overall similar to each other.[18,27,31] Previous Ames-2016 intensities suffered from a small intensity gap between the P and R branches. Now the intensity gap has been fixed, and evidence show the Ames-2021 DMS based S_{Ames} are much more accurate than $S_{Ames2016}$, S_{UCL296} (or

S_{HIT16}), or the $S_{UCL2021}$ update. In addition to the 3001*i*, 2001*i* and 00031 bands discussed in Section III.1 – III.3, it is reasonable to assume $S_{Ames2021}$ has general accuracy improvement for other bands, including those bands higher than 8000 cm^{-1}. This assumption requires more robust proof – such as from a random comparison with a high accuracy experiment, although the impact on a specific band or transition is hard to predict, and so is the magnitude of potential improvement.

Recently, the HITRAN2016 database[32] has been upgraded to HITRAN2020.[33] Karlovets et al (2021)[41] discussed the CO_2-related updates in detail, e.g., issues identified in HITRAN2016, new experimental and theoretical data, and the data source for every piece of addition or update. An inclusive and thorough comparison between the $S_{Ames2021}$, $S_{HITRAN2020}$, and $S_{CDSD2019}$[17] intensities will be useful for transitions >8000 cm^{-1}. However, this paper is focused more towards improving the uncertainty level from 1.0% to 0.1%. Considering that a very limited number of IR bands in HITRAN2020[33] or CDSD2019[17] have comparable experimental uncertainty (e.g., the S_{NIST} and S_{DLR} data), and experimental uncertainties associated with minor isotopologues are usually even larger, a complete and detailed comparison is beyond the scope of this paper, but can be separately reported in the future. The intensity comparisons given in this section are limited to those bands with intensity updates, or the new bands just added to HITRAN2020[33] (except for the S_{NIST} or S_{DLR} based data scaling which have already been discussed in Section III.1 and III.2). This choice is not strictly random, but it may better assess the Ames-2021 DMS and $S_{Ames2021}$ intensities, to support or disapprove our claims about their accuracy and consistency, as well as to identify any drawbacks or problems requiring immediate attention. Note the 4003*i* bands are added as a follow-up to our Ames-2016 line list paper.[18] For clarity, please note S_{Ames}= $S_{Ames2021}$= $S_{Ames-2021}$, S_{HIT16} = $S_{HITRAN2016}$, S_{HIT20} = $S_{HITRAN2020}$, S_{UCL} = S_{UCL296} (non-sensitive bands).

III.4.1. 40002-01101, 21113-01101 and 21113-11102 bands

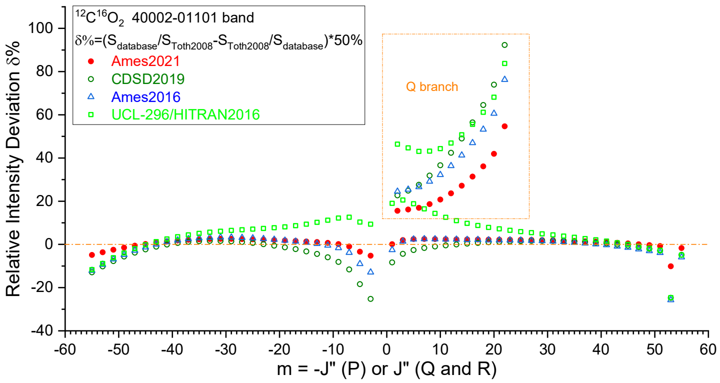

Figure 8. $^{12}C^{16}O_2$ 40002 – 01101 band comparison between the Toth et al (2008)[70] model and 4 line list databases. See text for details.

All the relative intensity errors in Fig.8 are computed with respect to Toth et al (2008),[70] which is the best experimental data available for 40002-01101 and 21113-01101 bands. The 10-15% rotational dependence in the HITRAN2016[32] (or UCL-296[27,31]) intensity for the 40002-01101 band is noticeable in both *P* and *R* branches. Karlovets *et al*[41] suggested it was caused by the Coriolis coupling between the 40002 and 21113 states which led to difficulty in the S_{UCL296} calculations. However, S_{Ames2016} and S_{Ames2021} do not contain such rotational dependence. One possible explanation could be the inaccuracy of the Ames-1 PES[23] used in the S_{UCL296} calculation.[27,31] The S_{Ames2016} and S_{CDSD2019} have similar *P* and *R* intensities for middle *J*s, but $S_{\text{Ame-2016}}$ has much smaller δ% deviations for the *P3* – *P*21 and *R*1 transitions. The HITRAN2020 update[41] chose S_{CDSD2019} over S_{Ames2016} for this band, but the S_{Ames2021} surely has the *best* agreement with Toth et al (2008).[70] Compared to S_{CDSD2019} and S_{Ames2016}, now the δ% at high *J* and low *J* ends are reduced by two thirds (*P* and *R*). The δ% of the *Q* branch is also reduced by 1/3 ~ 1/2. The disturbed *R*53e transition also has its δ% reduced from ~ -25% (S_{CDSD2019}, $S_{\text{HITRAN2016}}$ and S_{Ames2016}) to ~ -10% ($S_{\text{Ames-2021}}$).

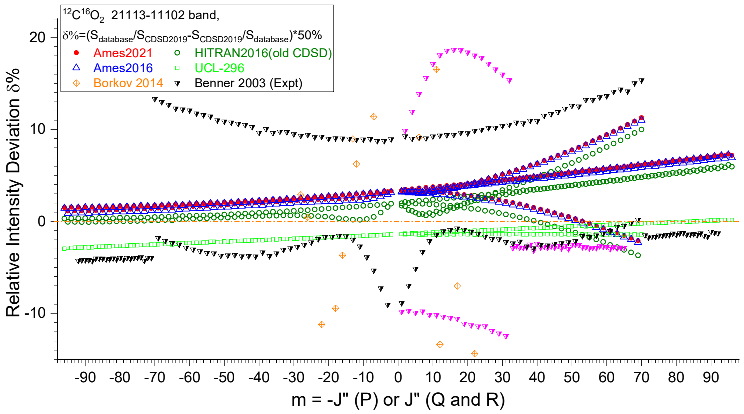

Figure 9. $^{12}C^{16}O_2$ 21113 – 11102 band comparison. HITRAN2020 (or CDSD2019) vs line lists and experiments : Borkov *et al* (2014, measured, 2 lines out of range),[73] and Benner (2003, fitted, magenta for *Q* branch).[74] See text for details.

The 21113-11102 band was one of the "sensitive" bands in Zak et al[31]. The HITRAN2016 adopted earlier CDSD2015[16] intensities instead of $S_{\text{UCL-296}}$. The HITRAN2020[33,41] adopted new CDSD2019[17] intensities after comparing line lists with Benner's (2003) unpublished experimental EDM model.[74] The comparison in Fig.9 uses S_{CDSD2019} (or $S_{\text{HITRAN2020}}$) as reference. The *e-f* (or odd *J* – even *J*) separation of Benner's EDM model is ~15%, much larger than the differences between the old CDSD and Ames intensities, so this band is not suitable for percent or sub-percent level analysis. However, the Ames and old CDSD intensities are in the middle of the EDM *e* and *f* branches, while the S_{CDSD2019} (and $S_{\text{UCL-296}}$) is very close to the lower side of *e* (odd *J*) lines. Therefore, S_{CDSD2019} may be the best candidate for half of the EDM intensities, but Ames and old CDSD intensities are better choices for overall representation. Fig.9 also includes 16 intensity values measured by Borkov et al (2014),[73] including 6 *R* lines with 15% uncertainty. If they were adopted by the CDSD models, the large uncertainty and limited *J* range might have also affected S_{CDSD2019}. On the other hand, a systematic discrepancy is observed between the reference S_{CDSD2019} (or $S_{\text{HITRAN2020}}$) and other line lists. From *P*96 to *R*96, the rotational (*J*) dependence of δ% is very similar between S_{Ames2016}, S_{Ames2021}, $S_{\text{HITRAN2016}}$ (or S_{CDSD2015}), and $S_{\text{UCL-296}}$, i.e., increased by ~5%. From Ames-2016 study,[18] it suggests linear residuals in the new EDM model of CDSD2019.[17] The $\delta\%_{\text{HITRAN2016}}$ (or $\delta\%_{\text{CDSD2015}}$) is 1.5% lower than $\delta\%_{\text{Ames}}$. The difference between $S_{\text{Ames-2016}}$ and $S_{\text{Ames-2021}}$ is less than 0.2-0.3%. For this band, new experiments and EDM models are desperately needed with higher accuracy.

The 3rd band in Fig.4 of Karlovets et al[41] is 21113-01101. The original S_{Toth2008} data had gaps at *P*80, *R*80, and *Q*40, see Fig.10a. Compared to the first two bands, theoretical calculations and experimental models agree very well on this band, but with *e*/*f* separations at high *J*. $S_{\text{HITRAN2016}}$ used old CDSD[16] intensities, while $S_{\text{HITRAN2020}}$ has adopted $S_{\text{Ames-2016}}$. Note the $S_{\text{UCL-296}}$ for *P*2-*P*9, *Q*1-*Q*2, and *R*1-*R*46 lines were taken from Toth et al,[70] so the corresponding $\delta\%_{\text{UCL-296}}$ are zeroes. The differences between $S_{\text{Ames-2016}}$ and S_{CDSD2019} are less than 1% for most *P*/*R* lines. Fig.10b plots the δ% with respect to $S_{\text{Ames-2016}}$. The $S_{\text{Ames-2021}}$ are 0.3-0.6% higher. The $\delta\%_{\text{HITRAN2016}}$ has the *e*/*f* separation and local minima near *J*″=10, like those in Fig.9. There is a tiny *J* dependence of 2% for $\delta\%_{\text{CDSD2019}}$ in *R* lines, but not in $\delta\%_{\text{HITRAN2016}}$.

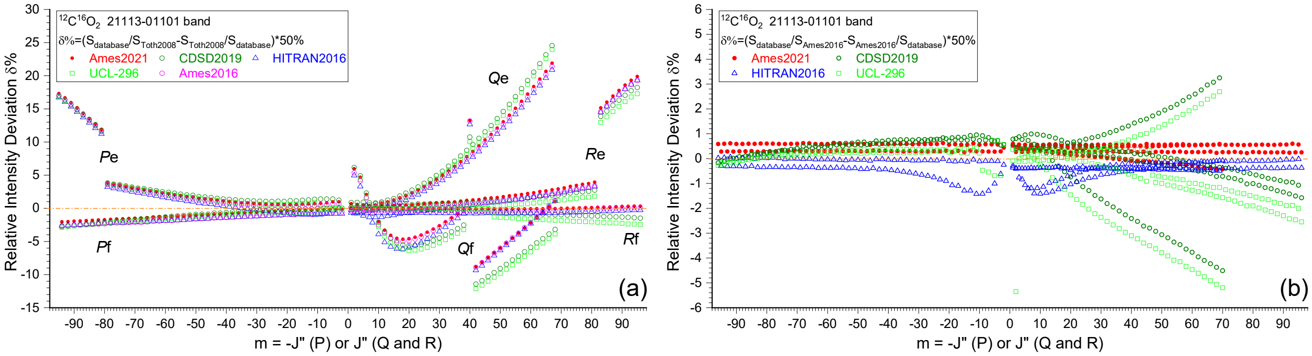

Figure 10. 21113-01101 band intensity comparison. (a) 5 line lists vs. Toth 2008 et al[70]; (b) 4 line lists vs. $S_{\text{Ames-2016}}$ (taken as $S_{\text{HITRAN2020}}$).

In short, improvement is confirmed on the 40002-01101 band. The changes on the two 21113 related bands are less than 1%, might be less than the experimental data uncertainty. Need more accurate experiment for evaluation. But there is no degrades, which is good for S_{Ames2021}.

III.4.2. 1110*i*-00001 bands (*i*=1-2) and 20003/12202-01101 bands

As reported before,[17,42] the Ames intensity in the 1800-2000 cm^{-1} range has considerable deviations for the 11101-00001 and 11102-00001 bands. They are linked to the sharp intensity variations caused by the strong Coriolis coupling with the anti-symmetric stretching fundamental band 00011-00001.[41] Fig.11 uses Tanaka 2006 et al[75] as experimental reference. Compared to $S_{\text{Ames-2016}}$, the δ% of $S_{\text{Ames-2021}}$ shows small increases for the 11101-00001 band but rises by nearly 50% (*R* branch) or about 1/3 (*P* branch) for the 11102-00001 band. These 40-100% relative errors are attributed to the sensitivity of the Coriolis interaction and the wavefunction inaccuracy resulting from the Ames-2 PES defects. Such deviations are expected to reduce on future more accurate PES refinements. However, the issue probably will remain for years before they can be reduced to ±1~5% level, i.e., similar to most other bands.

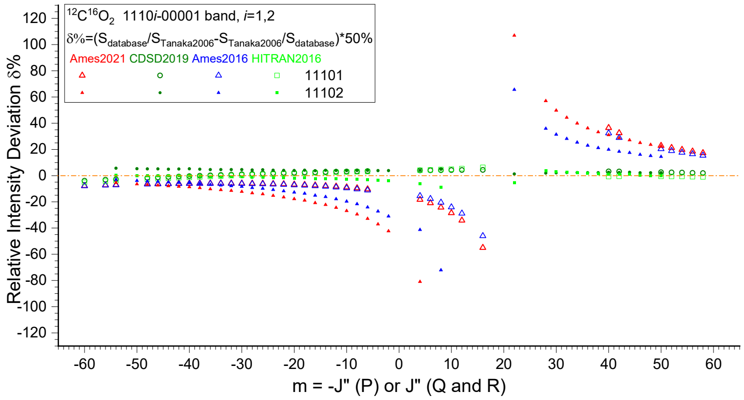

Figure 11. 11101-00001 and 11102-00001 band intensity comparison: line lists (database) vs Tanaka et al.[75]

To the best of our knowledge, the UCL *ab initio* intensities for these two bands were also impacted by the Coriolis coupling problem, but with a smaller magnitude. The recommended UCL-296[27,31] line list for 626 used CDSD2015[16] intensities for the 11101 *R*20-*R*34 and 11102 *R*10-*R*22 transitions. The HITRAN 2020 update has fully replaced the $S_{UCL\text{-}296}$ by $S_{CDSD2019}$ values.[41]

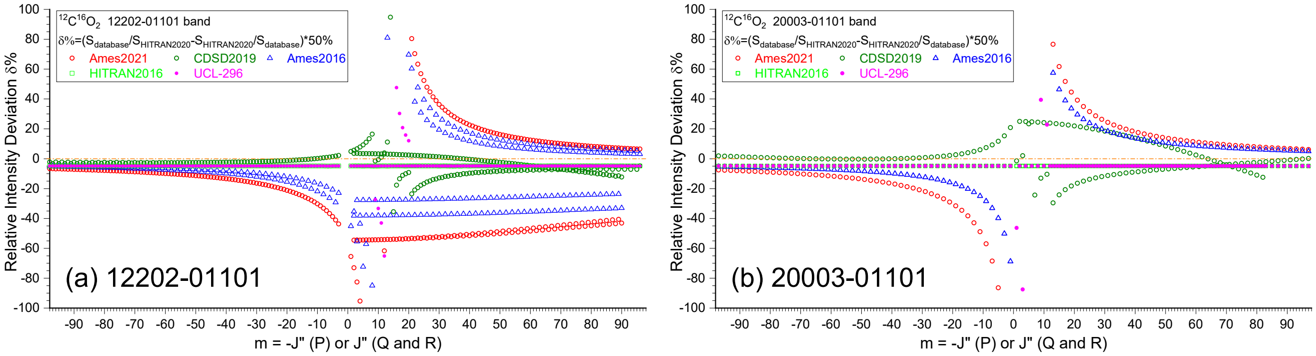

Figure 12. Intensity comparison with respect to HITRAN2020. (a) 12202-01101; (b) 20003-01101.

In the HITRAN2020 update, the $S_{HITRAN2016}$ intensity of the 20003-01101 and 12202-01101 hot bands near 1900 cm^{-1} were scaled by 1.05 to match the JPL ATM[76,77] values. These two bands are also affected by Coriolis Coupling. Karlovets et al[41] cited the 20003-01101 intensity source as UCL *ab initio*. But to our knowledge, the $S_{UCL\text{-}296}$ and $S_{HITRAN2016}$ *R1-R11* intensity of the 20003-01101 band were also taken from CDSD2015 due to 2 orders of magnitude deviation around *R*5,[16] just like the *R9-R20* intensity of the 12202-01101 band. The $S_{UCL\text{-}296}$ are represented by magenta dots in Fig.12, where 5 sets of intensities are compared to the new $S_{HITRAN2020}$. The $δ\%_{Ames\text{-}2021}$ are noticeably larger than the $δ\%_{Ames\text{-}2016}$, for all 3 *P*, *Q* and *R* branches, similar with the 11102-00001 band. Note that the δ% for the 20003-01101 *Q* branch go from -150~-100% to -400~-200%, so they are out of the range of Fig.12b. Again, future CO_2 PES refinement needs to put higher priority on the accuracy of vibrational states involved in Coriolis couplings. The S_{Ames} deficiency related to Coriolis couplings may have other factors, e.g., the affected *J* range for the 12202-01101 band is much wider than that of the original *ab initio* $S_{UCL-296}$. The sensitivity may also impact EDM models, e.g., the $\delta\%_{CDSD2019}$ for the $R1$-$R11$ of 20003-01101.

III.4.3. Above 8000 cm^{-1}

HITRAN2020[33,41] included new $^{12}C^{16}O_2$ bands up to 20,000 cm^{-1}, which were plotted as blue dots in Fig.13 of Karlovets et al.[41] Those bands utilized the UCL-4000[50] line intensity and CDSD2019[17] line positions, with a $S_{UCL-4000}$ (296K) cutoff at 1E-30 cm/molecule. The $S_{UCL-4000}$ intensities were computed using the Ame-1 PES[23] and UCL DMS 2015.[34] Abnormal intensity has been found in some new bands included in the HITRAN2020 update – see the black peaks in Fig.13a. Independent comparisons should have been done before the HITRAN update was finalized.

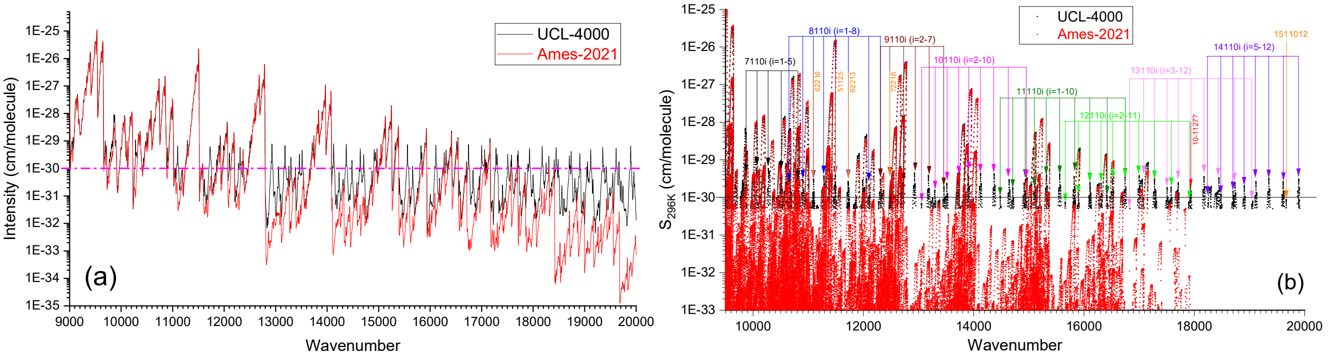

Figure 13. (a) $^{12}C^{16}O_2$ IR simulation at 300K, UCL-4000[50] vs Ames-2021, including all lines with S_{300K} > 1E-36 cm/molecule. See text for details. (b) Assignment of the irregular intensity peaks in UCL-4000, including UCL-4000 lines with S_{300K} > 5E-31 cm/molecule, and Ames-2021 lines with S_{296K} > 1E-33 cm/molecule, E'<19,500 cm^{-1}, and E'-E"<18,000 cm^{-1}.

In Fig.13a, the IR simulation at 300K reveals the atypical intensity in the UCL-4000[50] list (black peaks). In contrast, the Ames-2021 list (red) has very few lines above 17,000 cm^{-1} stronger than 1E-30 cm/molecule. The simulations took the line widths from the HITRAN2016[32] CO_2 line list by averaging over all values at a given J''. Self-broadening widths used in the calculations gave information on very high J values. The same partition function and line widths were adopted. A Voigt profile was used with the wing extent determined by a formula based on the line widths, doppler plus Lorentz, at a specific temperature and pressure.[78] All lines stronger than 1.E-36 cm/molecule at 300K were included. The data was then smoothed for plotting purposes using a Gaussian window function. Note this 300K simulation is not affected by the partition function value change from HITRAN2016[79] to HITRAN2020[80], at least not on this scale.

Those irregular intensity peaks in UCL-4000 became part of the HITRAN2020 update.[33,41] Apparently, they span from 10,000 cm^{-1} to 20,000 cm^{-1} with nearly identical peak heights and systematic intervals between the peaks. But some peaks may have sneaked into even lower wavenumber region.

These peaks were part of the Fig.4 in Yurchenko et al.[50], which should have ringed an alarm. Since first Ames-1 CO_2 line list paper[23], Ames 296K line lists[18,23,24,42] never had such irregular intensity below 24,000 cm^{-1} or stronger than 1E-34 cm/molecule. The 296K-300K simulations always look like the red line in Fig. 13a, during multiple PES and DMS updates (including the latest DMS series). In short, the non-standard wave of peaks should not have intensity as strong as 1E-29~1E-30 cm/molecule at room temperature. To our knowledges, none of those black peaks are experimentally confirmed.

Transition details are checked for those peaks stronger than 5E-31 cm/molecule. Most of them belong to the cold band series from 7110*i*, 8110*i*, 9110*i* … to 14-1-1-0*i*, in the range of 10,000 cm^{-1} to 20,000 cm^{-1}. See Fig.13b, where each series is marked by a unique color. Secondary contributions have also been identified from other bands, such as 5112*i* and 6221*i*. More band series can be found if the study is extended to below the 5E-31 cm/molecule cutoff. These noisy bands can be easily identified by the textbook style sharp *Q*-branches with intensities always larger than the nearly symmetric *P*- and *R*-branches. This textbook style intensity pattern between the *P/Q/R* branches is highly inconsistent with the other $^{12}C^{16}O_2$ bands in the range. From 7110*i* to 14-1-1-0*i*, the non-decreasing band intensities are inconsistent with a tightly bonded CO_2 molecule and a Boltzmann distribution. It also conflicts with other published theoretical or semi-empirical IR line lists (e.g., Refs.81,82), *and it is difficult to find a physics-related rationale to justify these peaks.* The UCL-4000[50] based IR simulation at 4000K has a much flatter slope for its total intensity in the range of 13000 – 18000 cm^{-1}, as shown in Fig.4 of Yurchenko et al.[50] The irregular bands found at room temperature probably make important contributions. A future paper on Ames hot CO_2 list will have more details. But the more important question is: where does the fake intensity come from?

The Ames-1 PES[23] is less accurate than the Ames-2 PES[18] adopted by $S_{Ames\text{-}2016}$ and $S_{Ames\text{-}2021}$, but it can be safely concluded that Ames-1 PES is not the source of those fake intensity peaks. The Ames-1 PES based line lists computed from 2012 to 2014[23,24,42] did not have this noise. Both Ames-1 and Ames-2 PESs are essentially similar up to 40,000 cm^{-1}, and both PESs do not cover the high-lying region (~30,000 cm^{-1}) for the triangular CO_2 isomer. The partition function and Boltzmann distribution at 300K do not support the wild guess that these intensities might be related to the triangular isomer region.

How about the dipole surface? Although the UCL DMS 2015[34] was fitted from points up to 15,000 cm^{-1}, both the Ames and UCL groups have strong enough confidence in its robustness. We also have run intensity calculation using the same Ames-2 PES wavefunction and an accurately refitted UCL DMS 2015, and obtained a spectra very similar to other Ames lists. "Accurately refitted" means fitting σ_{rms} = 0.5E-8 a.u. for more than 13,000 points up to 60,000 cm^{-1}, or 0.2E-8 a.u. for 8590 points up to

30,000 cm^{-1}. It is confidently concluded the UCL DMS 2015 itself *should be* fine. Hence, the fake intensities *should not* be part of the DMS.

The last and least possible guess is the TROVE[58] calculation behind the UCL-4000 list. Considering the success records of the ExoMol[25,82] group, it is always difficult to imagine any significant problem could happen there with a simple triatomic molecule, like CO_2. But if something really happened, it probably happened unnoticed at some transition stage. A wild guess is, the DMS re-expansion in the TROVE calculation unintentionally magnified the impurities in the original UCL DMS 2015, i.e., errors associated with "thetae_rad =3.141592". This deficiency prevented the DMS refits from obtaining σ_{rms} better than 1E-5 a.u.. When TROVE re-expanded the DMS, certain higher order terms might obtain extra flexibility. This may have ended up with values larger than expected, which then led to the appearance of the series of noise peaks.

Authors of the UCL-4000 line list[50] can re-run their calculations using thetae_rad=*dacos*(-1.d0) with the UCL DMS subroutine, or any Ames dipole surfaces (including the refitted UCL DMS 2015 or the Ames-2021 DMS attached as a supplement file). However, *if* the thetae_rad definition was already fixed – or the UCL DMS 2015[34] has already been regenerated with the constant corrected – *before* the UCL-4000 calculation, the wild guess would be plainly wrong and misleading, and the suggestion above would be totally useless. In that scenario, another option could be the DVR3D[59] line lists which the UCL group published[27,31] with an 8000 cm^{-1} cutoff. It would be interesting to see how their DVR3D intensities look in the range of 10000 – 20,000 cm^{-1}. Would the definition for π have any impact? We expect the impact to be much smaller, or negligible, at least on the scale used in Fig.11, because the DVR calculations do not re-expand the DMS.

At the end of this discussion, it should be noted that the Ames-2021 IR line lists attached to this paper already include CDSD[17] line positions determined from energy level matches, see Section III.5. As the best alternative to HITRAN2020 (except the Coriolis coupling affected lines), the Ames-2021 line lists also reliably cover the higher wavenumber range with CDSD line positions and vibrational polyad assignments, but without irregular or fake intensity peaks.

III.4.4. 10032-10002 and 01131-01101 bands

According to the HITRAN2020 update,[33,41] the $S_{HITRAN2016}$ for the 10032-10002 and 01131-01101 bands were scaled by 1.1346 and 1.0022, respectively, to match the $S_{DLR2021}$ measurements This means the $S_{UCL-296}$ was lower by about 12% and 0.22%, respectively. In Fig.14, 10032-10002 intensity of 6 line lists are compared to the original $S_{DLR2021}$.[40] The weighted "mean±σ" of $S_{DLR2021}/S_{Ames2021}$ differences is 4.95±5.93‰, or 0.5±0.6%. Compared to the -6.86‰ deviation of $S_{Ames2021}$ for the 00031-

00001 band (see Fig.4, Fig.5a and Table 4), the "mean" of 4.95‰ is still consistent within ±1%. This gives strong support for the $S_{Ames2021}$ consistency between the cold band and hot bands in the $3\nu_3$ series, i.e., cross-band consistency. The $S_{Ames2016}$ intensity was already better than $S_{CDSD2019}$ and $S_{HITRAN2016}$ by 1-7% and 7~12%, respectively. Compared to $S_{Ames2016}$, $S_{Ames2021}$ increases by 0.25% in the *R* branch, and 4.5% in the *P* branch which significantly reduced the δ%. This is evidence for the $S_{Ames2021}$ stability and noticeable improvement on the bands *not* strongly perturbed by Coriolis interactions. Current $S_{HITRAN2020}/S_{Ames2021}$ = 1.0047±0.0004. Recommend to re-run the HITRAN intensity scaling with $S_{Ames2021}$.

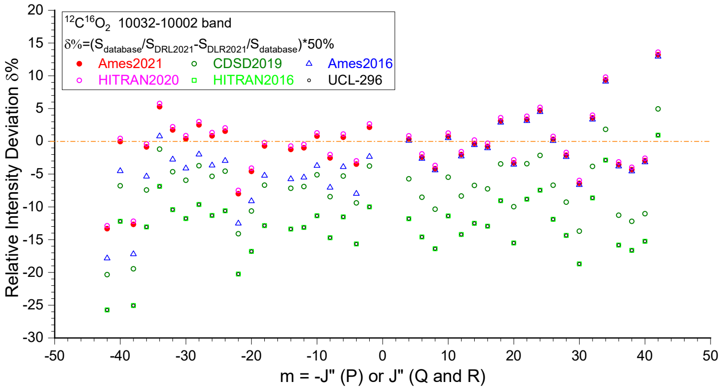

Figure 14. $^{12}C^{16}O_2$ 10032-10002 band intensity comparison at 296K, line lists and databases vs DLR2021.[40]

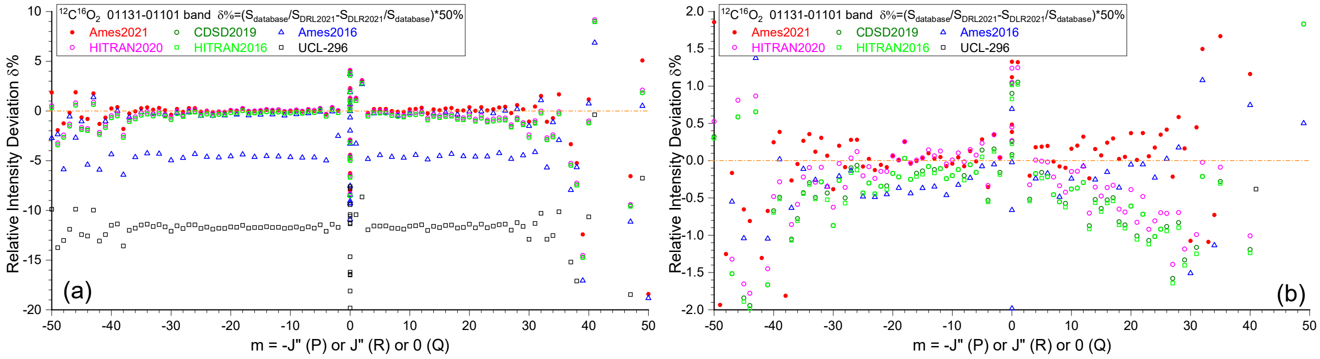

Figure 15. $^{12}C^{16}O_2$ 01131-01101 band intensity comparison: 5 line lists vs DLR 2021,[40] in full range (*a*) or ±2% range (*b*). The $\delta\%_{Ames2016}$ in panel *b* only includes *P* lines with odd *J*" and *R* lines with even *J*".

Another hot band of 00031-00001 is 01131-01101. It was one of the “sensitive” bands where HITRAN2016[32] took the $S_{CDSD2015}$[16] model intensity instead of $S_{UCL-296}$, According to Karlovets et al,[41] HITRAN2020[33] scaled the $S_{CDSD2015}$[16] by 1.0022 to match $S_{DLR2021}$. Analysis for this band further supports the $S_{Ames2021}$ accuracy claimed in this paper. See Fig.15 with *Q* branch data in the center. Taking the $S_{DLR2021}$ as reference, the weighted "mean±σ" of $S_{DLR/2021}/S_{Ames2021}$ differences is surprisingly small: -0.91 ± 0.25‰, vs. 4.8±0.37‰ for $S_{CDSD2019}$, or 25.6±2.0‰ for $S_{Ames2016}$. The improvement from $S_{Ames2016}$ to $S_{Ames2021}$ is significant. In Fig.15b, the $S_{Ames2021}$ shows similar agreement as $S_{HITRAN2020}$ for *P* lines, but clearly better agreement for *R* lines. Overall, S_{Ames} (i.e., S_{Ames2021}) has the best agreement with S_{DLR} (i.e., S_{DLR2021}) intensities. The S_{CDSD} and $S_{\text{HITRAN2020}}$ models have a small but recognizable *J* dependence on *R* lines. Note the UCL-296 deviation is consistent with that of 00031-00001, 12.3% vs 12.2%. Based on analysis of other strong bands in this paper, the S_{DLR2021} intensity for this band could have 0.2-0.3% uncertainty for the $J''\leq30$ range. Recommend new scaling with S_{Ames2021} to improve the accuracy of $S_{\text{HITRAN2020}}$, especially the *R* branch.

III.4.5. 30022/30023 of 628, 00041-01101 of 626: weak bands

The HITRAN2020 update[33,41] adopted S_{Ames2016} intensities as the better choice for these bands. Compared to other bands discussed in this paper, these are very *weak* bands, i.e., 1E-30 ~ 1E-29 cm/molecule at 296K with terrestrial abundance. How does the S_{Ames2021} compare to S_{Ames2016} intensities?

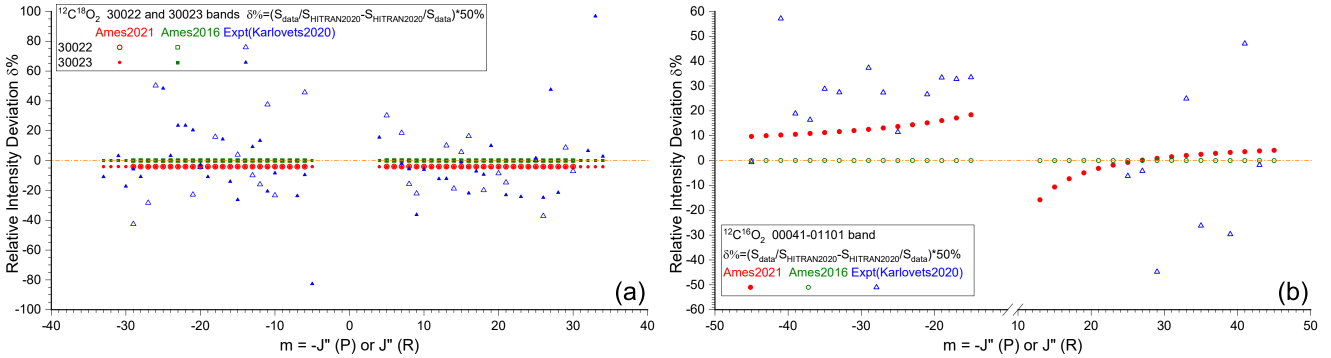

Figure 16. Comparison of experimental data and S_{Ames2021} with respect to $S_{\text{HITRAN2020}}$ (it uses S_{Ames2016}): (a) $^{16}O^{12}C^{18}O$ 30022 and 30023 bands; (b) $^{12}C^{16}O_2$ 00041-01101 band.

The measurements for the $^{12}C^{16}O^{18}O$ 30022/30023-00001 and $^{12}C^{16}O_2$ 00041-01101 bands were reported in Karlovets et al (2020).[83] They were not available in CDSD2019[17] or UCL-296.[27,31] Because the experimentally measured intensities have 20-40% uncertainties, the comparison in Fig.16 uses the $S_{\text{HITRAN2020}}$ (or S_{Ames2016}) as reference. In Fig.16a for the 30022 and 30023 bands, there is a -4% systematic difference between S_{Ames2016} and S_{Ames2021}. Given the experimental uncertainty, it is hard to tell if S_{Ames2021} is more accurate for the *P* branch. However, for the 30023 *R* branch, the $\delta\%_{\text{Ames2021}}$ (red dots) are visibly closer to the center of the experimental data (solid blue triangles), so $S_{\text{Ames-2021}}$ should be more reliable than S_{Ames2016}.

The 00041-01101 band comparison is given in Fig.16b. Assuming that Karlovets et al (2020)[83] has a similar uncertainty for this band, obviously the S_{Ames2016} underestimated the *P* branch intensities by 25-30%. The good news is the S_{Ames2021} intensity has reduced the $\delta\%_{\text{Ames2016}}$ deviations by 10-15%, i.e., the red dots vs. green circles. This is additional evidence for the overall enhancement brought by S_{Ames2021}

over $S_{Ames2016}$. Hope more accurate experiments in the future can help clarify the *R* branch intensities and the lower *J* range.

III.4.6. 41104-00001 band of 626/636/628: *Q* branch and isotopologues

Throughout the paper our discussion has been focused on *P*- and *R*-branches. In 2018, Čermák et al[84] reported their 41104-00001 band measurement for $^{12}C^{16}O_2$. They found that $S_{Ames2016}$ had the best agreement for the *Q*-branch, while S_{UCL296} and $S_{HITRAN2016}$ (it used $S_{CDSD2015}$) had overestimated both *Q*- and *R*-branch intensities.[84] See Fig.17. The symbols for $S_{Ames2021}$ and $S_{Ames2016}$ nearly overlap with each other. From $S_{Ames2016}$ to $S_{Ames2021}$, the range of intensity variations is 0.0-1.0% (*R*), -2.5 ~ -0.5% (*Q*) and 1.1-1.8% (*P*). But their agreement with experimental data (Expt 2018) scatter between -30% and +30%, mainly due to the experimental uncertainty (see Fig.17b). The Ames intensity changes are too small to evaluate the improvement. Compared to S_{Ames}, the fitted dipole model in $S_{CDSD2019}$ has similar or slightly better agreement for *P* and *R* branches, but its *Q* branch intensities were still overestimated.

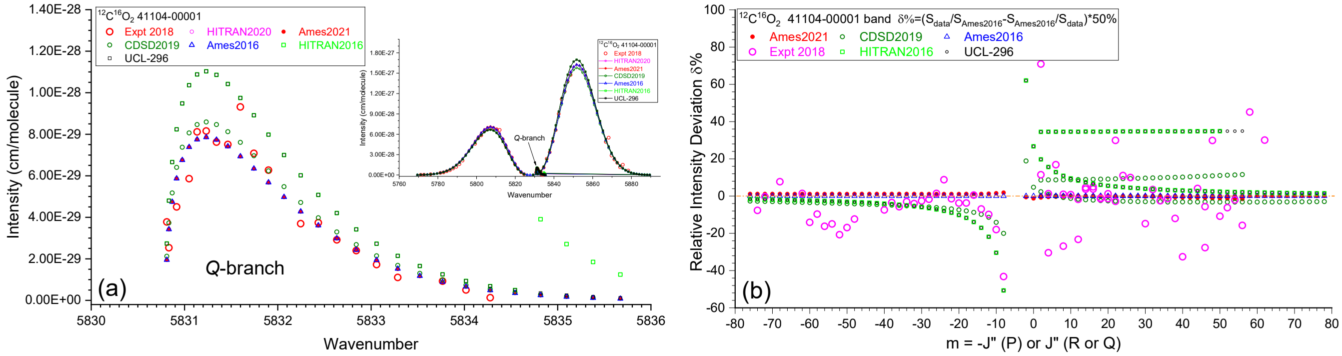

Figure 17. $^{12}C^{16}O_2$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance for the *Q* branch; experimental data (Expt 2018) was taken from Čermák et al (2018);[84] (*b*) δ% differences with respect to $S_{Ames2016}$ (or $S_{HITRAN2020}$).

Karlovets et al (2018)[20,85] also measured the 41104-00001 band intensities for $^{12}C^{16}O^{18}O$ and $^{13}C^{16}O_2$. As shown in Fig.10 of Ref.85, the $S_{CDSD2015}$ intensity (adopted in $S_{HITRAN2016}$) for $^{12}C^{16}O^{18}O$ had overestimated the *R* branch intensity by 50-100%, while S_{UCL}[28] slightly underestimated the *R* branch intensity. Therefore, $S_{Ames2016}$ was adopted by HITRAN2020[33,41] for the better agreement. Our comparison in Fig.18 does not include HITRAN2016[32] or CDSD2015.[16]

For $^{16}O^{12}C^{18}O$, the Ames intensity has maintained excellent consistency for most lines in Fig.18. With respect to $S_{Ames2016}$,[18] $S_{Ames2021}$ values only change by -1.0% ~ +0.25%, from *R*7 to *R*66. The *P*-branch intensity has a 1.2-5.2% increase from *P*44 to *P*9. Looking at the experimental data[85] (magenta circle), $S_{CDSD2019}$[17] (dark green circle) and $S_{UCL-296}$[28] (green square) overestimated the *R*-branch intensity. In short, the $S_{Ames2021}/S_{Expt}$ agreement has excellent consistency between the 626 and 628 isotopologues.

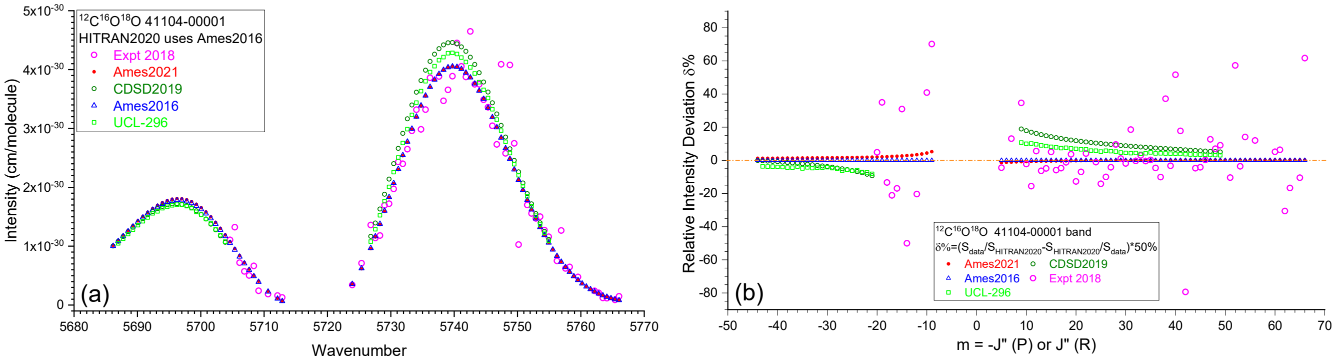

Figure 18. $^{12}C^{16}O^{18}O$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance; (*b*) δ% difference with respect to $S_{HITRAN2020}$ (or $S_{Ames2016}$).

For $^{13}C^{16}O_2$, the comparison in Fig.19 looks very different from the comparison in $^{18}O^{12}C^{16}O$ or $^{12}C^{16}O_2$. Overall, the intensity measured at 294K (Expt 294K) are noticeably higher than $S_{Ames2021}$ and other line lists, especially the *Q* and *R* branches. An exception is the experimental dipole model[20] (black +), which matched the peak region of the *P*-branch but the agreement deteriorates for the *Q*- and *R*-branches. From $S_{Ames2016}$ to $S_{Ames2021}$, the intensity changes on J>10 lines are just 0.5-1.5% (*R*), 5-6% (*Q*) and -2~0.7% (*P*). This is roughly consistent with those we have for $^{12}C^{16}O_2$. The changes are relatively larger (~10%) near J''=0.

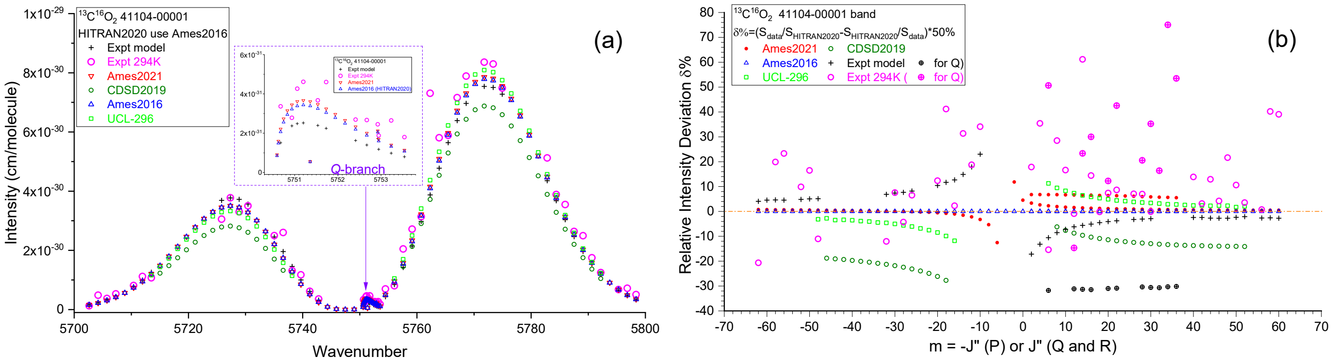

Figure 19. $^{13}C^{16}O_2$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance; (*b*) δ% difference with respect to $S_{HITRAN2020}$ (or $S_{Ames2016}$). Experiment: Karlovets et al (2018).[20]

These observations suggest significant underestimation across various line lists and models, for all three branches. This conflicts with the *Q*-branch agreement found for S_{Ames} ($^{12}C^{16}O_2$) and the *R*-branch agreement found for S_{Ames} ($^{12}C^{16}O_2$) and S_{Ames} ($^{16}O^{12}C^{18}O$). It will require additional studies to explain or clarify. The ^{13}C substitution is not supposed to cause such considerable changes in the intensity agreement, even if there might exist unknown intensity borrowing. If future experiments confirm the 10-30% underestimation of $^{13}C^{16}O_2$ intensity, it is obligatory to figure out the causes behind the isotopologue consistency breaking on this band. But for now, the S_{Ames}/S_{Expt} agreement for $^{12}C^{16}O_2$ 41104-00001 band first lends more support for our claim that the *n*110*i* (*n*=7-15, *i*=1~*n*+1) band series in UCL-4000 should not have 296K intensity as strong as 1E-30 ~ 1E-29 cm/molecule (see Fig.13).

III.4.7. 4003*i*-00001 and Summary

In the Ames-2016 line list paper,[18] the 4003*i*-00001 (*i*=2-4) bands were specifically discussed. The line intensities reported in Tan et al[19] were in the range of 4~70 × 10^{-30} cm/molecule. $S_{\text{Ames-2016}}$ agreed on the 40032-00001 band, but was substantially lower than the intensities reported for the 40033-00001 and 40034-00001 bands. Revisiting this vibrational polyad, we choose a pair of strong *P* and *R* transitions in each band, and list their intensity values from several line lists. The unit is 10^{-29} cm/molecule. The "*" indicates a blended line with experimental uncertainty 20-30%, other lines have uncertainty 5-10%.[19] The UCL-296 line list is not included because this band is higher than 8000 cm^{-1}.

Table 6. Intensity comparison for $^{12}C^{16}O_2$ 4003*i*-00001 (*i*=2-4) bands. All values are in 10^{-29} cm/molecule.

	40034		**40033**		**40032**	
	*P*16	*R*16*	*P*14	*R*14	*P*14	*R*12*
Expt. (Tan et al[19])	1.67	1.78	5.12	6.23	1.68	2.13
CDSD2019[17]	1.92	2.06	5.44	5.82	1.98	2.05
Ames-2016[18]	1.05	1.21	3.85	4.32	1.91	2.06
Ames-2021 (this work)	0.87	1.00	3.17	3.60	1.65	1.79
UCL-4000[50]	1.29	1.47	4.10	4.61	1.41	1.54
Ames DMS Series	**0.96±0.14**	**1.10±0.16**	**3.17±0.45**	**4.01±0.45**	**1.60±0.22**	**1.90±0.24**

Compared to $S_{\text{Ames-2016}}$,[18] the $S_{\text{Ames-2021}}$ intensities have been further reduced by 1/6 for all three bands. Compared to S_{CDSD2019}[17] which was fit from experimental data (Tan et al[19]), the $S_{\text{UCL-4000}}$[50] are 30% lower, while S_{Ames2021} are lower by ~50% (40034), ~40% (40033), and ~15% (40032). To better understand these differences (or underestimation), statistical "mean±σ" are computed for each line intensity over the Ames DMS series, which has more than 25 DMS fits (see Fig.3 and Fig.6). As shown at the bottom of Table 6, the ratios between "σ" and "mean" is approximately 15%, which represents the relative uncertainty inherited from the DMS used in Ames calculation. In contrast, the σ range for the 2001*i* and 3001*i* bands is less than 0.3% in Fig.3. Theoretical analysis on this 15% range suggests the following: 1) the weak 4003*i* bands are more sensitive to DMS fits, but the Ames DMS series should have included some DMS good for these bands; 2) the S_{Ames2016} and S_{Ames2021} intensities are still consistent with each other; 3) the 30-50% difference between Ames and experiment for the 40032 and 40033 bands is real, it requires a physically meaningful explanation. One possible explanation is some unknown defects in the Ames-2 potential energy surface.

In this section, band by band analysis is presented for those CO_2 bands mentioned in the HITRAN2020 intensity update,[33,41] and the 4003*i* bands. The latest S_{Ames2021} intensities computed using the Ames-2021 DMS are compared to S_{Expt}, S_{CDSD}, S_{HITRAN}, S_{UCL} and S_{Ames2016}. For the bands that are not perturbed by Coriolis coupling, $S_{Ames2021}$ is found to be more accurate than $S_{Ames2016}$ for several bands: 40002-01101,10032-10002, 01131-01101, 00041-01101, 30022/30023 (628), while there is no significant change for the 20013-11102, 21113-01101, 41104-00001 (626, 636, 628) bands. Excellent consistency is confirmed between cold bands and hot bands (00031 series), and between the 626 and 628 isotopologues (41104-01101). The worse performance on the Coriolis coupling related bands is acknowledged for 1110*i*-00001,12202-01101, and 20003-01101. Improving these bands probably requires a PES enhancement. The consistency breaking for the 41104-00001 (636) or 4003*i*-00001 (626) bands will stay on the watch list for future CO_2 work. But it can be confirmed that the intensity of the *n*110*i* (*n*=7-15, *i*=1~*n*+1) band series was significantly overestimated in UCL-4000[50] (and current HITRAN2020), where other bands also contributed fake intensity as minor sources.

List of findings from the $S_{Ames\text{-}2021}$ vs. $S_{Ames\text{-}2016}$ comparisons:

a) 40002-01101: Improvement confirmed. No *J* dependence. More accurate than S_{CDSD}.
b) 21113-11102: Changes are trivial. $S_{CDSD2019}$ ($S_{HITRAN2020}$) probably has linear residual. Better to use $S_{Ames2021}$, or $S_{HITRAN2016}$ (old $S_{CDSD2015}$).
c) 21113-01101: Changes are trivial. *Q* branch better than $S_{CDSD2019}$.
d) 10032-10002 & 01131-01101: Improvement confirmed. Best agreement vs $S_{DLR2021}$.
e) Weak 30022/30023 (628): Changes are small, but *R* branch seems improved.
f) Weak 00041-01101: Improvement confirmed for the *P* branch.
g) Weak 41104-00001 (626): Changes are trivial. *Q* branch better than $S_{CDSD2019}$.
h) Weak 41104-00001 (628): Changes are trivial. Still the best for the *R* branch
i) Weak 41104-00001 (636): Changes are trivial. Calls for more studies.
j) Weak 4003*i*-00001 (626): 1/6 reduction. Now 30-50% below S_{Expt} and S_{CDSD}.
k) 1110*i*-00001,12202-01101,20003-01101 [Coriolis coupling bands]: Worse, requires more accurate PES.
l) Above 8000 cm^{-1}: No significant changes. Fake intensity peaks identified in $S_{UCL\text{-}4000}$ and $S_{HITRAN2020}$.

III.5. Ames-2021 296K Line Lists

New 296K IR line lists have been computed for 13 CO_2 isotopologues of $^{12/13/14}C$ and $^{16/17/18}O$, assuming 100% abundances and 1E-31 cm/molecule cutoff. Rovibrational energy levels below 18,000 cm^{-1} were included in the intensity calculation. To obtain the best intensity accuracy and isotopologue consistency, the intensity gap between the *P*- and *R*- branches of symmetric isotopologues has been fixed. Energy levels and related IR transitions are rejected if they are forbidden by nuclei-spin statistics. The computed energy levels were locally matched to CDSD[17] levels. The product line lists are compressed and attached to this paper as supplementary files. For each transition, $S_{Ames-2021}$ and Einstein A_{21} coefficient are reported along with two sets of information. One set has the original Ames-2 PES[18] based line position and lower state energy, and leading CI basis and coefficients generated by the VTET program.[57] The other set has the CDSD[17] based line position, lower state energy, and vibrational polyad labeling for upper and lower states. To our knowledge, this is a flexible and easy-to-track combination between the best line positions and the best *ab initio* IR intensities. The transition intensities affected by Coriolis coupling should still use more reliable, experimental data based CDSD values.

The reliability of the "Ames vs CDSD" local match degrades at high energy and/or high *J*'s, e.g., see Fig.2 of Ref.18, so please use with caution. As CDSD[17] does not have intensity data down to 1E-31 cm/molecule (with 100% abundance) for minor isotopologues, CDSD intensity values are not included in the Ames-2021 line lists for individual isotopologues. Interested readers can compare it with the published CDSD database.

Together with the Ames-2021 296K IR line lists, the Ames-2 PES, Ames-2021 DMS and $S_{Ames-2021}$ intensity values for 2001*i*, 3001*i* and 00031 bands are also supplied as supplementary files. They are already available at http://huang.seti.org. Please note that all $S_{Ames-2021}$ intensities are reported with 7 significant figures, because 1‰ or higher level comparisons will need *at least* 5-6 figures to prevent the noises caused by data precision loss, e.g., those minor oscillations in Fig.2a. This will be more important for the five symmetric minor isotopologues in HITRAN2020,[32,33,41] i.e., 636/727/737/828/838, because their intensities have only 3 significant figures.

IV. Conclusions

We report a new, highly accurate DMS for CO_2 IR intensity and line list studies. The Ames-2021 DMS targets both lower energy accuracy and higher energy coverage. It was fit from the extrapolated CCSD(T)/(d-)aug-cc-pV(T,Q,5)Z(O) finite-field dipoles of 8590 geometries under 30,000 cm^{-1}, with fitting σ_{rms} = 8.5E-7 a.u., or σ_{rms} = 3.8E-7 a.u. for 4443 geometries below 15,000 cm^{-1}. See Fig.1. The basis set for the O atoms was doubly augmented to help describe the polarization of the molecular orbitals due to an external field. The impacts of *ab initio* methods, geometry sets, and energy cut offs are investigated to ensure the stability and convergence of the Ames-2021 DMS. Using the best available PES for CO_2, Ames-2, new theoretical IR intensities ($S_{Ames-2021}$) have been computed and compared to reference experimental data and other databases or line lists.

Compared to the CRDS intensity[36,38] that the NIST group reported with high accuracy in 2019 and 2020, the Ames-2021 intensity has reached an -1.0±1.3‰ agreement for the 20013 and 30012/3/4 bands, or -0.8±1.0‰ agreement with $S_{NIST-HIT16}$ (|*m*|≤30). The mean differences of $S_{NIST-HIT16}/S_{Ames}$ for the two OCO-2 bands, 20013 and 30013, are 1.4‰ and 2.2‰, respectively. Such consistency should be good for the OCO-2 mission data analysis. In *R*12+*R*18 based comparison with $S_{NIST-HIT16}$, the mean deviation was reduced by 85~90%, from the DMS-N2[42] based $S_{Ames-2016}$ (-6.8‰ ± 1.5‰) to Ames-2021 DMS based $S_{Ames-2021}$ (-0.85±1.04‰). Compared to $S_{UCL2021}$[39] (-0.63±4.96‰) and $S_{UCL-296}$[27,31,32] (0.95±6.59‰), the uncertainty is also reduced by 80-85%, i.e., more than half an order of magnitude. The larger uncertainty in S_{UCL} and $S_{UCL2021}$ was mainly attributed to the Ames-1 PES[23] used in their calculations, which is less accurate than the Ames-2 PES. As demonstrated, a less accurate PES ("X01d") raised the σ from 1‰ to 4‰.

The DLR 2021 FTIR study[40] in 6000 – 7000 cm^{-1} provided more reliable intensity ratios for 3001*i* bands. With respect to S_{DLR}, Ames-2021 intensities are 5‰ higher for 30012 and 30011 bands. The "mean±σ" of $S_{DLR}/S_{Ames2021}$ differences is 1.9±3.7‰. Due to the 3-5% deviations on 30011 band, the "mean±σ" of $S_{UCL2015}$ agreement was 15±20‰, which has been reduced to 10±14‰ in $S_{UCL2021}$. The Ames-2021 DMS still yields one of the best overall agreements with the $S_{DLR2021}$ intensity, including both 'mean' and 'σ'. Discussions in Section III.2.4 explain in detail why the Ames-2021 DMS is still our best choice and should be preserved. Another top candidate is the CCSD(T)/aug-cc-pwCVQZ level DMS fit. The ±0-2‰ intensity agreement for 30013 band between S_{DLR}, S_{NIST}, S_{Ames} and $S_{UCL-296}$ is also supportive for the OCO-2 mission. More accurate experimental studies are needed for the 30011 and 2001*i* bands, and $^{13}C^{12}O_2$, etc.

After the detailed comparisons with NIST and DLR studies, we feel more confident to claim that the $S_{Ames-2021}$ (296K) computed using the Ames-2 PES and Ames-2021 DMS gives the best theoretical intensities available for $^{12}C^{16}O_2$ and isotopologues, including sub-percent accuracy for many unperturbed bands below 8000 cm^{-1}. "Best" means least noise, smallest uncertainty, and best consistency. For example, excellent consistency for the $3\nu_3$ series. The weighted mean of S_{DLR}/S_{Ames} differences are -6.86‰ for 00031-00001, -0.91±0.25‰ for 01131-01101, and 4.95±5.93‰ for 10032-10002. See III.2 and III.4.4.

The impact of more accurate *ab initio* intensities ($S_{Ames2021}$) is evaluated for the VPDB $^{13}C/^{12}C$ ratio analysis reported in Fleisher et al.[39] Substituting $S_{UCL-2021}$[39] with $S_{Ames-2021}$, we get a new $^{13}C/^{12}C$ ratio of 0.011147±14. Compared to the published value, it is 2‰ higher with an uncertainty that has been reduced by 2/3. Further replacing S_{NIST} with S_{DLR}[40] for the 3001*i* bands, a second $^{13}C/^{12}C$ ratio is 1‰ lower than the published value, with 2/3 of the original uncertainty, i.e., 0.011112±30. Both new ratios are within the range given by Fleisher et al.[39] This evaluation confirms the value and reliability of the Ames-2021 theoretical intensity. Note that the cross-band, cross-isotopologue intensity consistency is largely an unexploited territory.

The accuracy and consistency of $S_{\text{Ames-2021}}$ is further assessed upon analysis of the vibrational bands highlighted in the recent HITRAN2020 update.[33,41] See the list of findings at the end of Section III.4. The consistency of $S_{\text{Ames-2021}}$ and the improvements over $S_{\text{Ames-2016}}$[18] are truly remarkable, except for those bands affected by Coriolis interactions. The permille level agreement with S_{DLR} and S_{NIST} is not accidental. Such accuracy and consistency have overwhelmed the old *ab initio* intensities computed using Ames-1 PES[23] (less accurate), Ames DMS-N2[42] (less accurate) or UCL DMS 2015[34] (less accurate and potentially contaminated) and UCL DMS 2021[39] (partially improved upon DMS 2015). For the benefit of high-resolution IR line list databases and atmospheric or spectroscopic studies, the Ames-2021 DMS should be adopted for future CO_2 IR intensity calculations, and Ames-2021 intensity is recommended for most vibrational bands and minor isotopologues. For example, the S_{Ames2021} for certain bands are better inputs for the scaling to match highly accurate experiments. The latest CDSD or experimental intensities are recommended for the bands perturbed by Coriolis interactions, or the bands with large discrepancies confirmed.

The most important lesson we have learned from this study is: to achieve 0.1% (or 1‰) consistency and accuracy for the intensity of multiple bands, it absolutely requires both the *best* PES and the *best* DMS. They are not available yet, but Ames-2021 DMS is the closest one (for now) on the right path towards 0.1%. This probably will take at least 2-3 rounds of major improvements on the current Ames-2 PES and Ames-2021 DMS to make the permille level agreement available for most medium to strong bands up to 10,000 cm^{-1}, excluding Coriolis coupling affected ones. The improvements must be global and consistent, not some patches or fixes on specific bands or lines. Although the PES accuracy is regarded as the principal factor limiting the uncertainty of current theoretical intensities, please remember it is very hard to predict the impacts on an individual band or line, especially in the sub-percent arena.

Today, only a limited number of $^{12}C^{16}O_2$ IR bands have their intensities measured with sub-percent accuracy, and even less with uncertainty less than 2-3‰. But there are many reasons to feel optimistic about the future synergy between experiments and theories. In next 10-20 years, theoreticians expect that more accurate CO_2 PESs, DMSs and line lists will benefit from new experimental data acquired on higher energies, weaker bands, higher temperatures, and minor isotopologues.

The Ames-2021 DMS, Ames-2 PES, and 296K IR line lists are reported as supplementary files, and available at huang.seti.org.

Supporting Information:

Supplementary files associated with this article include: 1) Ames-2 PES, Ames-2021 DMS subroutines and coefficient files; 2) Ames-2021 296K IR intensity of 00031, 2001*i* and 3001*i* bands, with 100% abundances for the 4 most abundant isotopologues (626, 636, 628, 627); 3) Ames-2021 296K IR line lists for 626, 636, 628, and 627, with 100% abundances; 4) Ames-2021 296K IR line list for "natural" CO_2, using terrestrial abundances for 13 isotopologues; 5) ORIGIN project file containing all the figures and data analysis presented in this paper, please use Origin Viewer to open and extract data. All these files can be found online at https://doi.org/10.1016/j.jqsrt.2022.xxxxxx (to be updated).

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Table 1. List of recent theoretical studies for CO_2 semi-empirically refined PES, *ab initio* DMS, intensity and IR line lists. Cutoffs are for intensity (cm/molecule) and transition wavenumber range, e.g., 8K for 8000 cm^{-1}. Note the UCL DMS 2021 based line list is not publicly available.

Table 2. Partial list of high accuracy CO_2 IR intensity measurements. Those in bold are used in this work.

Table 3. Comparison of the Ames-2021 DMS with the Ames DMS-N2, the UCL DMS 2015 and the 2021 update.

Table 4. Statistical difference between $S_{Toth2008}$, scaled $S_{UCL/HIT16}$, scaled S_{Ames}, and S_{Ames} for 3001*i* and 00031 bands, $|m| \leq 30$.

Table 5. Weighted average, or "mean", of the relative intensity differences $(S_1/S_2-1)\cdot 1000$‰ for 6 bands measured in NIST and DLR studies. In parentheses are the numbers of corresponding transitions. Statistics for a row is given in first column, as 'mean±σ'. All values are in permille (‰).

Table 6. Intensity comparison for $^{12}C^{16}O_2$ 4003*i*-00001 (*i*=2-4) bands. All values are in 10^{-29} cm/molecule.

Figure 1. Grid point distribution and fitting deviations of the Ames-2021 DMS, along the increasing energy.

Figure 2 (*a*) $S_{Ames2021}$ vs. $S_{NIST\text{-}HIT16}$ intensity comparison for 4 CO_2 IR bands, with unweighted mean$\pm\sigma_{rms}$ of $(S_{Ames}/S_{NIST\text{-}HIT16}-1)\cdot 1000$. Note $S_{NIST\text{-}HIT16}$ (or S_{HIT20}) was the S_{HIT16} intensity scaled with the β values reported in Long et al (2019)[38] and Fleubaey et al (2020)[36]. Part of the fluctuations in this plot are because UCL-296 and HITRAN provide only 4 significant figures for the intensities. (*b*) measured S_{NIST} vs $S_{Ames2021}$ intensity comparison for 4 CO_2 IR bands, with weighted mean$\pm\sigma_{rms}$ of $(S_{NIST}/S_{Ames}-1)\cdot 1000$. The S_{NIST} and relative uncertainty associated with a specific transition was the weighted average from multiple measurements. See text for more details about weights and uncertainties.

Figure 3. Calc vs Expt ($S_{NIST\text{-}HIT16}$) intensity agreement for selected Ames DMS fits. The number of points in the geometry sets at corresponding energy cutoffs are: 30KS – 2320 or 2531 pts; 30KL – 7667 pts; 30KF – 8590 pts; 40KF – 11155 pts; 45KF – 12096 pts, where "30K" = 30,000 cm^{-1} above PES minimum and so on. Notations: "a(w)vxz" – aug-cc-p(w)CVXZ, "davxzO" – d-aug-cc-pVXZ basis on O atoms and aug-cc-pVXZ basis on C atom, *X*=T,Q,5; "2013" – the published surface DMS-N2; "rel" – relativistic correction at CCSD(T)/cc-pVTZ-DK level; "daug-O" – 2nd diffuse function effect on O atoms computed as the differences between the extrapolated (d-)aug-cc-pVXZ(O) dipoles and aug-cc-pVXZ dipoles, *X*=T,Q,5; "core" – all-electron correlation effects computed with specified basis or 2-point extrapolated aug-cc-pCV(T,Q)Z.

Figure 4. The NIST [Refs.36,38] and DLR (2021) [Ref.40] experiments vs. Ames-2021 theoretical IR intensities [this work] for the $^{12}C^{16}O_2$ 20013, 3001*i* and 00031 bands. The DLR data was downloaded from https://zenodo.org/record/6573418 on 05/23/2022. The $(S_{NIST}/S_{Ames}-1)\cdot 1000$ value at a specific *m* is averaged from multiple measurements with weights defined as the inversed squares of relative uncertainty.

Additional 0.05% system uncertainty was included for the band specific mean±σ statistics of S_{NIST}/S_{Ames}. Please note the Y-scale is in thousandth, or permille.

Figure 5. a) 00031 band (left) intensity comparison between S_{DLR}, S_{Ames}, S_{UCL}, $S_{DLR\text{-}UCL}$, and $S_{DLR\text{-}Ames}$; b) 30011 band (right) intensity comparison between S_{DLR}, S_{Ames}, S_{CDSD}, $S_{Toth2008}$, S_{HIT16} and S_{HIT20}.

Figure 6. Calc vs "Expt" intensity agreement for selected Ames DMS fits, including Ames-2021. $S_{'Expt'}$ uses $S_{DLR\text{-}HIT16}$ for 30012/3/4 bands, and $S_{DLR\text{-}Ames}$ for 30011 band. See Fig.3 for the notation details. The UCL2015 results are based on $S_{UCL2015}$ (30011) ≅ 1.052*$S_{HITRAN2012}$, , based on Fig.9 of Zak et al.[31]

Figure 7. (a) New uncertainty estimate using $S_{Ames\text{-}2021}$ with the experimental data cited in Fleisher et al[39], including PTB2021,[61] NIST2019,[38] NIST2020,[36] and DLR 2021.[40] Thick black lines are from the $S_{NIST/PTB}/S_{Ames\text{-}2021}$ comparison, and light grey lines are from the $S_{DLR/NIST/PTB}/S_{Ames\text{-}2021}$ comparison. The figure follows the style of Fig.S1 in Fleisher et al.[39] (b) New $^{13}C/^{12}C$ ratios derived with S_{NIST}, S_{DLR} (for $^{12}C^{16}O_2$ 3001*i* bands) and $S_{Ames\text{-}2021}$ (for $^{13/12}C^{16}O_2$), compared to the Fleisher et al value and other reference values therein. The figure follows the style of Fig.3c in Fleisher et al.[39] See text for details.

Figure 8. $^{12}C^{16}O_2$ 40002 – 01101 band comparison between the Toth et al (2008)[70] model and 4 line list databases. See text for details.

Figure 9. $^{12}C^{16}O_2$ 21113 – 11102 band comparison. HITRAN2020 (or CDSD2019) vs line lists and experiments : Borkov *et al* (2014, measured, 2 lines out of range),[73] and Benner (2003, fitted, magenta for *Q* branch).[74] See text for details.

Figure 10. 21113-01101 band intensity comparison. (a) 5 line lists vs. Toth 2008 et al[70]; (b) 4 line lists vs. $S_{Ames\text{-}2016}$ (taken as $S_{HITRAN2020}$).

Figure 11. 11101-00001 and 11102-00001 band intensity comparison: line lists (database) vs Tanaka et al.[75]

Figure 12. Intensity comparison with respect to HITRAN2020. (a) 12202-01101; (b) 20003-01101.

Figure 13. (a) $^{12}C^{16}O_2$ IR simulation at 300K, UCL-4000[50] vs Ames-2021, including all lines with S_{300K} > 1E-36 cm/molecule. See text for details. (b) Assignment of the irregular intensity peaks in UCL-4000, including UCL-4000 lines with S_{300K} > 5E-31 cm/molecule, and Ames-2021 lines with S_{296K} > 1E-33 cm/molecule, E'<19,500 cm^{-1}, and E'-E"<18,000 cm^{-1}.

Figure 14. $^{12}C^{16}O_2$ 10032-10002 band intensity comparison at 296K, line lists and databases vs DLR2021.[40]

Figure 15. $^{12}C^{16}O_2$ 01131-01101 band intensity comparison: 5 line lists vs DLR 2021,[40] in full range (*a*) or ±2% range (*b*). The $\delta\%_{Ames2016}$ in panel *b* only includes *P* lines with odd *J*" and *R* lines with even *J*".

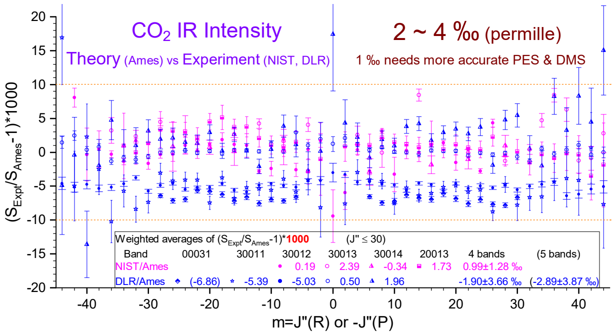
Figure 16. Comparison of experimental data and $S_{Ames2021}$ with respect to $S_{HITRAN2020}$ (using $S_{Ames2016}$): (a) $^{16}O^{12}C^{18}O$ 30022 and 30023 bands; (b) $^{12}C^{16}O_2$ 00041-01101 band.

Figure 17. $^{12}C^{16}O_2$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance for the *Q* branch; experimental data (Expt 2018) was taken from Cěrmak et al (2018);[84] (*b*) δ% differences with respect to $S_{Ames2016}$ (or $S_{HITRAN2020}$).

Figure 18. $^{12}C^{16}O^{18}O$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance; (*b*) δ% difference with respect to $S_{HITRAN2020}$ (or $S_{Ames2016}$).

Figure 19. $^{13}C^{16}O_2$ 41104-00001 intensity comparison. (*a*) absolute intensity with terrestrial abundance; (*b*) δ% difference with respect to $S_{HITRAN2020}$ (or $S_{Ames2016}$). Experiment: Karlovets et al (2018).[20]

TOC Graphic



100% size (8.25 cm x 4.45 cm)