



Utilizing Experimental-based Line Positions for Semi-empirical IR Line Lists

- Highlights of Ames BTRHE Line Lists for CO₂, N₂O, CS₂, OCS
 - What we learned: OCS and N₂O examples

Prediction-oriented, Consistency-based

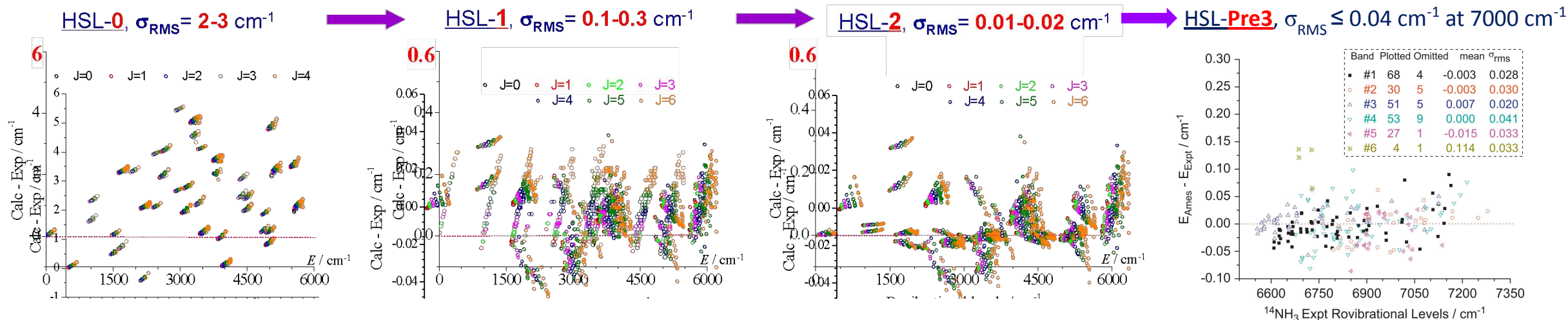
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Theory + Experiment ☐ BTRHE IR Line Lists



☐ Best Theory + Reliable High-resolution Experiment ☐ Prediction oriented

Complete, Reliable, Consistent predictions for missing bands, weak bands, and isotopologues
accuracy and consistency across isotopologues, J, and vibrational band series

- ☐ *ab initio* potential energy surface (PES) refinement ☐ $\sigma_{\text{rms}} = 0.01\sim 0.04 \text{ cm}^{-1}$ ☐ *Experimental energy levels*
- ☐ High quality *ab initio* dipole moment surface (DMS) ☐ intensity prediction accuracy within a few percent
- ☐ PES accuracy and DMS accuracy are equally important for sub-pct intensity prediction accuracy



Expt-based Position : Need Correct Matches

- Integrate theoretical IR intensities predictions with experimental based line positions
- require **correct match** between:
 - Theoretical energy levels calculated on a refined PES
 - Empirical energy levels derived from experiments and models (e.g., RITZ, MARVEL)
- Measured data (Expt/Obs/EH) □ overall easy, state by state, case by case
 - Global EH models □ difficult, program-aided, molecule/model/PES-dependent
- We prefer **accurate and consistent** empirical energy levels, or corrections
- We have tried several different approaches on different molecules, under different scenarios, for different purposes
 - e.g., (simplest) three SO₂ lists: Ames + Obs line pos; Ames + EH levels; Ames + MARVEL levels.
 - e.g., mass-dependent corrections on EH(Ames) parameters for SO₂ minor iso (MW)

Ames BTRHE IR Line Lists (2017 – 2024)

CO₂

- Ames-2016 (13 iso) Huang, Schwenke, Freedman, & Lee, *JQSRT* (2017) 203:224 (*Ames-2 PES & DMS-N2*)
- Ames-2021 (13 iso) Huang, Schwenke, Freedman, & Lee, *JPCA* (2022) 126:5940 (*Ames-2 PES & DMS-2021*)
- AI-3000K** (4 iso) Huang, Freedman, Tashkun, Schwenke, & Lee, *JMSpec* (2023) 392:111748 (*X01d + DMS-2021-40K*)

SO₂

- Ames 296K (5 iso) Huang, Schwenke, & Lee *JQSRT* (2019) 225:227 ; MW line list (30 iso) *JQSRT* (2019) 230:222

N₂O (12 iso)

- Ames-1 296K Huang, Schwenke, & Lee *Mol.Phys.* (2023), e2232892 (Tim Lee Memorial Issue)
- ABG-IMRHT** (*paper in preparation*) and **AI-1000K**

CS₂ (20 iso)

- Ames-296K (20 iso) and **A+I.296K** (1 iso)
Huang, Gordon, Tashkun, Schwenke, and Lee, *ApJS* (2024) 272,17

OCS (12 iso)

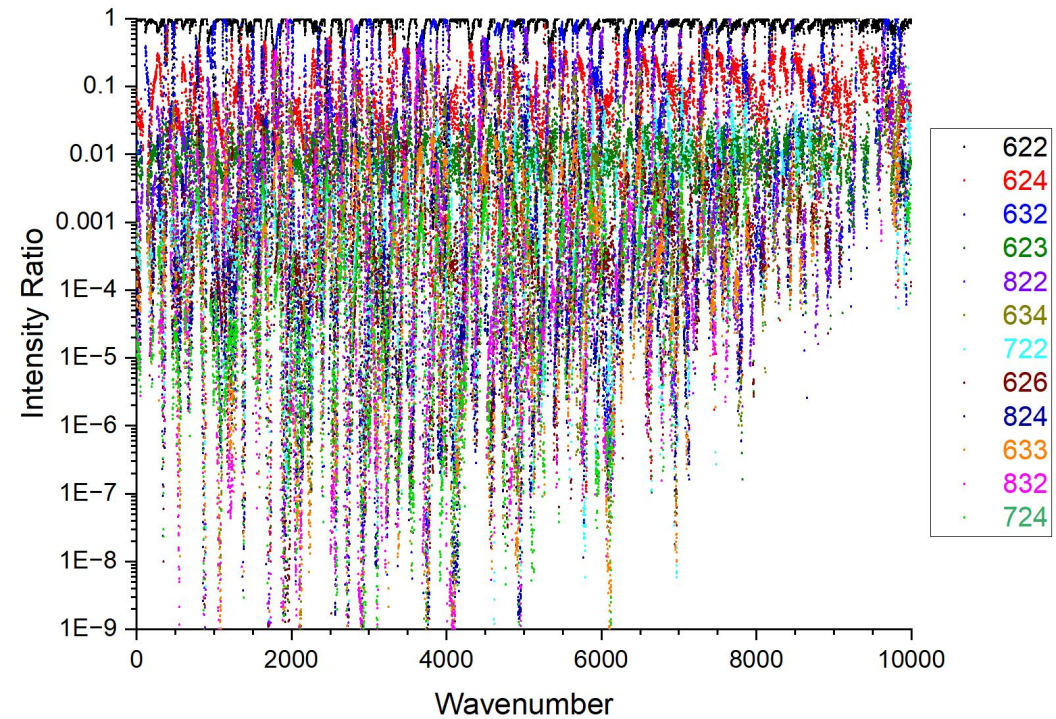
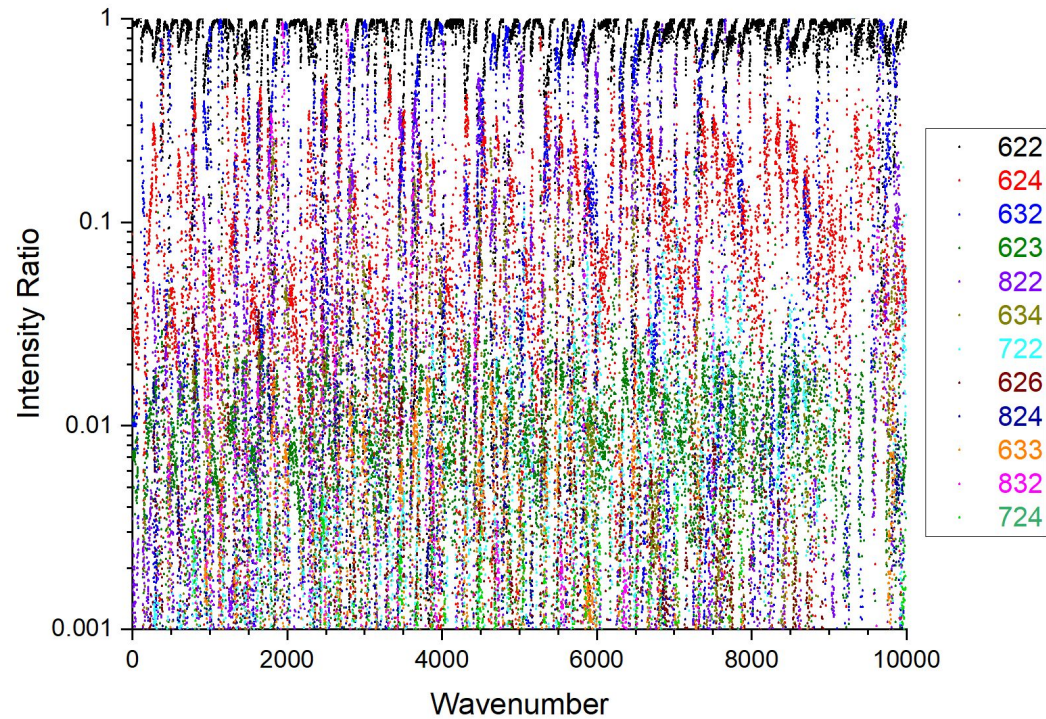
- Ames-1 296K line list: online available 11/2021 (AMSD), reported in 75th ISMS (06/2022).
- Ames-2024** (*paper in preparation*) and **Ames-1000K**



Dr. Timothy J. Lee (1959-2022)



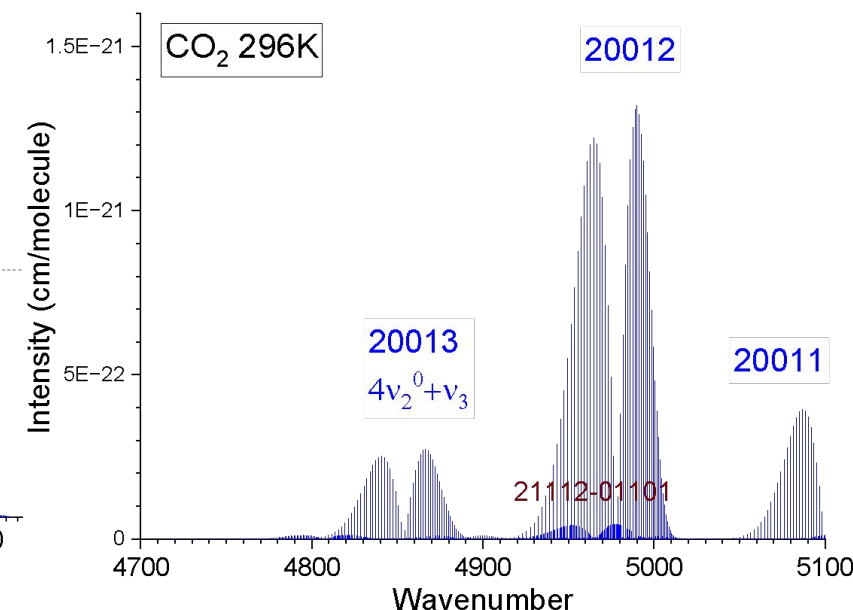
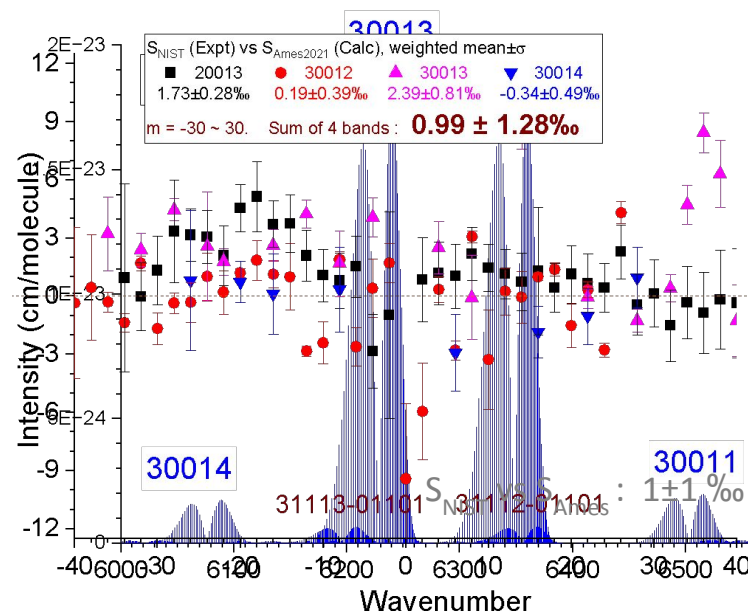
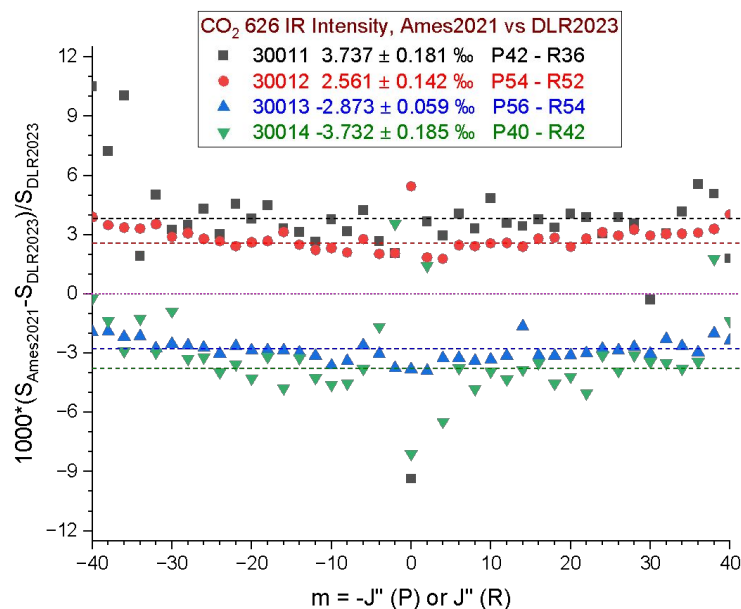
Isotopologue Contributions : OCS Example



Minor isotopologue IR absorptions may dominate certain cm^{-1} ranges: e.g., 832 (#11) under 3000 cm^{-1}

CO₂: 2-4‰ for OCO bands (Ames-2021)

- ✓ CCSD(T)/CVQZ+0.5ACPF/VTZ PES refined using pure experimental levels ($\sigma_{\text{rms}} = 0.02 \text{ cm}^{-1}$) + CCSD(T)/CBS DMS
- ✓ 2-4 permille agreement for 2001*i* and 3001*i* bands (DLR 2023, 0.2% larger than DLR 2021, new $u_{\text{sys}} < 0.06\%$)

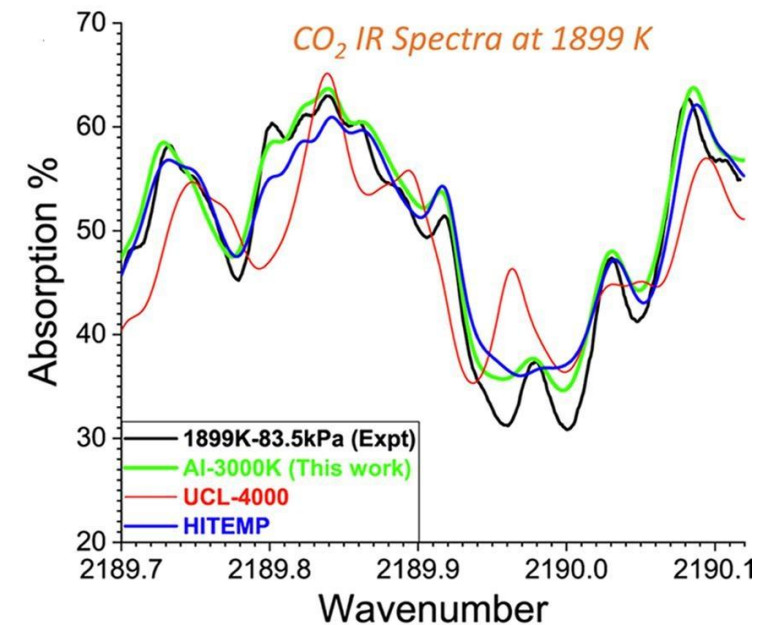
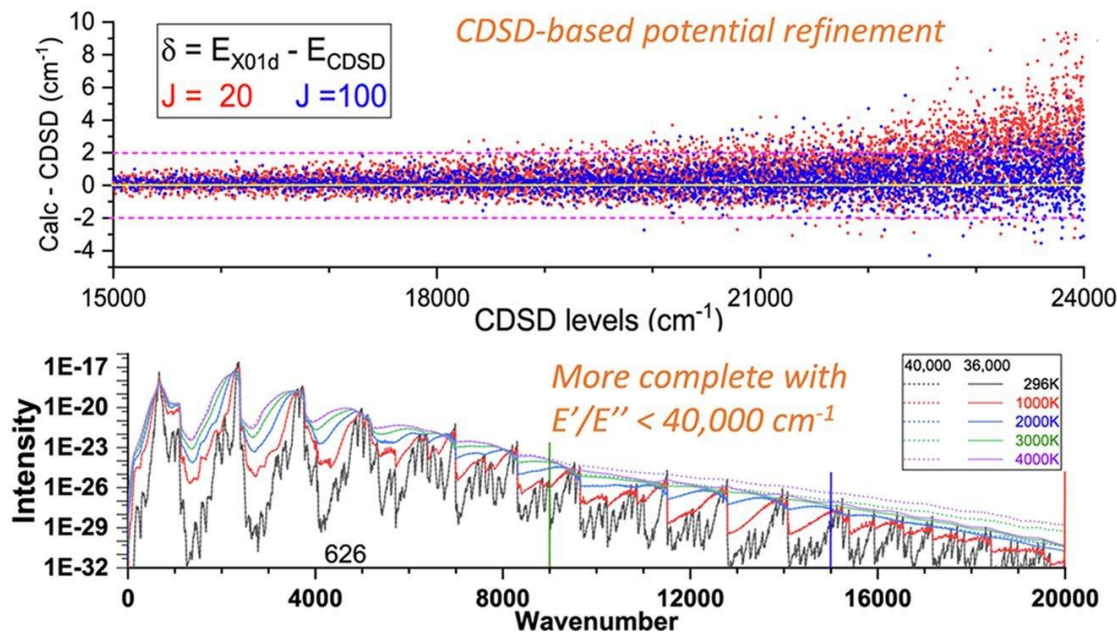


- ✓ Use CDSD-2019 global EH model energies
 - More efforts are needed for accurate ν_2 intensity (2%), or at $0.7 \mu\text{m}$ --- require more accurate PES & DMS

Hot CO₂: from Ames-1000K to AI-3000K

✓ Ames + IAO (CDSD global EH model) □ new PES refinement (X01d) using CDSD levels

(X01d + Ames-2021-40K) line list + (Ames-2 + Ames-2021) A_{21} + CDSD Energy levels = AI-3000K
 Upgraded Reliable IR Prediction More Accurate IR Intensity Accurate Line Position for hot CO₂

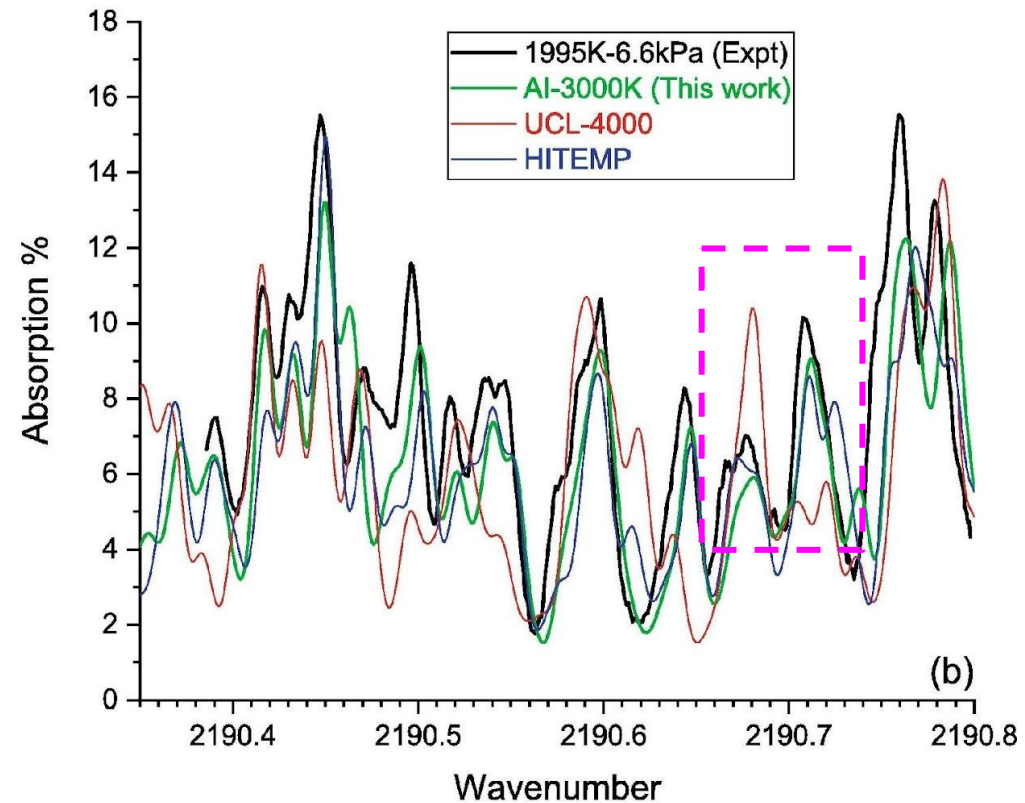
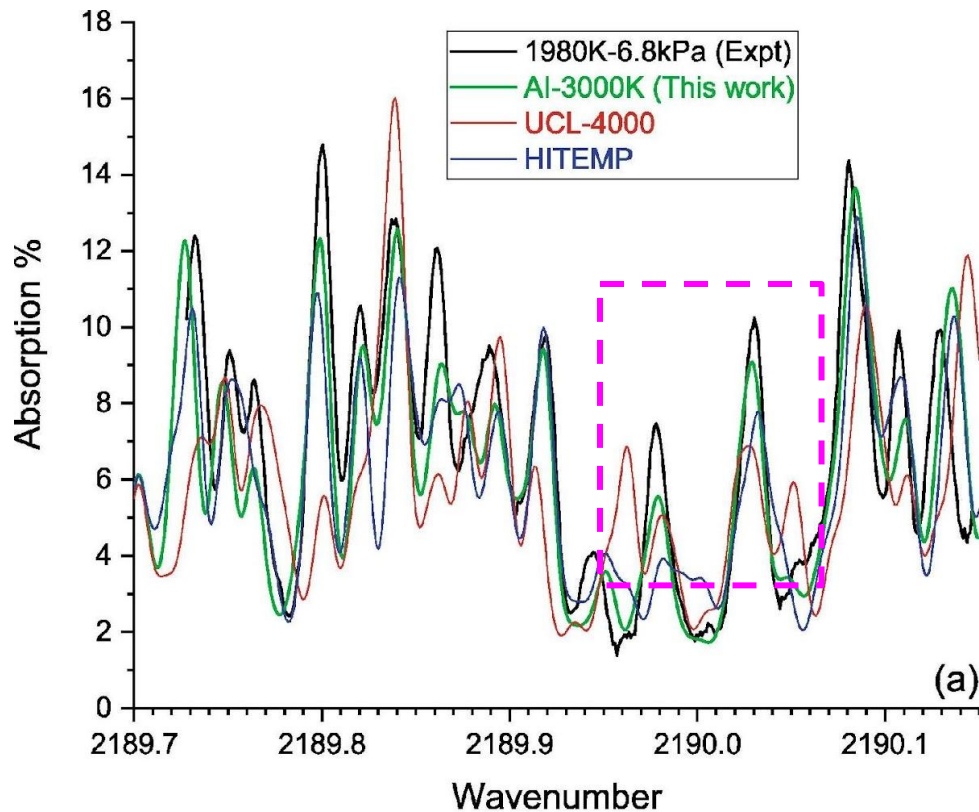


- Next: Ames-3 PES; $\log(A_{21})/\sqrt{0.001 \cdot E/1000}$ test beyond 0.8 micron; etc.



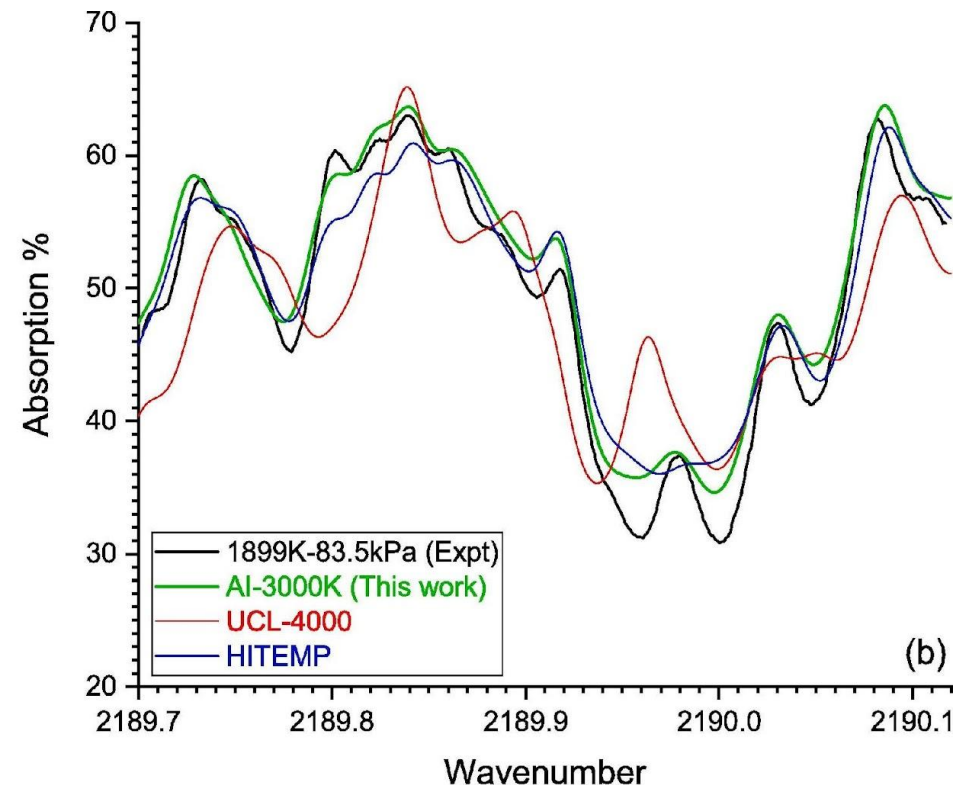
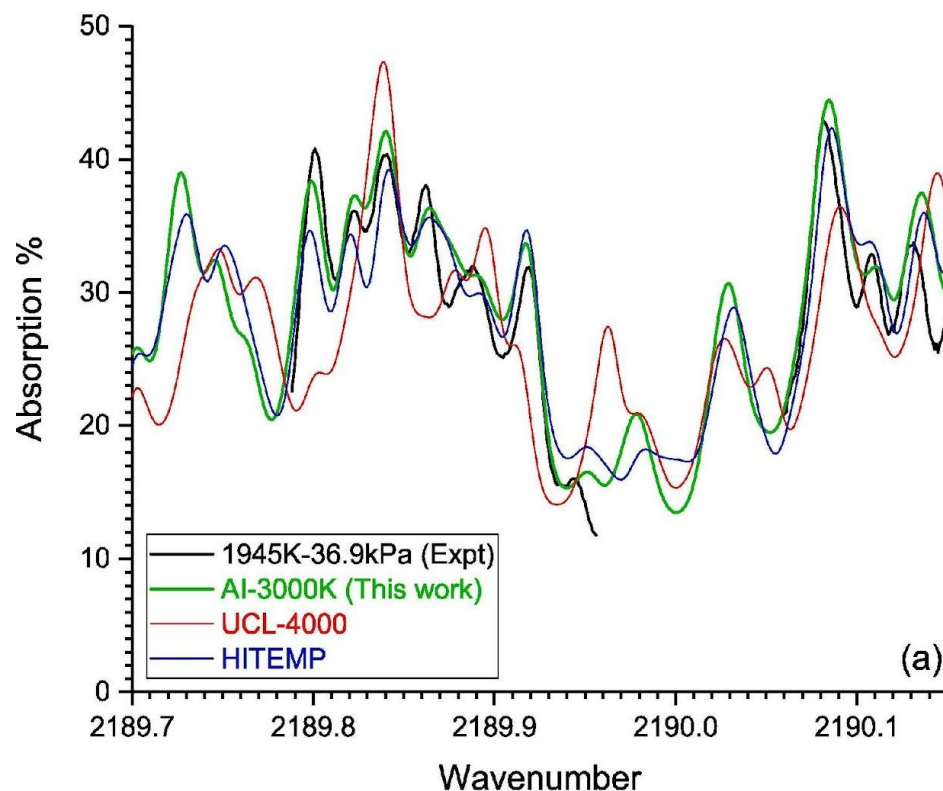
Hot CO₂: AI-3000K vs Experiment at 2000K

Shock tube IR spectra (Expt, black) compared to AI-3000K, UCL-4000, and HITEMP



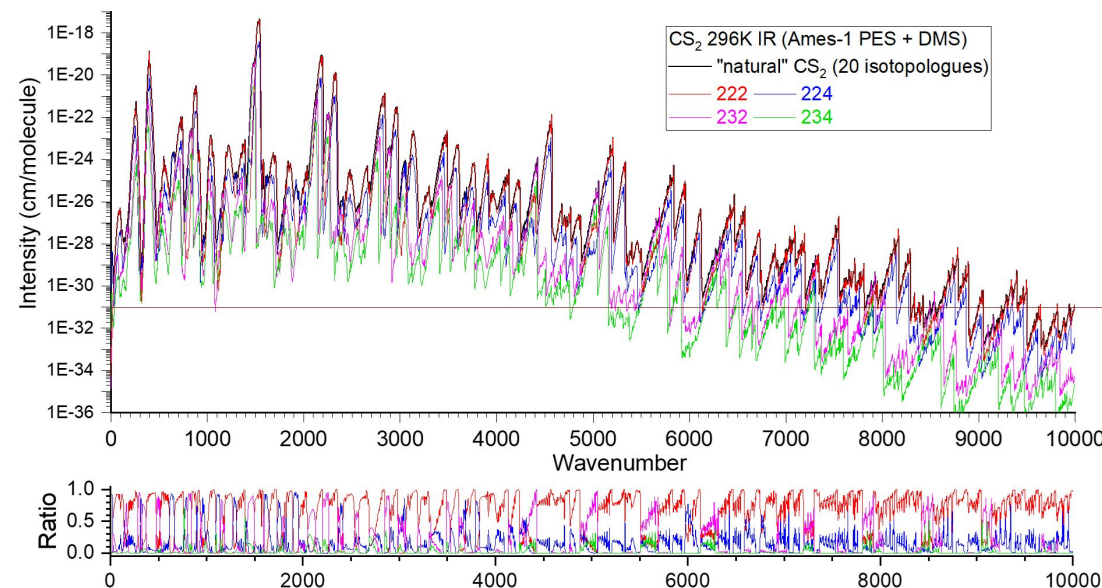
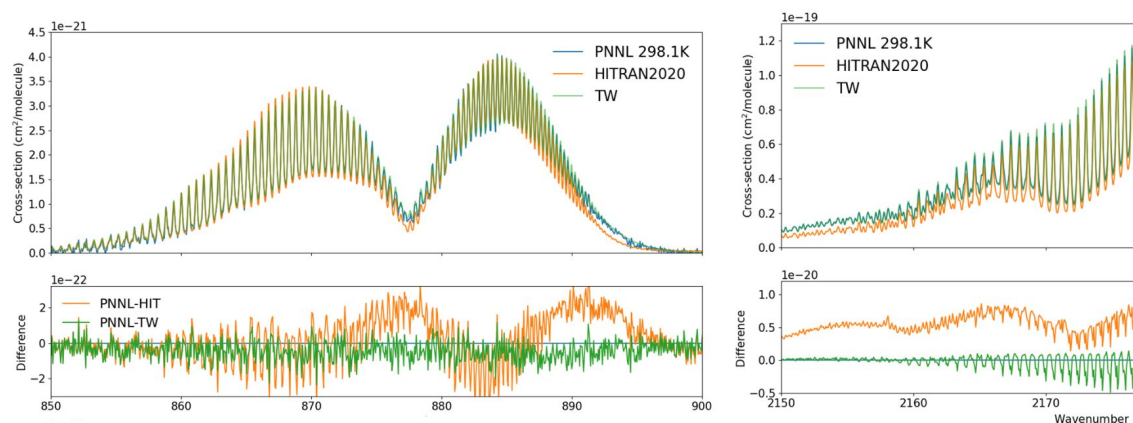
Hot CO₂: AI-3000K vs Experiment at 2000K

For high temperature line list, refining PES with respect to reliable global EH models (if available) is a good choice
but it will sacrifice the quality at low energy, so need A_{21} from a more accurate room-temp line lists



CS₂ : natural list (20 iso) & A+I.296K (¹²C³²S₂)

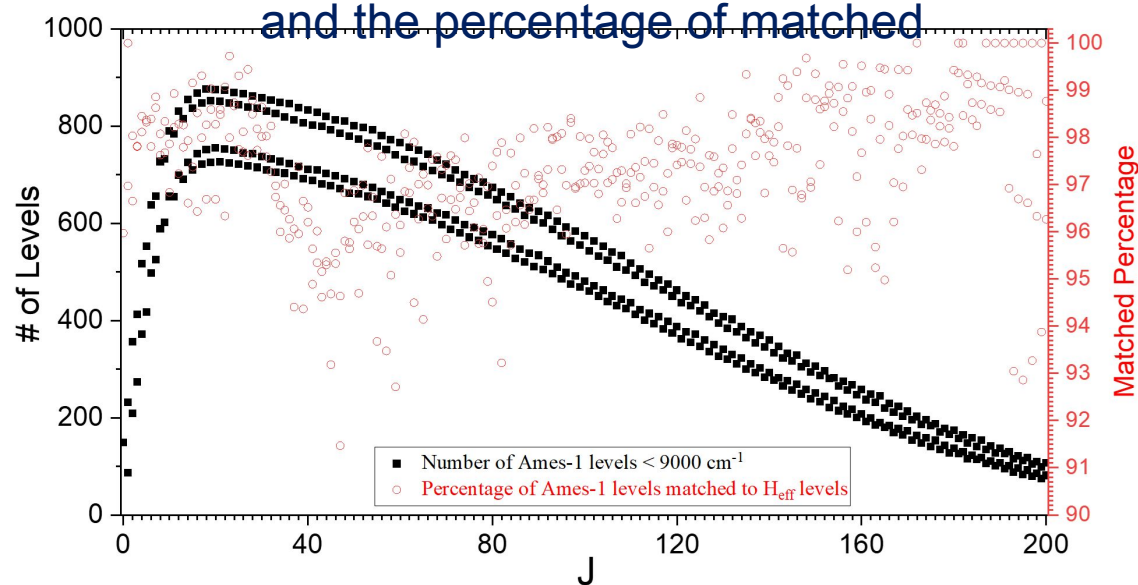
- ✓ CCSD(T)/aug-cc-pV(Q+d)Z PES refined using HITRAN experimental data collection, $\sigma_{\text{rms}} = 0.017 \text{ cm}^{-1}$
- ✓ CCSD(T)/aug-cc-pV(T/Q/5+d)Z DMS, $\sigma_{\text{rms}} = 6.0 \times 10^{-6} \text{ a.u.}$, 0 – 20,000 cm⁻¹
- ✓ Line list (20 isos): J=0-200, E' < 13,700 cm⁻¹, S_{296K} > 10⁻³¹ cm⁻¹/molecule.cm⁻², 0 – 10,000 cm⁻¹,
- ✓ ¹²C³²S₂ (A+I.296K) : Ames + IAO Global EH Model; Use reliable E_{HITRAN} for iso 224, 223 and 232.
- ✓ Validation against PNNL cross-sections.
- ✓ Next: PES refinement at higher energies



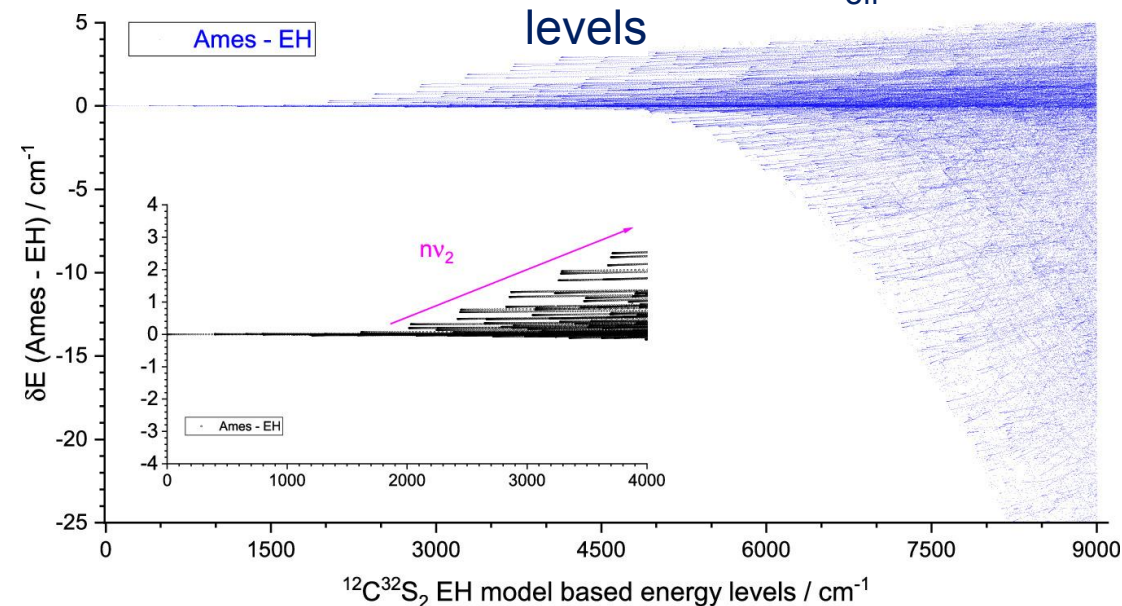
Use Global EH Model: $^{12}\text{C}^{32}\text{S}_2$

Number of $^{12}\text{C}^{32}\text{S}_2$ levels below 9000 cm^{-1}

and the percentage of matched



Energy difference between
Ames-1 PES based levels and H_{eff} model
levels



- We need a program to match E_{ames} and EH levels:
easiest one, ~ 1 month, iterative fix/check, v_3 quanta helps
- Different priority, criteria, and matching strategies

OCS : Ames-1 (11/2021) Ames-2024

Determine Consistent and Accurate Line Positions
for the Ames-296K OCS IR Line List

- Ames-296K line list
- Compare to experiments and datasets
- How to use CDMS + HITRAN + MARVEL data

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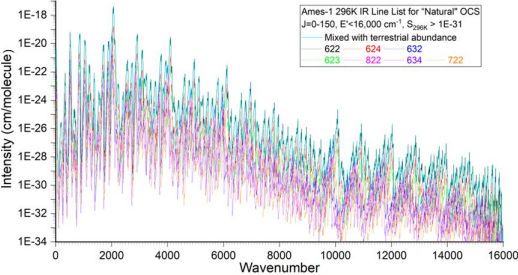
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TH04 06/18/2024

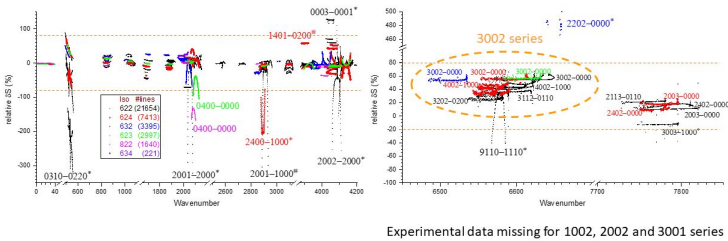
A “natural” OCS line list: 7 isotopologues



Ames-1 based, 0 – 16,000 cm ⁻¹ , iso lists: S _{296K} > 1E-36 (100%) “natural” list: S _{296K} > 1E-31		
Iso	Abundance	# lines
622	0.937395	2,803,468
624	0.0415828	1,374,314
632	0.0105315	1,062,057
623	7.39908E-3	893,896
822	1.87967E-3	654,976
634	4.67176E-4	485,770
722	3.49539E-4	416,931
Sum	0.999604765	7,691,412

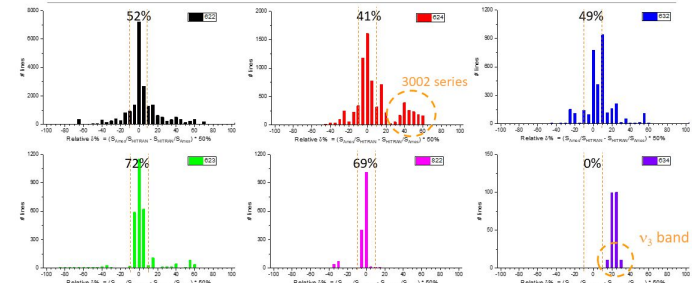
Ames-1 PES, DMS and 296K “natural” line list are available at <http://huang.seti.org>

Line Intensity: Ames-1 vs HITRAN (6 isos)



Experimental data missing for 1002, 2002 and 3001 series

Line Intensity: Ames-1 vs HITRAN (6 isos)



Percentage of relative $|\delta\%| < 10\%$

- PES: CCSD(T)/aug-cc-pV5Z, refined with HITRAN levels, $\sigma_{\text{rms}} = \mathbf{0.007\text{ cm}^{-1}}$
 $\sigma_{\text{rms}} \approx \mathbf{0.01\text{ cm}^{-1}}$ for E_{MARVEL} subset; $\pm 0.01\text{-}0.02\text{ cm}^{-1}$ for obs bands $> 10,000\text{ cm}^{-1}$
- DMS: CCSD(T)/aug-cc-pV(T/Q/5+d)Z, 0 – 20,000 cm⁻¹, $\sigma_{\text{rms}} = 5.8 \times 10^{-7}\text{ a.u.}$
DMS-2024: 12,000 dipoles, 0 – 15,000 cm⁻¹, $\sigma_{\text{rms}} = \mathbf{1.35 \times 10^{-7}\text{ a.u.}}$
- 296K line lists: J=0-150, E’<16,000 cm⁻¹, S_{296K} > 10⁻³¹ cm⁻¹/molecule.cm⁻²
- 1000K line lists (2023): E’< 22,500 cm⁻¹, S_{296K} > 10⁻³³ cm⁻¹/molecule.cm⁻²
- “natural” 296K list (2024): 12 most abundant isotopologues, 9.1 million lines
- **Ames-2024:** HITRAN & Ames-vs-MARVEL comparison-based line positions

OCS: Identify outliers, Correct assignments

Accuracy and consistency across isotopologues*, J, and vibrational band series

HITRAN (partially from Toth 2010 list or JPL list for HITRAN2008):

IR intensity issues

- 623 22⁰1-10⁰ intensity, overestimated by 40 times
- 822 04⁰0-00⁰ intensity, overestimated by 220%
- 622 00⁰3-00⁰1 intensity, underestimated by 65%
- 622 03¹0-02²0 intensity, overestimated by 320%

Line Position / energy level:

- 622 5002 levels, off by 0.384 cm⁻¹
- 624 2001 (J=83-93) and 623 2001 (J=74-81): non-matchable
- 622 4112 and 9110 levels, off by ~0.10 cm⁻¹;
7440 J=29 doubly assigned (from Expt 2014);
- 632 3800 J55e doubly assigned, 1440 J58e misassigned to 1001;
- 623 J=5/6 levels, off by 0.02-0.05 cm⁻¹
- EH model over extrapolations:

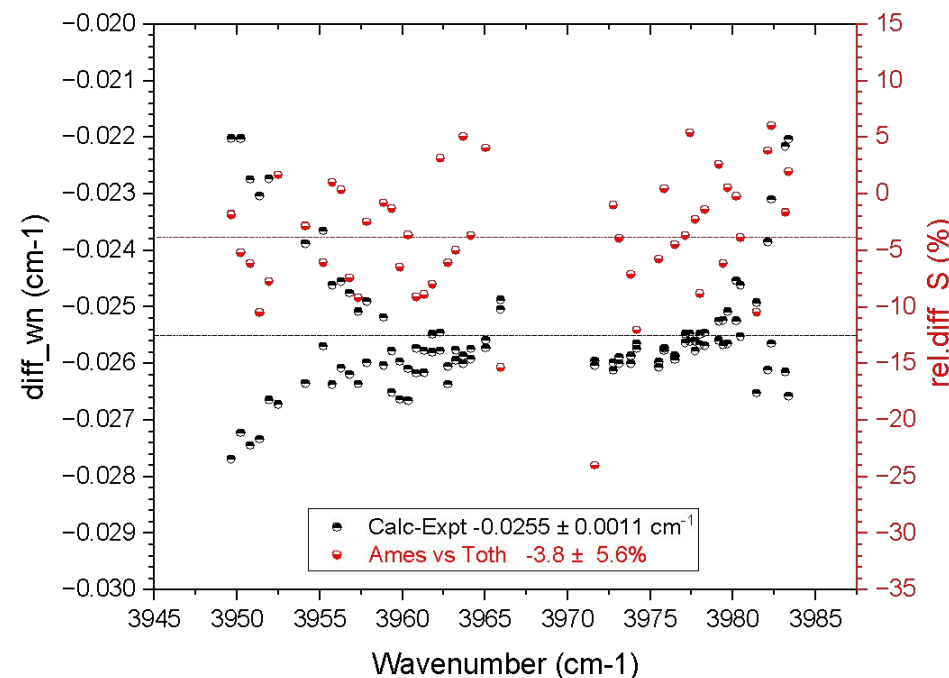
622 0002, 0421, 1002, 1201, 1401, 1421, 2002, and 2113

* Huang, X.; Schwenke, D. W.; Lee, T. J. JQSRT (2019) 230:222; HITRAN2020: Gordon, I. E., Rothman, L. S., Hargreaves, R. J., et al. JQRTS (2022) 277:107949

Toth 2010: Toth, R. A., Sung, K., Brown, L. R., & Crawford, T. J. JQSRT (2010) 111:1193

622 90⁰0-00⁰ band in Toth 2010 is 632 02²2-02²0

¹⁶O¹³C³²S 02²2-02²0, Ames (This work) vs Toth (2010)



-5 ± 5% difference between S_{Ames} and S_{Toth}

N₂O : from Ames-296K to ABG-IMRHT

Ames-1 296K IR Line Lists for N₂O Isotopologues

1. Background
2. Methodology
3. Results & Comparison
4. Future work

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TC05 06/21/2022

Accurate IR Intensity Prediction for N₂O Analysis as a Potential Biosignature Molecule in Planetary and Exoplanetary Atmospheres: *Uncertainty and Upgrades*

1. Ames-296K intro
2. Compare to Expt/NOSL-296
3. Unc Estimate
4. DMS Upgrade

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RL07 06/22/2023

More Accurate N₂O IR Line List Enhanced with Experimental-based Line Positions

1. Ames-296K Published
2. PES & DMS upgrades
3. Line Position Upgrades

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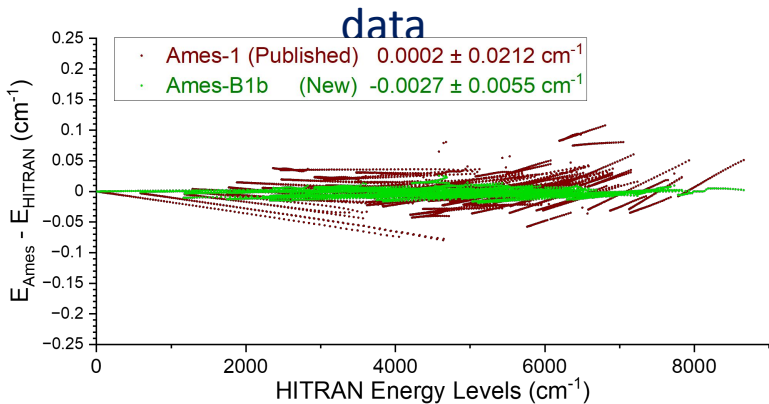
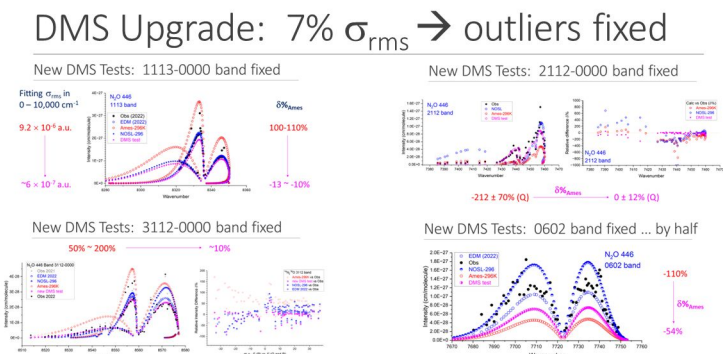
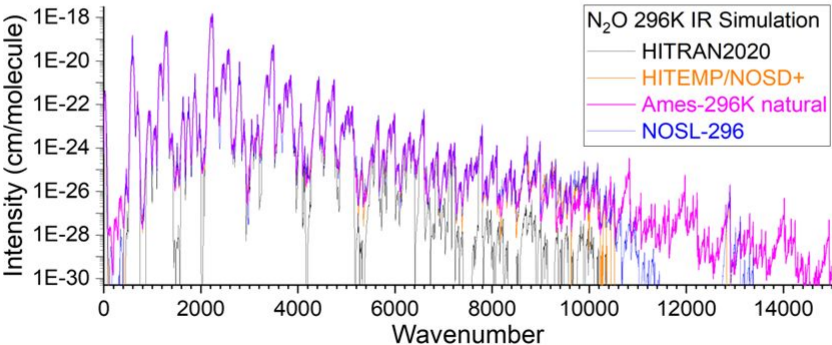
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WI04 06/19/2024

2021: HITRAN based PES refinement
CCSD(T)/aug-cc-pVT/Q/5Z DMS
 $\sigma_{\text{rms}} = 0.02\text{-}0.03 \text{ cm}^{-1}$, and $\pm 20\%$ (S_{296})

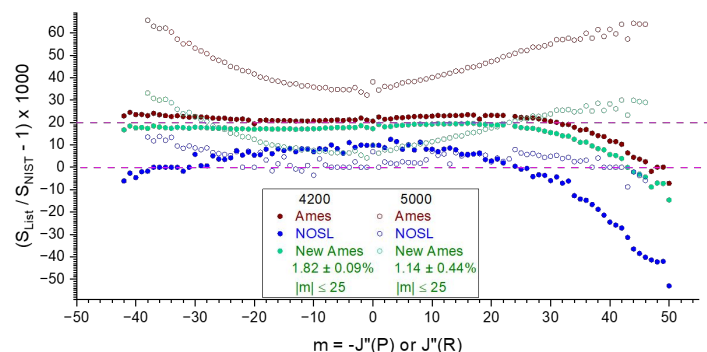
2023: Ames-296K published
vs. NOSL/Expt $\square$ DMS upgrade
Uncertainty estimate

2024: new PES (B1b) $\sigma_{\text{rms}} = 0.006 \text{ cm}^{-1}$
more accurate line pos and intensity
Use **IAO-MARVEL-RITZ-HITRAN-Toth**



N₂O : from Ames-296K to ABG-IMRHT

- ✓ 42⁰0 and 50⁰0 bands: 1-2%
Ames vs NIST 2021 (HITRAN2020)

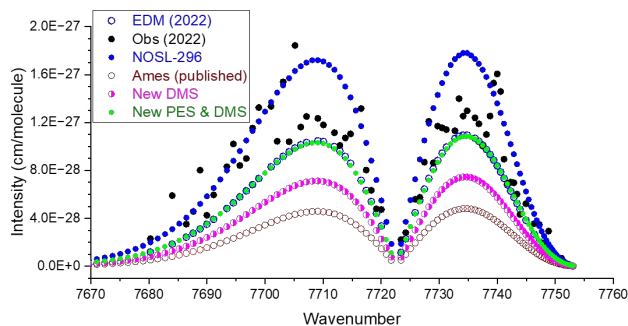


$\delta = 1.1\%$ and 1.8% vs S_{NIST}

All large $\delta S\%$ fixed

Good constraints on S_{Ames}

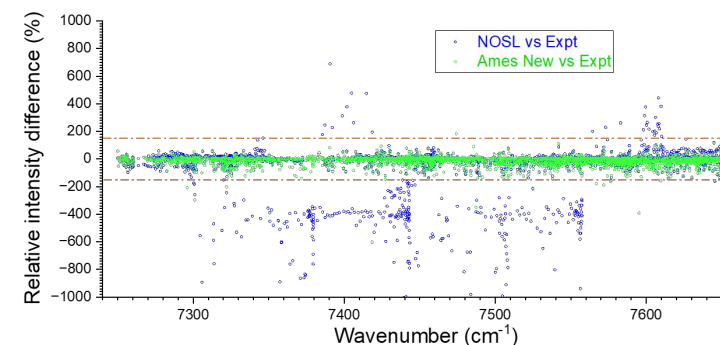
- ✓ 06⁰2 band: Ames vs Karlovets et al (2022)
-110% □ -54% □ better than NOSL



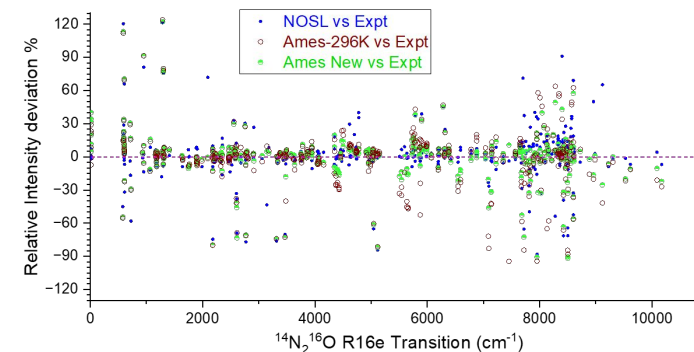
Most $|\delta\%| < 15\%$

Pure ab initio test
Medvedev test

- ✓ S_{Ames} and S_{NOSL} vs Karlovets et al (2023)
all outlier bands are fixed



- ✓ R16e intensity comparison
Ames vs NOSL vs Experimental data collection



N₂O : Line Pos & Intensity vs. HITRAN/JPL(Toth)

- Obs/EDM-based intensity in SISAM.n₂o list as adopted in HITRAN.

446 bands need attention:

$$1000-0110 \text{ PNNL} \approx S_A \approx 1.4 \cdot (S_N \approx S_H = S_T)$$

$$[S_{\text{HIT20}} = S_{\text{Toth}} \neq S_{\text{Ames}} \approx S_{\text{NOSL}}]$$

$$3000-2000 S_A \approx S_N \approx 3 \cdot (S_H = S_T)$$

$$0400-0310 S_A \approx S_N \approx 2.8 \cdot (S_H = S_T)$$

$$2220-1220 S_A \approx S_N \approx 2 \cdot (S_H = S_T)$$

$$2200-1200 S_A \approx S_N \approx 2 \cdot (S_H = S_T)$$

$$1331-0330 S_A \approx S_N \approx 0.5 \cdot (S_H = S_T)$$

$$0440-0330 S_A \approx S_N \approx 2 \cdot (S_H = S_T)$$

$$0441-0330 S_A \approx S_N \approx 0.5 \cdot (S_H = S_T)$$

$$0441-0440 S_A \approx S_N \approx 0.5 \cdot (S_H = S_T)$$

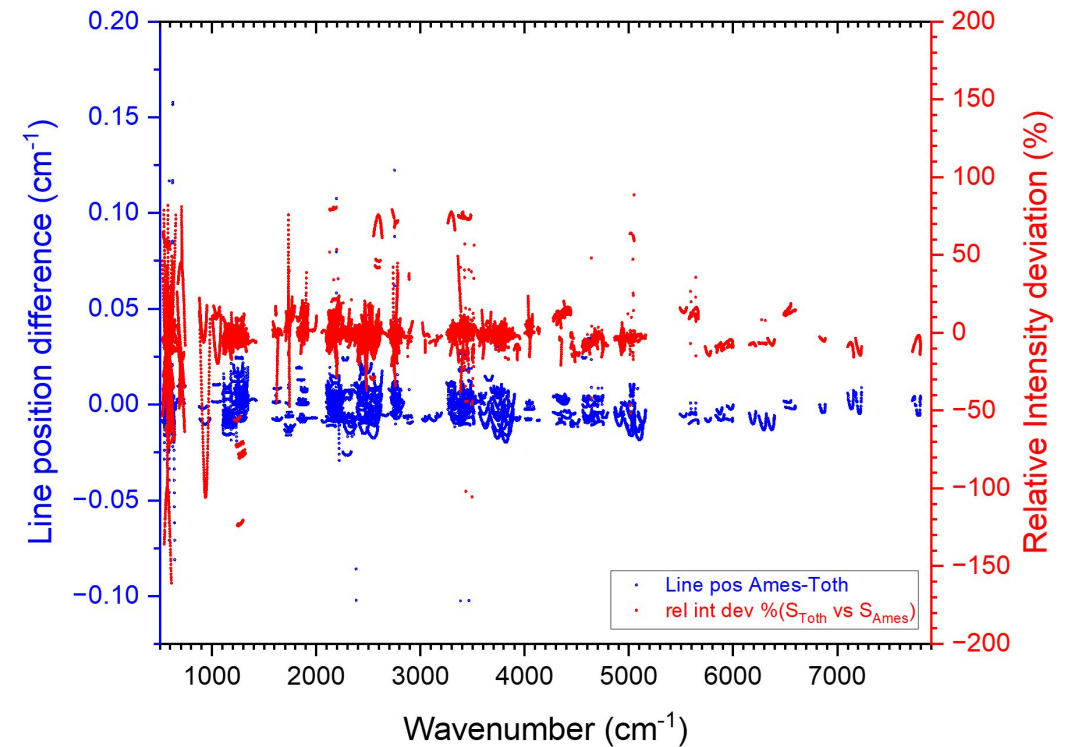
$$0420-0330 S_A \approx S_N \approx 0.6 \cdot (S_H = S_T)$$

$$0531-0330 S_A \approx S_N \approx 0.5 \cdot (S_H = S_T)$$

456 band needs attention

$$1201-1000 S_H = S_T \approx 40 \cdot S_A$$

- High consistency across isotopologues and band series
- identify unreliable data and issues



447 1111-0110 lines (66); 456 1201-1000 lines (17)

The synergy between theory and experiment has allowed us to identify unreliable data and issues in expt and datasets

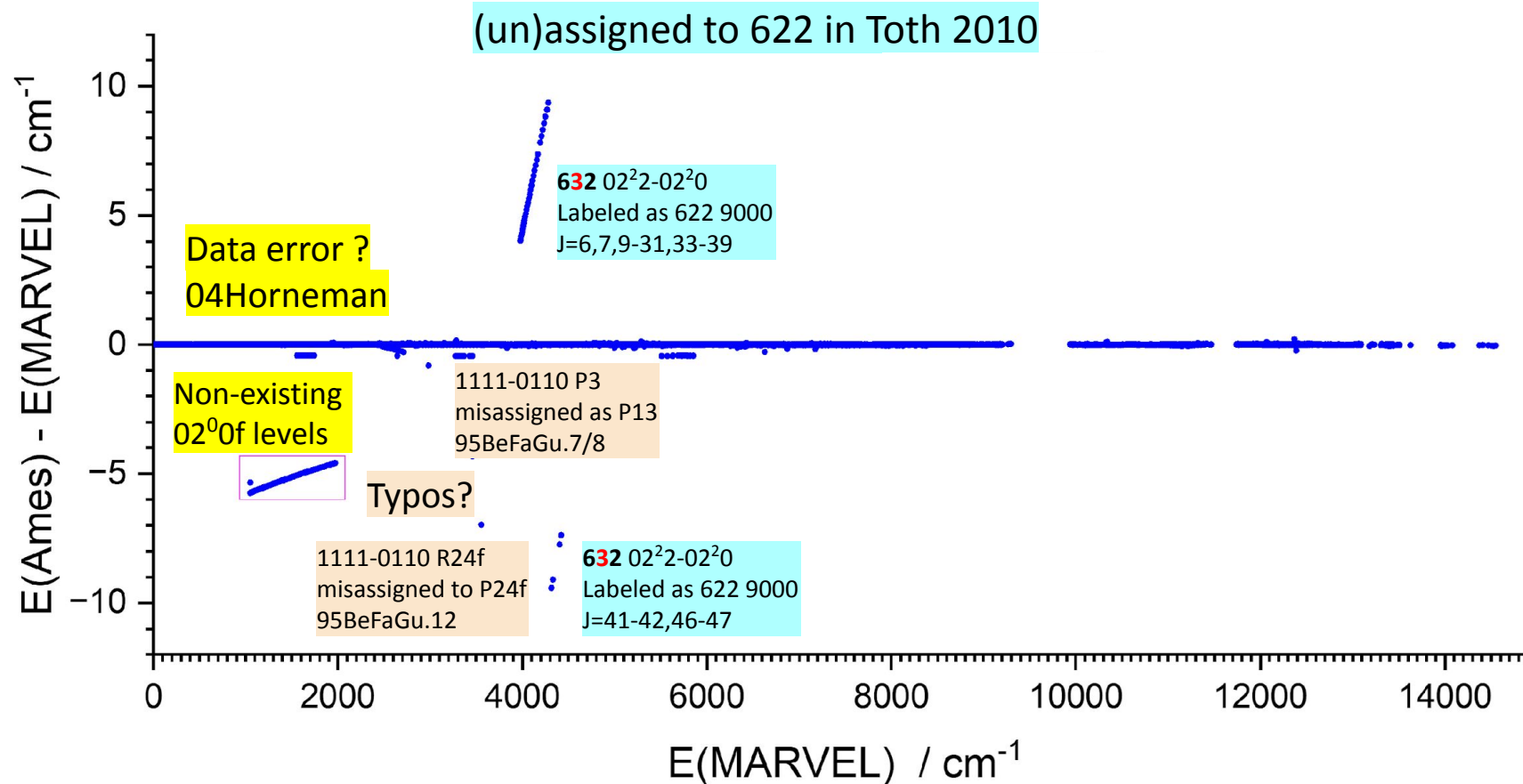
SISAM.n₂o (Toth) list: https://mark4sun.jpl.nasa.gov/data/spec/N2O/RAToht_N2O.tar



What we have learned

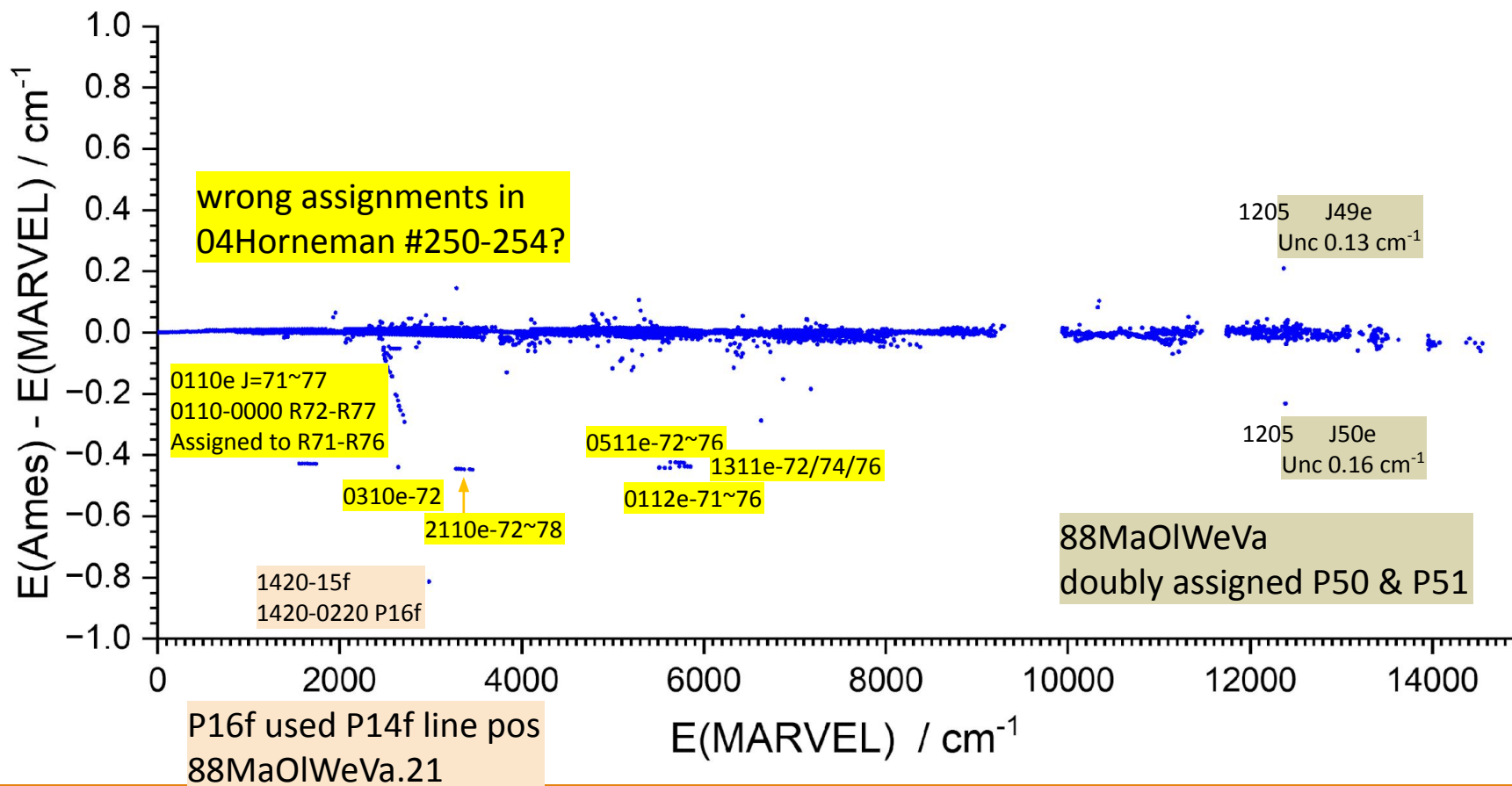
- Pure Experimental or MARVEL set – not ideal for direct use in high-resolution line list
- $^{16}\text{O}^{12}\text{C}^{32}\text{S}$: 0th-2nd order adjustments on E(Ames), comparison based
- $^{16}\text{O}^{12}\text{C}^{32}\text{S}$: Resonance analysis for $3\nu_3$ state
- OCS MW transitions – adjustment on calculated levels
- $^{14}\text{N}_2^{16}\text{O}$: 0th-2nd order adjustments on E(NOSL), comparison based
- Strongly recommend iterative improvement of “MARVEL + PES (refinement)”

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$: data errors in MARVEL level set



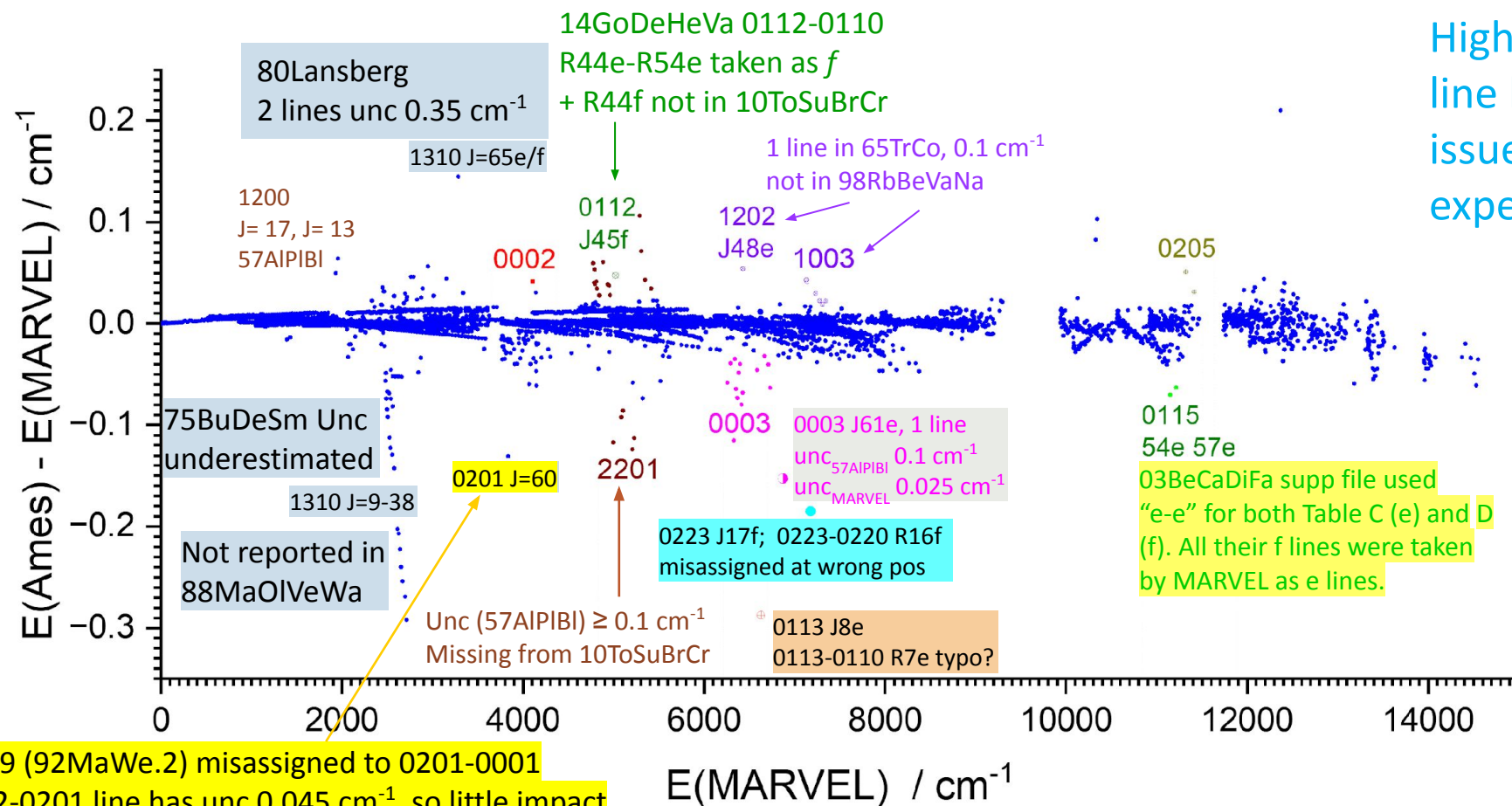
Spectroscopic Network (SN) based MARVEL analysis does not know symmetry or isotopologue

^{16}O ^{12}C ^{32}S : assignment errors in MARVEL level set



Errors may propagate in the network (SN); MARVEL procedure does not check consistency among levels

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$: more deficiencies in MARVEL set



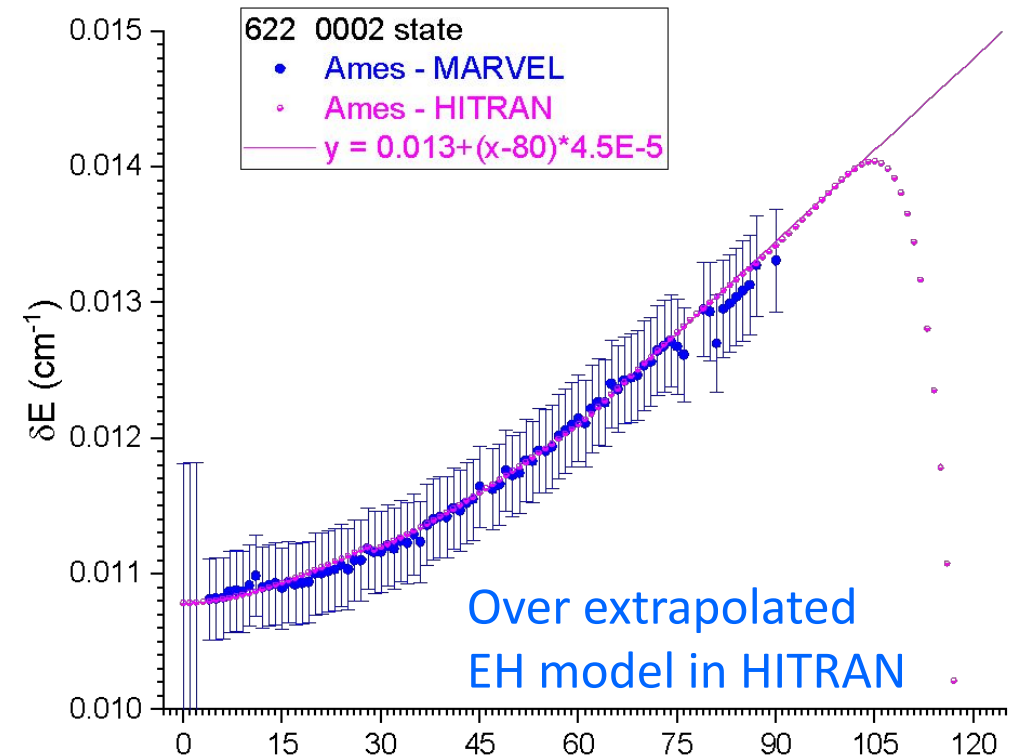
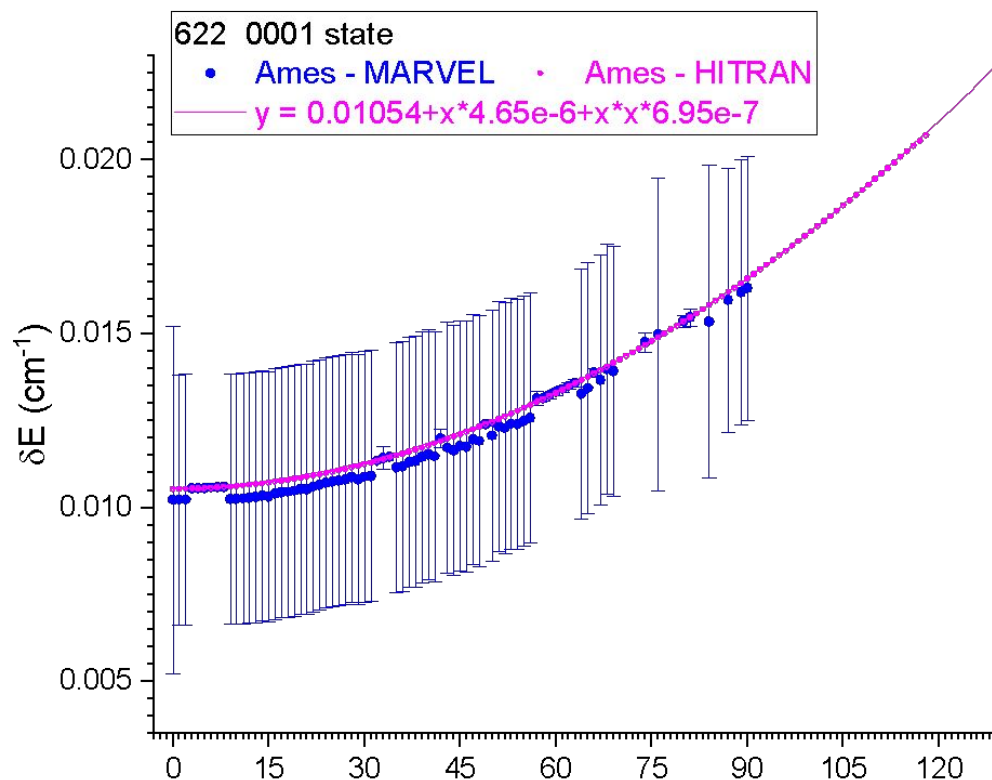
High-quality semi-empirical
line list can identify and fix
issues and inconsistencies in
experiment or MARVEL data

Our $\sigma_{\text{rms}} \approx 0.01 \text{ cm}^{-1}$
for a less contaminated
 E_{MARVEL} subset (5592 levels)

Accuracy, uncertainty, and coverage vary by experiments □ deficiencies in MARVEL data

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$ Levels: HITRAN vs Ames vs MARVEL

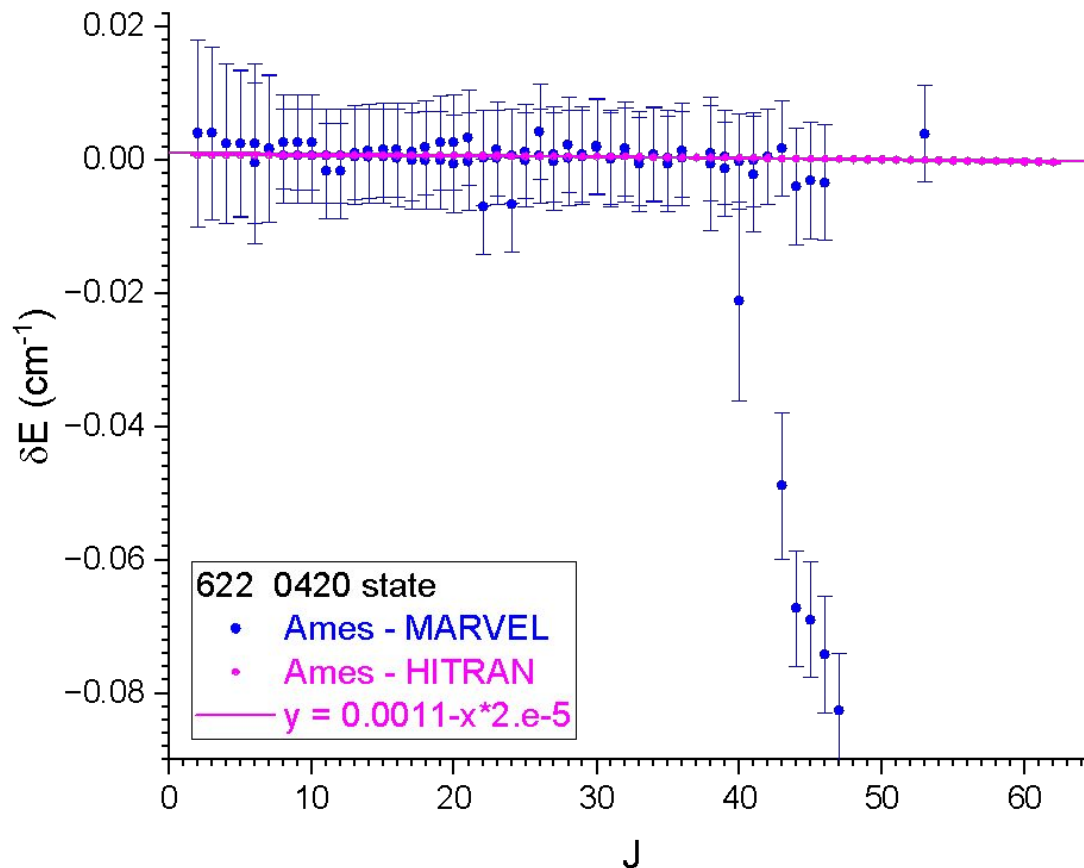
1) which dataset better for line list; 2) which model is over extrapolated; 3) what correction to use at extrapolations



Best energy values: $E_{\text{EH(HITRAN)}} + 0^{\text{th}} - 2^{\text{nd}}$ order corrections fitted from Ames-HITRAN-MARVEL comparison



e/f split check: 04^20 at 2100 cm^{-1}



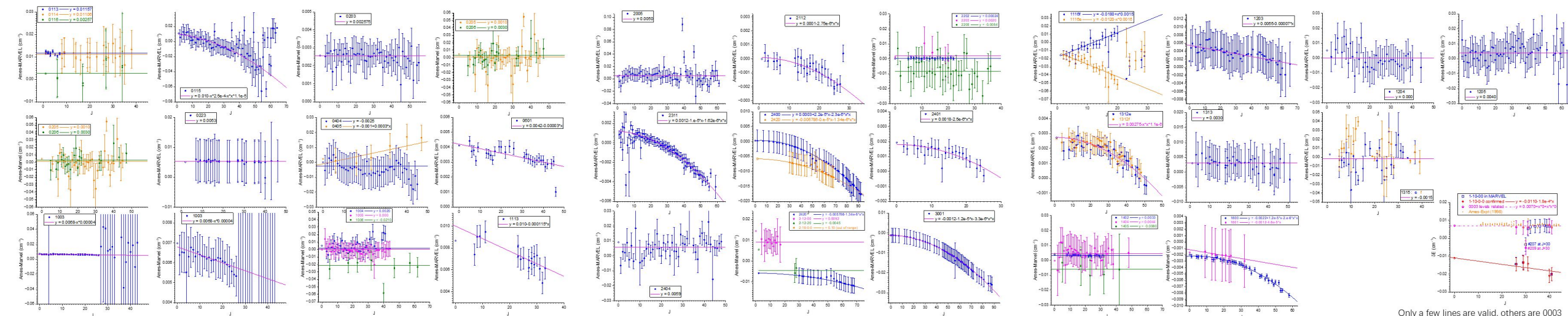
76MeDuMe, 04^20 - 02^20 lines
doubly assigned to both e & f
Many Js are contaminated, but only
noticed when they dominate

Use HITRAN energies
+ linear extrapolation

Best energy values: $E_H(\text{HITRAN})$ or $E_{\text{Ames}} + 0^{\text{th}}\text{-}2^{\text{nd}}$ order corrections fitted from Ames-HITRAN-MARVEL comparison

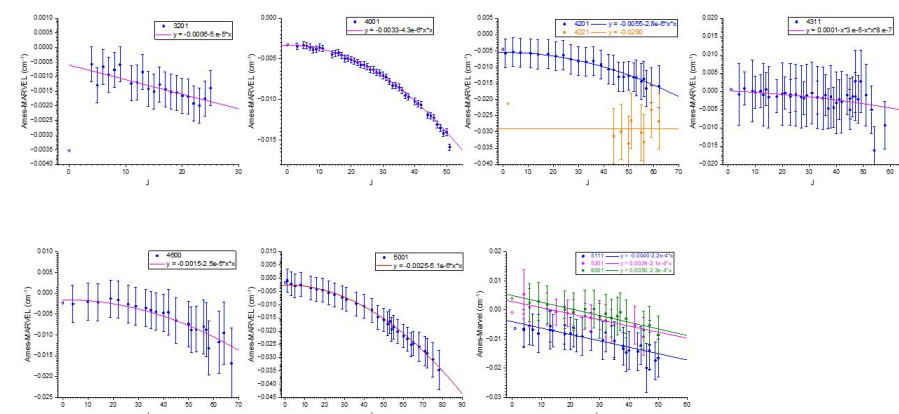


State-by-state: Ames-MARVEL corrections



Only a few lines are valid, others are 0003

- ✓ determined for all (50+) vibrational states beyond HITRAN
- ✓ Interpolate corrections for missing Js
- ✓ Extrapolate corrections beyond the J range of expt data
- ✓ Uncertainties estimated
- ✓ Use 2014 EH model for vibrational state labels



Best energy values: EH(HITRAN) or $E_{\text{Ames}} + 0^{\text{th}}\text{-}2^{\text{nd}}$ order corrections fitted from Ames-HITRAN-MARVEL comparison



Rovibrational levels: Use HITRAN (EH) first

□ Data exceptions identified in HITRAN

- 622: 5002 levels, off by 0.384 cm^{-1}
- 624: 2001 (J=83-93) and 623 2001 (J=74-81): non-matchable
- 622: 4112 and 9110 levels, off by $\sim 0.10 \text{ cm}^{-1}$ (from Expt 2014);
7440 J=29 doubly assigned (from Expt 2014);
- 632: 3800 J55e double assigned, 1440 J58e misassigned to 1001;
- 623: J=5/6 levels, off by $0.02\text{-}0.05 \text{ cm}^{-1}$

□ Over extrapolation of EH model fits:

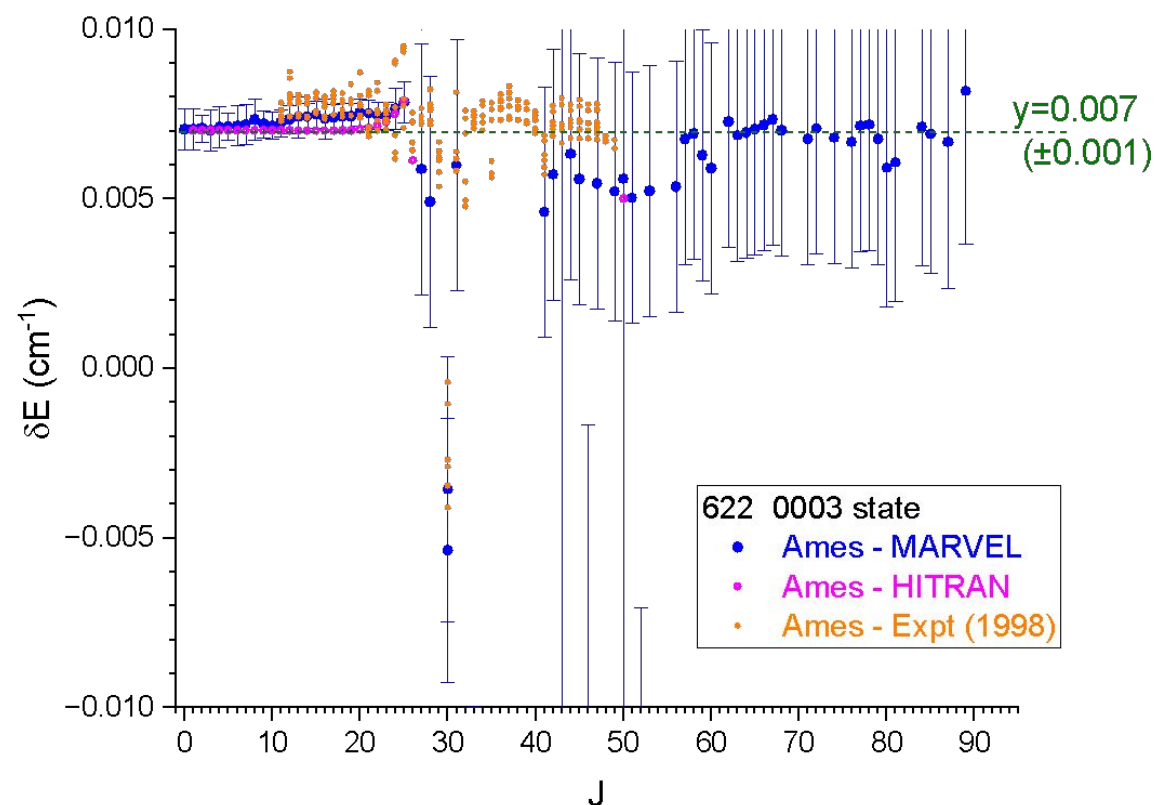
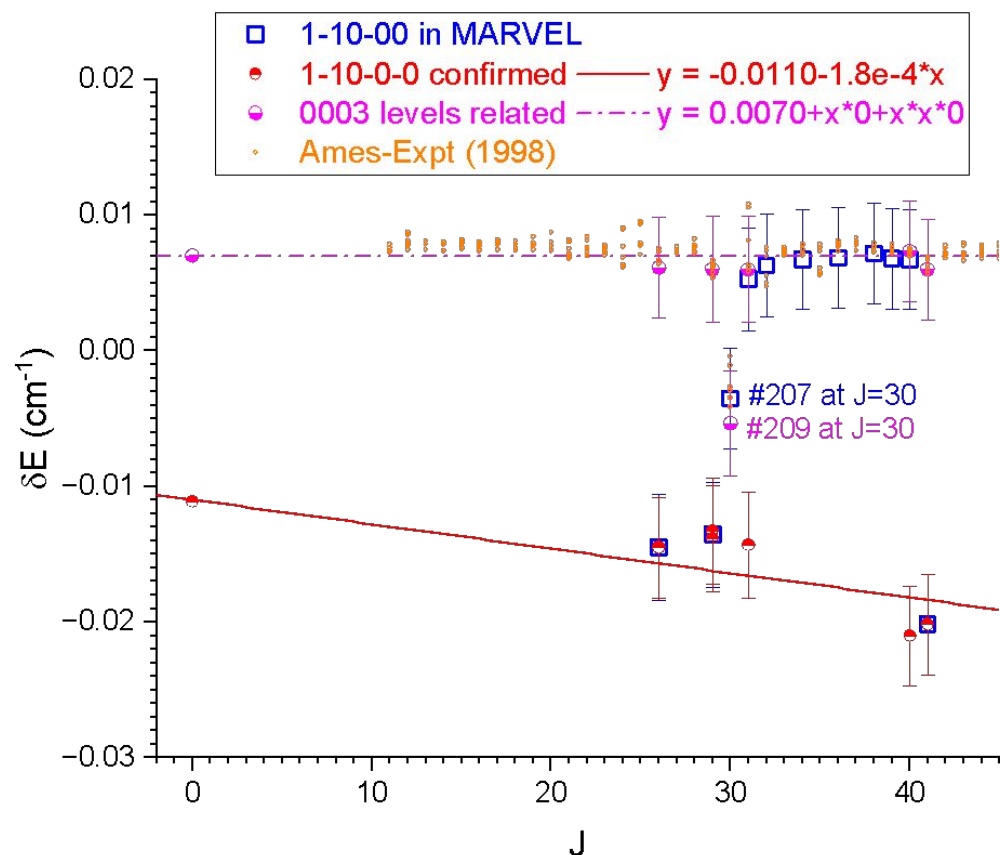
- 622: 0002, 0421, 1002, 1201, 1401, 1421, 2002, and 2113
- 624: 0002, 1002;
- 632: 0112f, 1002;
- 623: 0002, 1002;
- 634: 0003

□ Vibrational state labels

- 622: 4002 and 9000 levels, assignment exchanged

Exceptions and overextrapolations are fixed by constant or linear inter/extrapolations of reliable $\delta_{\text{Ames-HITRAN}}$

$^{16}\text{O}^{12}\text{C}^{32}\text{S}$: $3\nu_3$ (00^03) resonance clarified



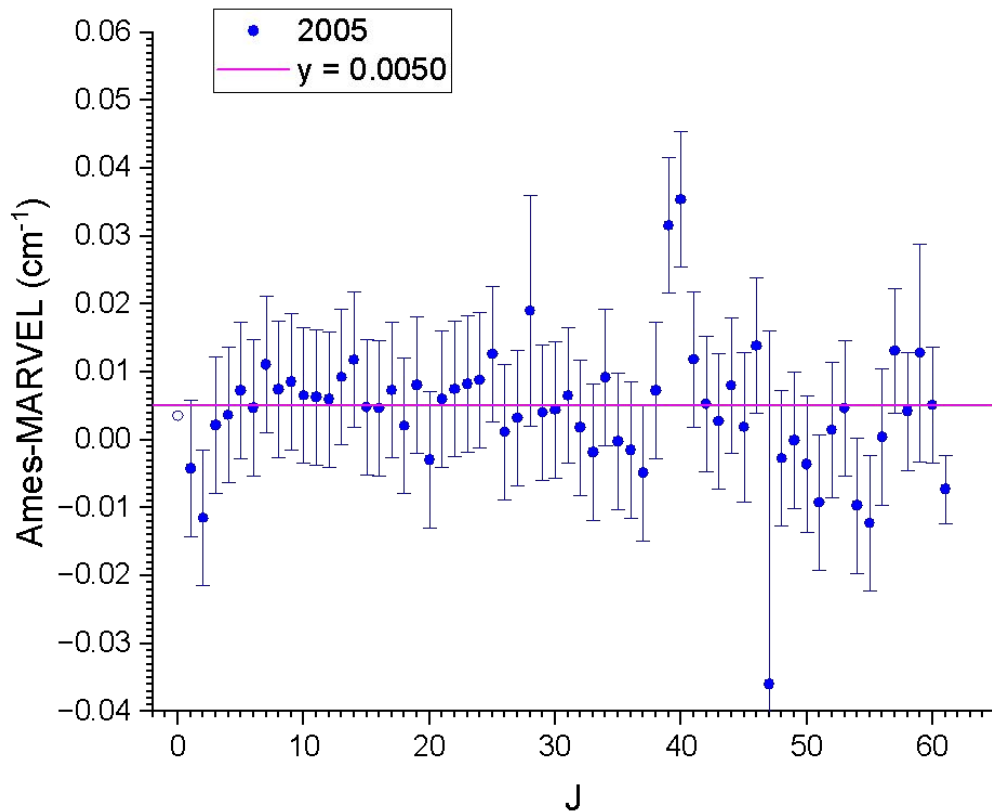
Accuracy of Ames-296K line list may facilitate spectra analysis, and separate states in resonance

Best energy values: E_{HITRAN} or $E_{\text{Ames}} + 0^{\text{th}} - 2^{\text{nd}}$ order corrections fitted from Ames-HITRAN-MARVEL comparison



Resonance Exceptions: case by case

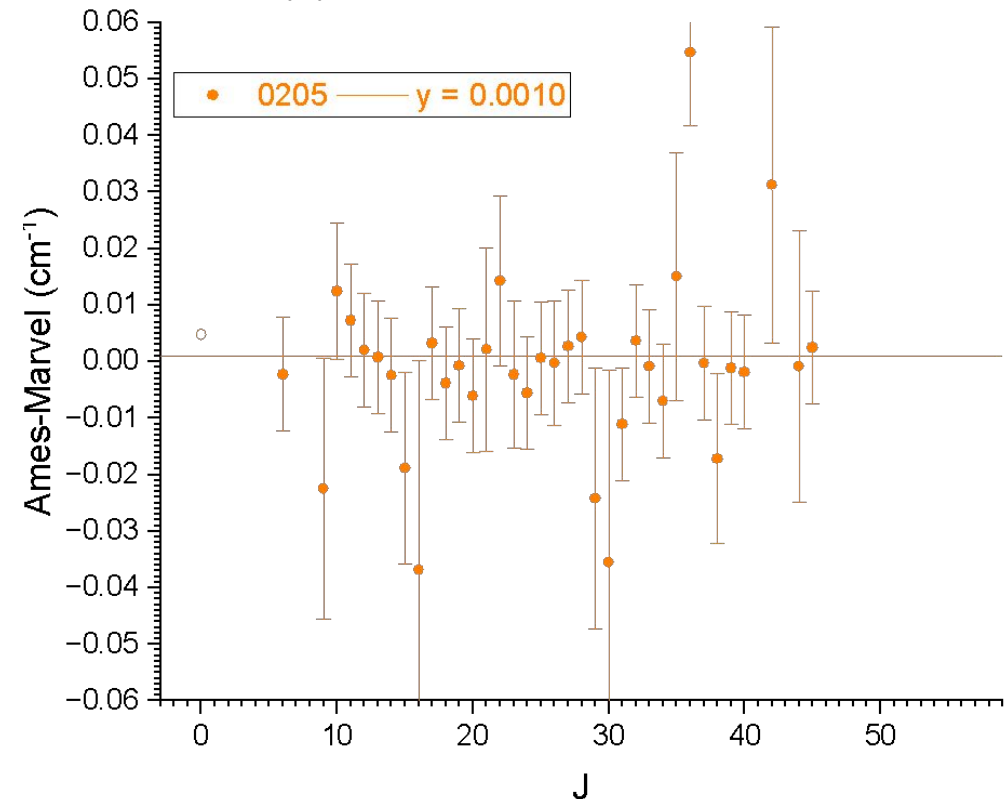
Perturbations confirmed at J=39-40 and 47



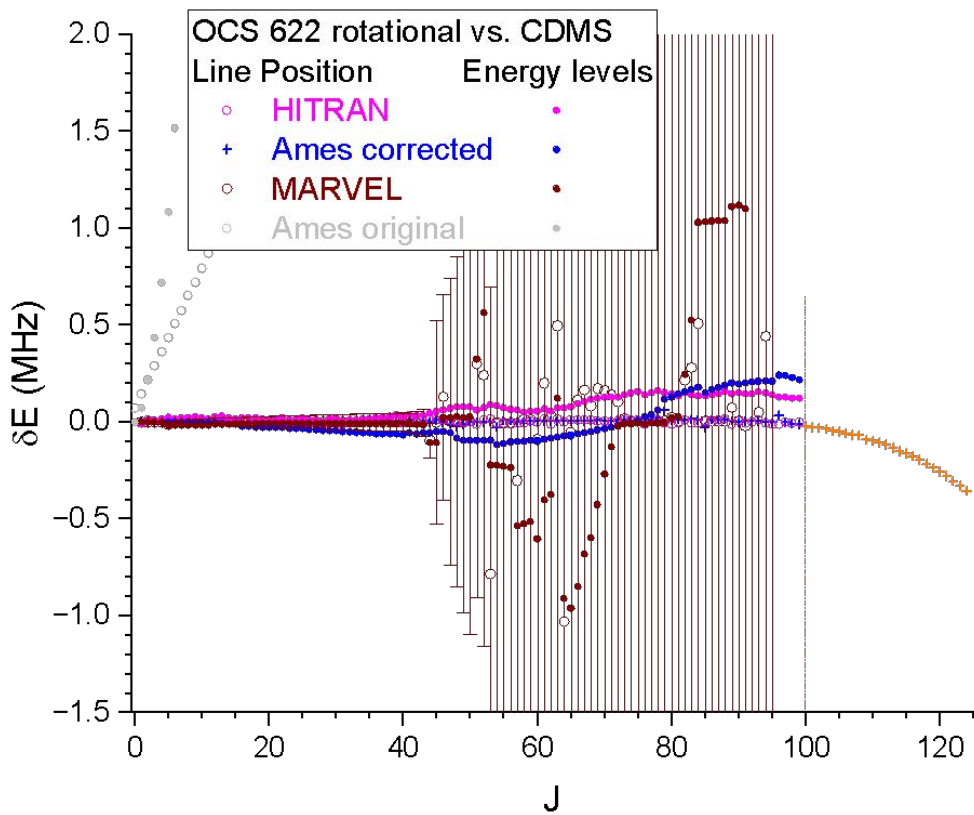
(1) Ames and EH(2014) agree on R34 / R35

$$\sigma_{EH} = 0.05 \text{ cm}^{-1}, \delta_{\text{Ames-EH}} = 0.0068 \text{ cm}^{-1}$$

(2) no resonance was found in J=25-45 calc



OCS: Adjust GS rotational levels wrt CDMS (11 iso)



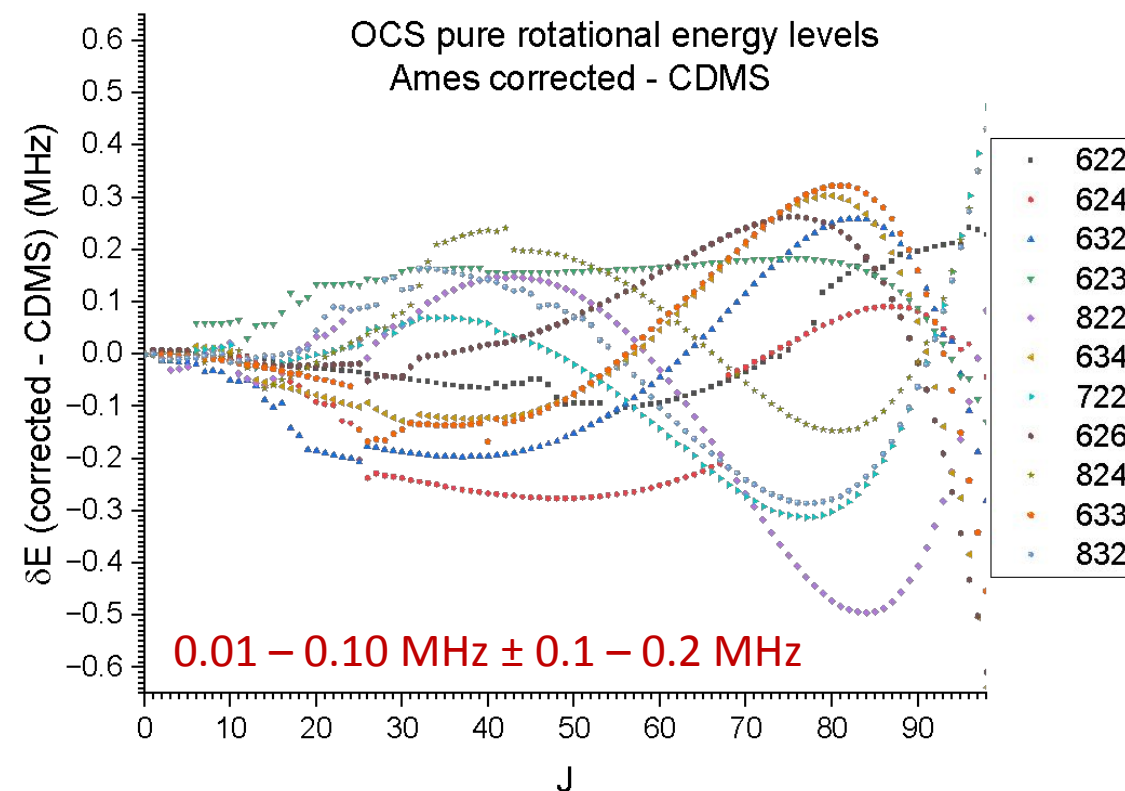
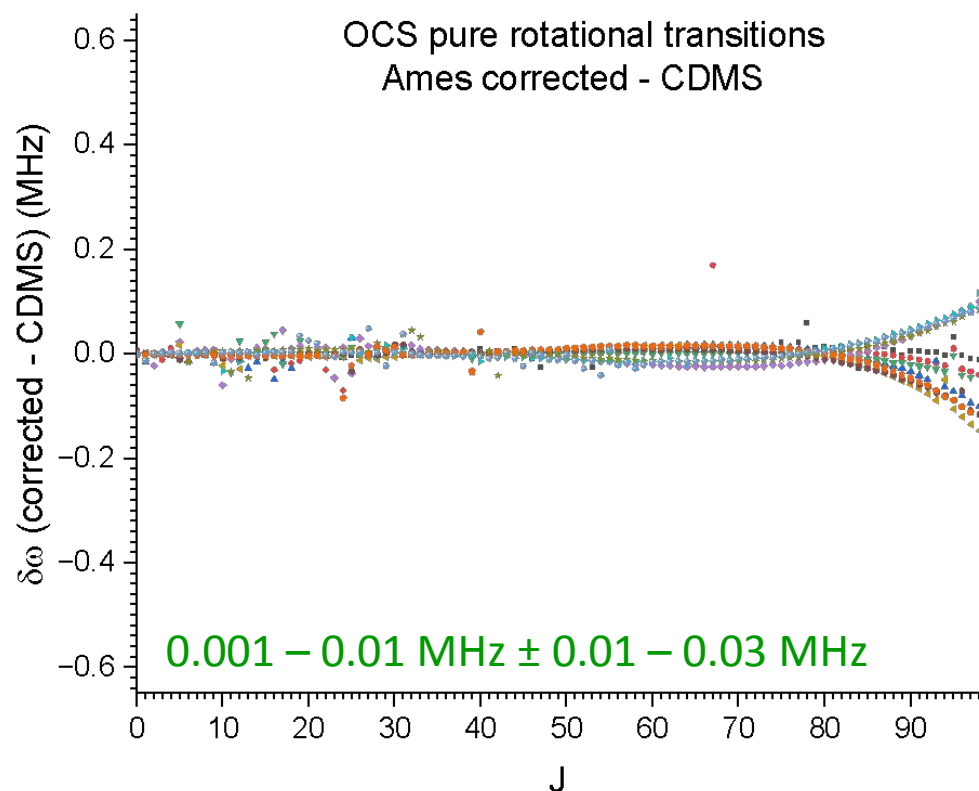
For $J=0-99$, $E_J' = E_J(\text{Ames}) + a \times 10^{-6} \times J \times (J+1) + b \times 10^{-12} \times J^2 \times (J+1)^2$

Iso	$a \times 10^6$ cm ⁻¹	$b \times 10^{12}$ cm ⁻¹	Corrected δE MHz	Corrected $\delta \omega$ MHz	J_{max}^*
626	-1.205	+1.76	0.003±0.100	0.002±0.013	>99
624	-0.225	+6.82	-0.108±0.136	0.001±0.021	>99
632	-1.725	+10.45	0.040±0.158	-0.004±0.023	86
623	-0.676	+3.25	0.124±0.068	0.001±0.013	>99
822	+3.869	-0.307	-0.088±0.207	0.002±0.027	85
634	-0.734	+7.25	-0.007±0.188	-0.008±0.032	80
722	+1.556	+5.4	-0.049±0.165	-0.006±0.025	79
626	+0.490	+28.65	0.038±0.173	-0.007±0.026	78
824	+4.700	+17.55	0.054±0.135	0.005±0.023	81
633	-1.2945	+46.73	0.019±0.167	-0.005±0.027	82
832	+3.372	-2.95	-0.011±0.167	0.005±0.024	77

$\delta \omega / u_{\text{CDMS}} = 0.1 \sim 1$

OCS: Adjust GS rotational levels wrt CDMS (11 iso)

Mixture of observed data and fitted data □ small gaps or kinks in energy level agreements



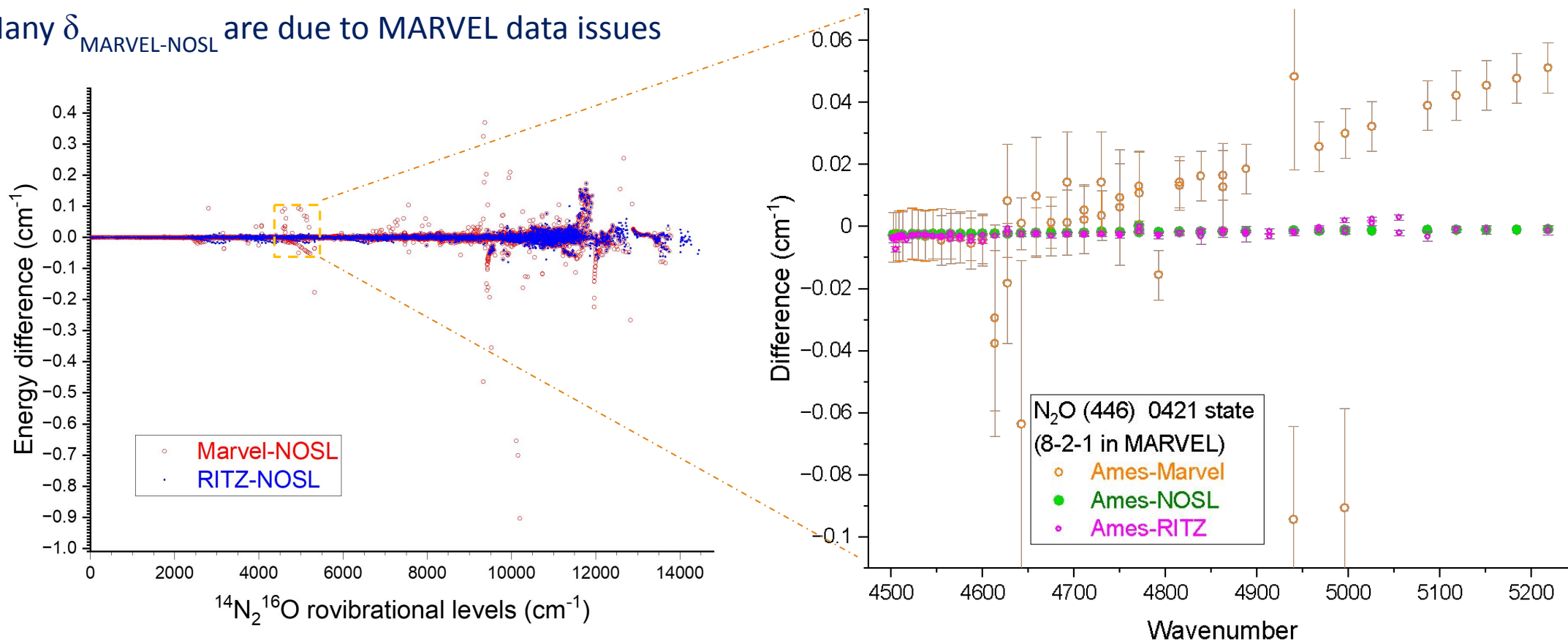


N₂O: Experimental-based Energy Levels

ISO	HITRAN	RITZ	OBS_Lines	EH	NOSL (EH)	MARVEL	SISAM (EH)
446	(6915)	19892	√	J=0-125	311676	17561	√
456	1769	8606	√	J=0-125			√
546	1952	9341	√	J=0-125			√
448	1894		2912	J=0-125			√
447	828		969	J=0-125			√
556		5225	√	J=0-125			√
458							107
548							105

$^{14}\text{N}_2^{16}\text{O}$: NOSL is the best choice for most levels

Many $\delta_{\text{MARVEL-NOSL}}$ are due to MARVEL data issues



Compared to E_{MARVEL} , RITZ levels are more consistent with NOSL

Ames - MARVEL: $0.0022 \pm 0.026 \text{ cm}^{-1}$

Ames - NOSL: $-0.0019 \pm 0.0006 \text{ cm}^{-1}$

Use Global EH Model (NOSL): $^{14}\text{N}_2^{16}\text{O}$

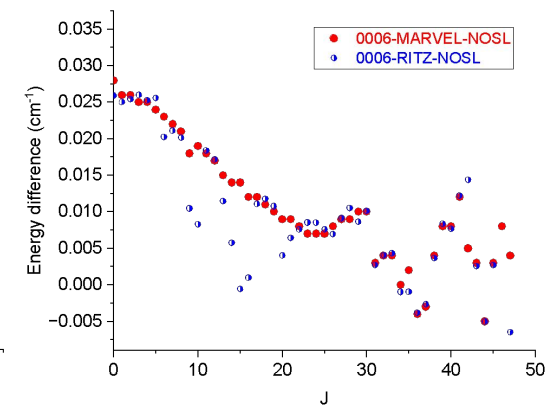
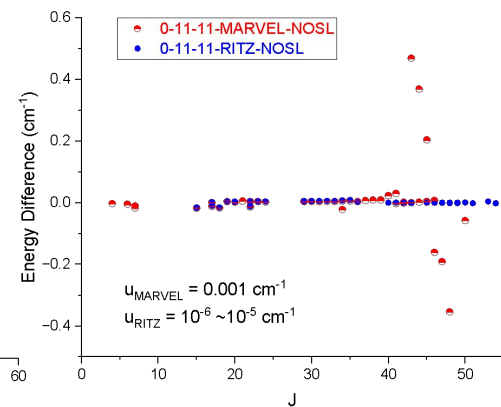
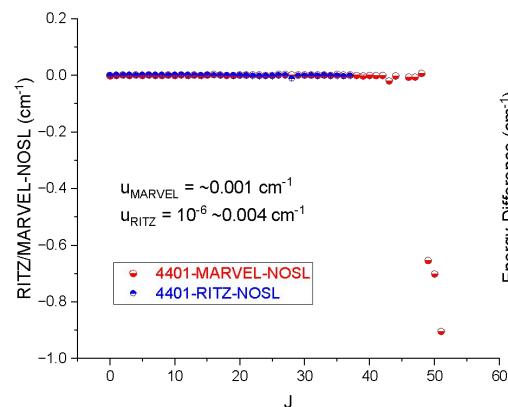
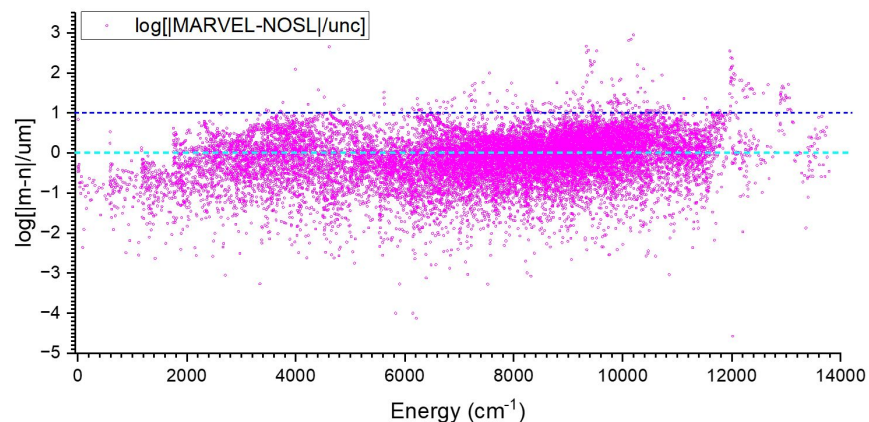
Global EH Model: $I_2 = 0-30$, $J=0-125$, $0-15,000 \text{ cm}^{-1}$, 310,676 levels
(experiment data based, up to Karlovets et al 2023)

- ✓ Begin with automatic search-to-match program (specific for N_2O)
 - ☐ Check all matches up to $11,000 \text{ cm}^{-1}$ (~100,000 levels)
 - ☐ hundreds of corrections at state crossing and perturbations
 - ☐ all $J=0-125$ levels up to $11,000 \text{ cm}^{-1}$ are matched and verified
- ✓ Use IR line intensity to help match higher energy levels
 - ☐ extract all IR active levels ($S_{296\text{K}} > 10^{-31} \text{ cm/molecule}$)
 - ☐ match all active levels with $S_{296\text{K}} > 10^{-28} \text{ cm/molecule}$
- ✓ Use additional levels in MARVEL/RITZ list, *if necessary*

[Independent NOSL-RITZ-MARVEL comparison also available from Dr. Tashkun]

Ames-B1b vs NOSL (446), MARVEL (446), HITRAN (446,456,546,448,447), EH (446,456,546,448,447,556), RITZ (446,456,546,556), Toth (458, 457)

$^{14}\text{N}_2$ ^{16}O : Empirical adjustments on E_{NOSL}

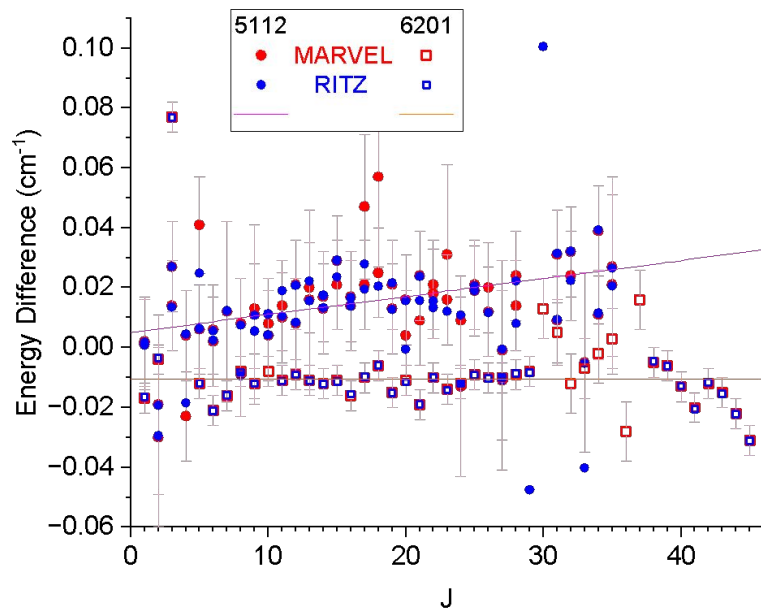


marvellevels - marvellevels.matched *		Long Na		Units		P		I		n		J		E(Y)		F(Y1)		G		H		I(Y)		J(X2)		K		L		M		N		O(Y2)		P(X3)		Q(Y3)		R(Y3)		S(Y3)		T(Y)		U(Y)		V		W(X)		Y(Y)		Z		AA		AB		AC		A		AE(Y3)		AF(Y3)		AG(Y3)		AH(Y3)		AI(Y3)		AJ(Y3)		AK(Y3)		AL(X4)		AM(Y4)	
marvellevels - marvellevels.matched *		Long Na		Units		P		I		n		J		E(Y)		F(Y1)		G		H		I(Y)		J(X2)		K		L		M		N		O(Y2)		P(X3)		Q(Y3)		R(Y3)		S(Y3)		T(Y)		U(Y)		V		W(X)		Y(Y)		Z		AA		AB		AC		A		AE(Y3)		AF(Y3)		AG(Y3)		AH(Y3)		AI(Y3)		AJ(Y3)		AK(Y3)		AL(X4)		AM(Y4)	
Units		P		I		n		J		E(Y)		F(Y1)		G		H		I(Y)		J(X2)		K		L		M		N		O(Y2)		P(X3)		Q(Y3)		R(Y3)		S(Y3)		T(Y)		U(Y)		V		W(X)		Y(Y)		Z		AA		AB		AC		A		AE(Y3)		AF(Y3)		AG(Y3)		AH(Y3)		AI(Y3)		AJ(Y3)		AK(Y3)		AL(X4)		AM(Y4)					
Comment		P		I		n		J		E(Y)		F(Y1)		G		H		I(Y)		J(X2)		K		L		M		N		O(Y2)		P(X3)		Q(Y3)		R(Y3)		S(Y3)		T(Y)		U(Y)		V		W(X)		Y(Y)		Z		AA		AB		AC		A		AE(Y3)		AF(Y3)		AG(Y3)		AH(Y3)		AI(Y3)		AJ(Y3)		AK(Y3)		AL(X4)		AM(Y4)					
Fix=		P		I		n		J		E(Y)		F(Y1)		G		H		I(Y)		J(X2)		K		L		M		N		O(Y2)		P(X3)		Q(Y3)		R(Y3)		S(Y3)		T(Y)		U(Y)		V		W(X)		Y(Y)		Z		AA		AB		AC		A		AE(Y3)		AF(Y3)		AG(Y3)		AH(Y3)		AI(Y3)		AJ(Y3)		AK(Y3)		AL(X4)		AM(Y4)					
17534	22	0	4	15	1	12060	28284	2	e	4	5	0.006E-4	1	0	0	5	12061	38235	12060	32724	1	0.0951	1	0.0511	-0.04440	3	0	0	4	1	0	0	5	2	15	1	1011	1	398E-26	-0.1	-1.86	1.53	-88.696764	1	947908	0.000501	88.697																																		
17535	22	0	4	13	1	12037	08032	2	e	3	6	0.003E-4	1	0	0	5	12037	85796	12037	13746	0	0.7764	0	0.72050	-0.05714	3	0	0	4	1	0	0	5	2	13	1	992	1	368E-26	1.8	-1.39	1.25	-95.177911	1	978536	0.000600	95.178																																		
17536	9	1	9	66	1	7554	71957	1	f	1	0	0.010046	4	1	1	0	7554	62103	7554	61542	-0.09854	0.00561	0.10415	3	5	5	0	2	5	1	0	1	66	1	74	2	043E-27	-159	29.76	-29.799	99.571128	1	998133	0.001046	99.571																																				
17537	14	2	15	40	2	9436	44253	2	e	1	0	0.001001	5	4	2	0	9436	37139	9436	33804	-0.07114	0.03335	0.10449	6	0	0	0	1	12	2	0	2	40	2	363	6	809E-29	-13.6	-3.47	3.471	104.381219	2	018622	0.001001	104.381																																				
17538	22	0	4	4	2	11972	22137	2	e	4	0	0.001063	1	0	0	5	11972	08011	11972	34891	-0.14126	-0.26880	-0.12754	2	0	0	4	1	0	0	5	2	4	2	611	4	39E-27	-25.9	-0.58	0.488	-121.1218	2	083222	0.001063	121.122																																				
17539	6	2	3	29	2	3995	96249	1	f	1	2	0.015E-4	1	4	2	0	3995	98069	3995	96766	0.02720	0.02003	-0.02517	0	6	2	0	0	6	2	0	1	29	2	20	1	54E-23	-7.7	-31.17	31.153	-122.6997	2	088843	0.002005	122.700																																				
17540	16	2	11	48	2	10383	07567	2	e	1	0	0.001003	-1	-1	-1	1	10383	30351	10383	20239	0.22784	0.10112	-0.12672	1	11	1	1	5	2	2	1	2	48	2	460	1	178E-29	-14.1	0.76	-0.759	-126.3398	2	10154	0.001003	126.340																																				
17541	22	0	4	9	1	12000	26852	2	e	4	6	0.006E-4	1	0	0	5	12000	51220	12000	34879	0.24398	0.16341	-0.08027	3	0	0	4	1	0	0	5	2	9	1	901	1	154E-26	10.6	-0.69	0.81	-133.5878	2	125767	0.000601	133.588																																				
17542	22	0	4	8	2	11993	05726	2	e	4	6	0.006E-4	1	0	0	5	11993	20737	11993	14901	0.15011	0.05746	-0.00265	3	0	0	4	1	0	0	5	2	8	2	861	1	038E-26	15.7	-0.6	0.726	-138.9917	2	142989	0.000667	138.992																																				
17543	15	1	8	45	1	9405	86719	2	e	1	0	0.001001	3	1	2	9405	06915	9405	01597	0.20196	0.05318	-0.14878	4	0	0	1	3	1	2	2	45	1	336	8	345E-28	80.5	-1	1.083	-148.6337	2	172117	0.001001	148.634																																						
17544	22	0	4	11	1	12017	07852	2	e	4	4	4.24E-4	1	0	0	5	12017	45308	12017	14466	0.37458	0.30852	-0.08204	3	0	0	4	1	0	0	5	2	11	1	957	1	291E-26	4.8	-1.1	1.01	-149.2798	2	174001	0.000442	149.280																																				
17545	15	1	7	46	2	9443	64864	2	e	1	0	0.001001	0	11	1	9443	85988	9443	80959	0.21122	0.05027	-0.16095	0	9	1	1	3	5	1	1	2	46	2	336	5	611E-28	41.5	1.52	-1.503	-160.7859	2	206248	0.001001	160.786																																					
17546	17	1	10	38	1	10270	91072	1	f	1	0	0.01004	3	3	1	2	10271	18864	10271	07276	0.27792	0.11588	-0.16204	4	2	1	3	3	1	2	1	38	1	412	2	666E-28	-108.1	0.98	-0.912	-161.3895	2	207875	0.001004	161.390																																					
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17548	15	1	7	47	1	9482	30093	2	e	3	0	0.001001	0	11	1	9482	53922	9482	49317	0.23829	0.04605	-0.19224	0	9	1	1	3	5	1	1	2	47	1	336	3	445E-28	-50.7	1.62	-1.611	-192.0482	2	228341	0.001001	192.048																																					
17549	15	1	7	45	1	9404	67623	2	e	1	0	0.001001	0	11	1	9404	50392	9404	47346	-0.17231	0.03046	0.20277	0	9	1	1	0	11	1	1	2	45	1	335	3	745E-28	31.3	-1.57	1.543	202.57013	2	306675	0.001001	202.570																																					
17550	20	0	27	10	2	12009	18319	2	e	2	3	0.005E-4	8	0	0	1	12009	46750	12009	25198	0.29431	0.21552	-0.06879	9	0	0	0	6	0	0	2	2	10	2	933	1	031E-29	-704	0.82	-0.905	-228.9324	2	359707	0.000301	228.932																																				
17551	22	0	4	7	1	11990	05466	2	e	4	4	0.003E-4	1	0	0	5	11990	71836	11990	75040	0.06370	-0.03204	-0.09574	2	0	0	4	1	0	0	5	2	7	1	814	8	881E-27	22.8	-0.55	0.651	-239.1694	2	378705	0.000601	239.169																																				
17552	16	2	10	23	1	9334	10811	2	e	1	0	0.00101	-1	-1	-1	1	9333	83890	9333	78580	-0.27191	0.05310	0.32501	0	13	1	0	12	2	1	2	23	1	413	2	939E-28	0.0	-0.95	0.944	-335.0081	2	251194	0.001001	335.008																																					
17553	22	0	4	3	1	11990	05464	2	e	4	4	0.001001	1	0	0	5	11990	71836	11990	75040	0.06370	-0.03204	-0.09574	2	0	0	4	1	0	0	5	2	7	1	814	8	881E-27	22.8	-0.55	0.651	-239.1694	2	378705	0.000601	239.169																																				
17554	22	0	4	2	1	11996	00520	2	e	3	4	4E-4	1	0	0	5	11996	40481	11996	74675	-0.15919	-0.30074	-0.14155	2	0	0	4	1	0	0	5	2	2	414	2	247E-27	43.4	-0.58	0.428	-135.0753	2	254849	0.000400	353.875																																					
17555	15	1	7	48	2	9521	70372	2	e	3	0	0.001001	0	11	1	9522	10006	9522	05539	0.39694	0.04227	-0.35467	0	9	1	1	3	5	1	1	2	48	2	336	2	032E-28	-55.3	1.84	-1.849	-354.32038	2	254396	0.001001	354.320																																					
17556	15	1	7	44	2	9367	76034	2	e	1	0	0.001001	0	11	1	9367	47106	9367	39081	-0.34298	0.02625	0.36923	0	5	1	1	0	11	1	1	2	44	2	335	2	751E-28	-54.7	-1.63	1.644	-368.8641	2	256686	0.001001	368.864																																					
17557	7	1	1	40	1	9155	62678	1	f	1	2	0.006E-4	0	7	0	9155	62966	9155	67308	-0.09722	-0.00552	0.09170	0	4	2	1	0	3	1	1	40	1	23	3	29E-23	-13.4	-16.55	16.544	-448.00889	2	264941	0.00026	446.007																																						
17558	15	1	7	43	1	9331	54126	2	e	1	0	0.001001	0	11	1	9331	98744	9331	50054	0.44598	0.01796	-0.46394	2	10	4	0	2	1	3	1	43	1	336	2	249E-29	-145.2	0.89	-0.932	-463.4019	2	266032	0.001001	463.401																																						
17559	16	2	10	2	1	11992	3	2	e	2	0	0.001001	3	2	0	2	11992	27004	11992	3	0.7123	0.01587	-0.16425	0	10	1	4	1	4	2	1	2	49	1	411	2	181E-28	-41.5	2	-2.223	-440.44912	2	266496	0.001001	440.449																																				
17560	16	2	10	2	1	10110	19177	2	e	1	0	0.00101	3	2	0	2	10110	10155	10110	96453	0.72129	0.07151	-0.18472	0	10	1	4	1	4	2	1	2	49	1	411	2	181E-28	-41.5	2	-2.223	-440.44912	2	266496	0.001001	440.449																																				
17561	16	2	10	2	1	10110	19177	2	e	1	0	0.00101	3	2	0	2	10110	10155	10110	96453	0.72129	0.07151	-0.18472	0	10	1	4	1	4	2	1	2	49	1	411	2																																													

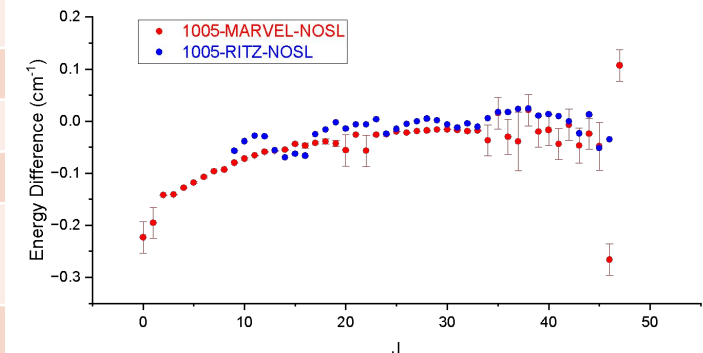


$^{14}\text{N}_2^{16}\text{O}$: Empirical adjustments on E_{NOSL}

✓ Adjustments on E_{NOSL} for ~ 20 vibrational states $> 10,000 \text{ cm}^{-1}$



P- I_2 -n	$v_1 v_2 l^2 v_3$	$J_{\min}/J_{\max}$	#levels	E to use (cm^{-1})	P- I_2 -n	$v_1 v_2 l^2 v_3$	$J_{\min}/J_{\max}$	#levels	E to use (cm^{-1})
15-1-7 e	0-11-11e	7/34	6	$E_{\text{NOSL}} - 0.016$	n/a	1006	2/33	26	$E_{\text{NOSL}} - 0.011$
15-1-20	2113/3910	(J25f)	1	$E_{\text{NOSL}} - 0.071$	n/a	1115	7/25	38	$E_{\text{NOSL}} + 0.016$
17-1-7	2113/3910	(J25f)	1	$E_{\text{NOSL}} + 0.071$	n/a	2203	1/49	45	$E_{\text{NOSL}} - 0.008$
17-1-4	1313	3/20	31	$E_{\text{NOSL}} - 0.10 + J \cdot 0.004$	19-1-10	2313	1/35	68	$E_{\text{NOSL}} - 0.016$
18-0-23	6201	1/45	44	$E_{\text{NOSL}} - 0.0104$					
19-1-8	3113	2/41	77	$E_{\text{NOSL}} + 0.02 - J \cdot 0.0005$	20-0-19	1-10-02	3/15	13	$E_{\text{NOSL}} + (J-1) \cdot 0.0058$
19-1-17	5112	1/35	64	$E_{\text{NOSL}} + 0.005 + J \cdot 0.0006$	20-0-19	1-10-02	16/27	12	$E_{\text{NOSL}} + 0.087$
20-0-15 *	5202	19/33	15	$E_{\text{NOSL}} + (J-19) \cdot 0.005$					
20-0-21	8001	2/23	22	$E_{\text{NOSL}} + 0.153 - J \cdot 0.002$					
20-0-23 *	4402	6/22	17	$E_{\text{NOSL}} + 0.130$					
20-0-27	6002	1/10	10	$E_{\text{MARVEL}} (E_{\text{RITZ}} \text{ n/a})$					
22-0-4	1005	0/47	48	$E_{\text{N}} - 0.17 + J \cdot 0.011 - J^2 \cdot 0.0019$					
24-0-2	0006	0/47	48	E_{MARVEL}					



NOSL-(Ames)-RITZ-MARVEL comparison $\square$ 0th – 2nd order adjustments on NOSL energies



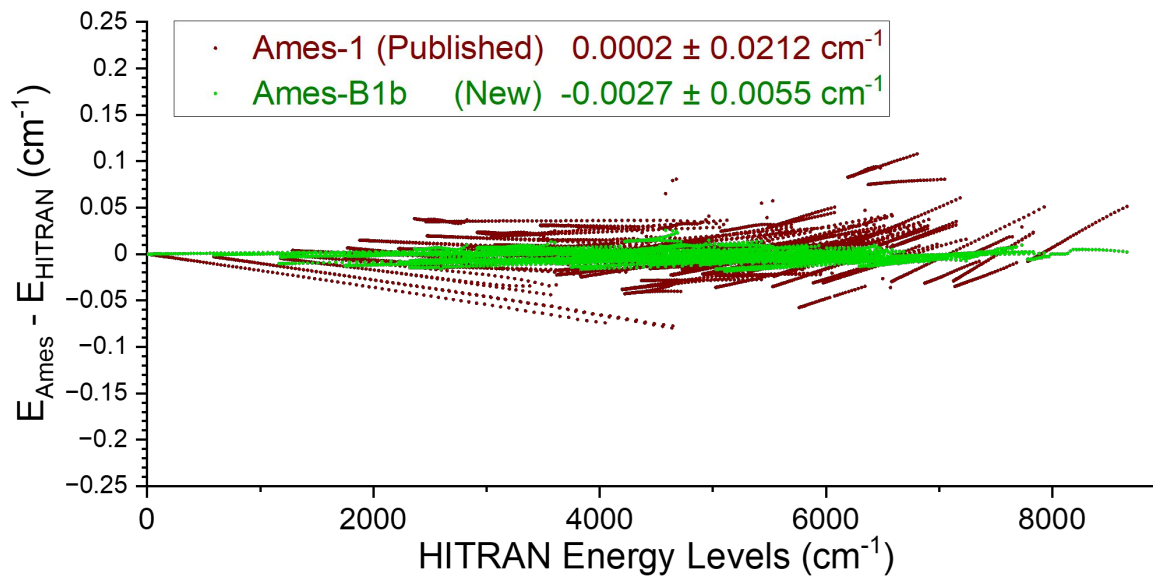
What we have learned

- Pure Experimental or MARVEL set – not ideal for direct use in high-resolution line list
 - $^{16}\text{O}^{12}\text{C}^{32}\text{S}$: 0th-2nd order adjustments on E(Ames), comparison based
 - $^{16}\text{O}^{12}\text{C}^{32}\text{S}$: Resonance analysis for $3\nu_3$ state
 - OCS MW transitions – adjustment on calculated levels
 - $^{14}\text{N}_2^{16}\text{O}$: 0th-2nd order adjustments on E(NOSL), comparison based
 - Strongly recommend iterative improvement of “MARVEL + PES (refinement)”
- Reliable Global EH models are the best choice – if available
 - room temperature – program-aided match, molecule/data dependent
 - high temperature – refine PES wrt EH Model, + A_{21} from room-temperature list
 - reliability of global EH model – use isotopologue consistency

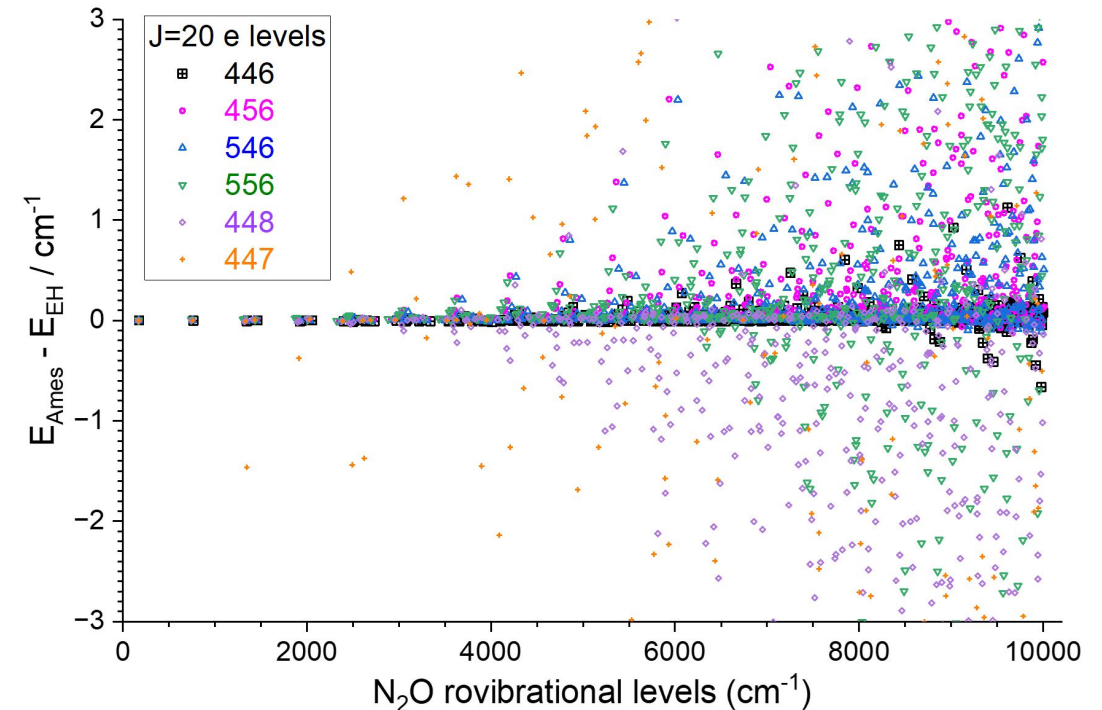


Not all global EH models are reliable: N₂O

Ames-B1b PES refinement using Benjamin Schröder's Comp I PES (2015): Intermediate, < 10,000 cm⁻¹



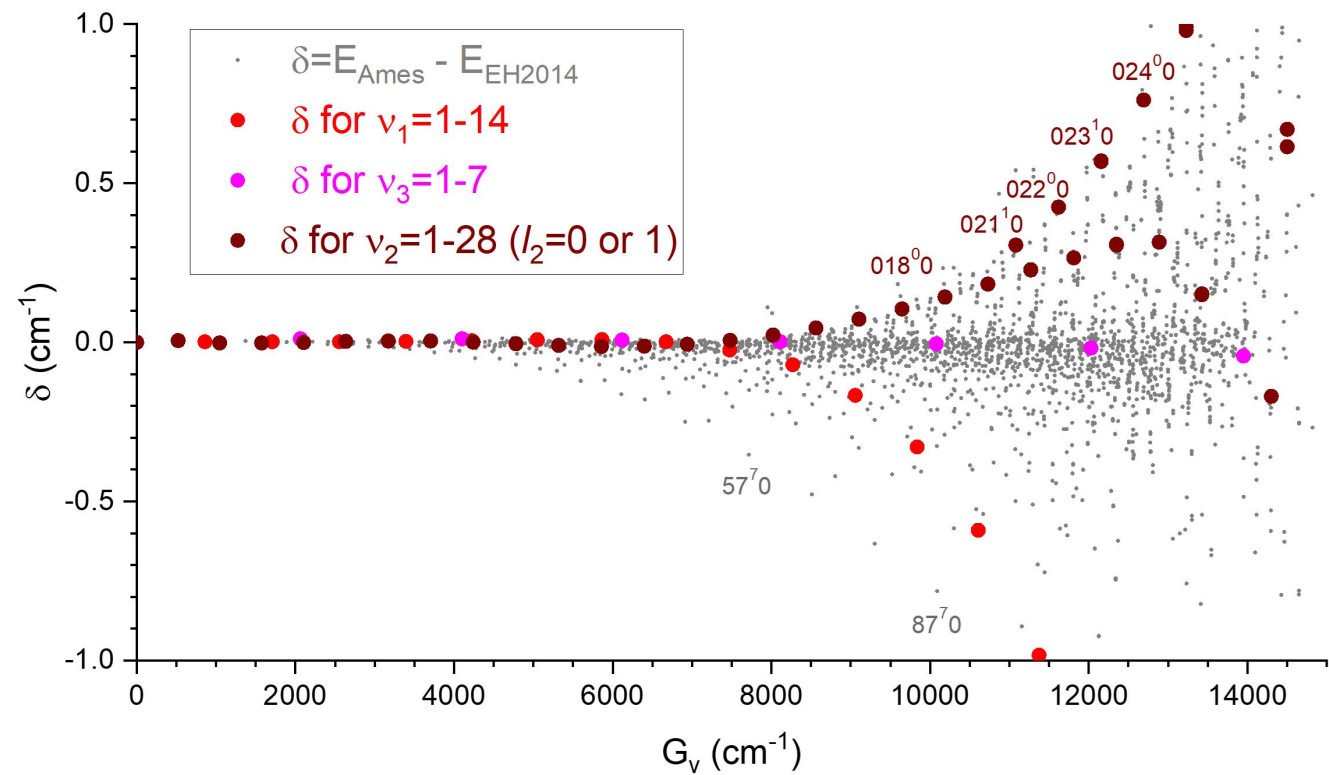
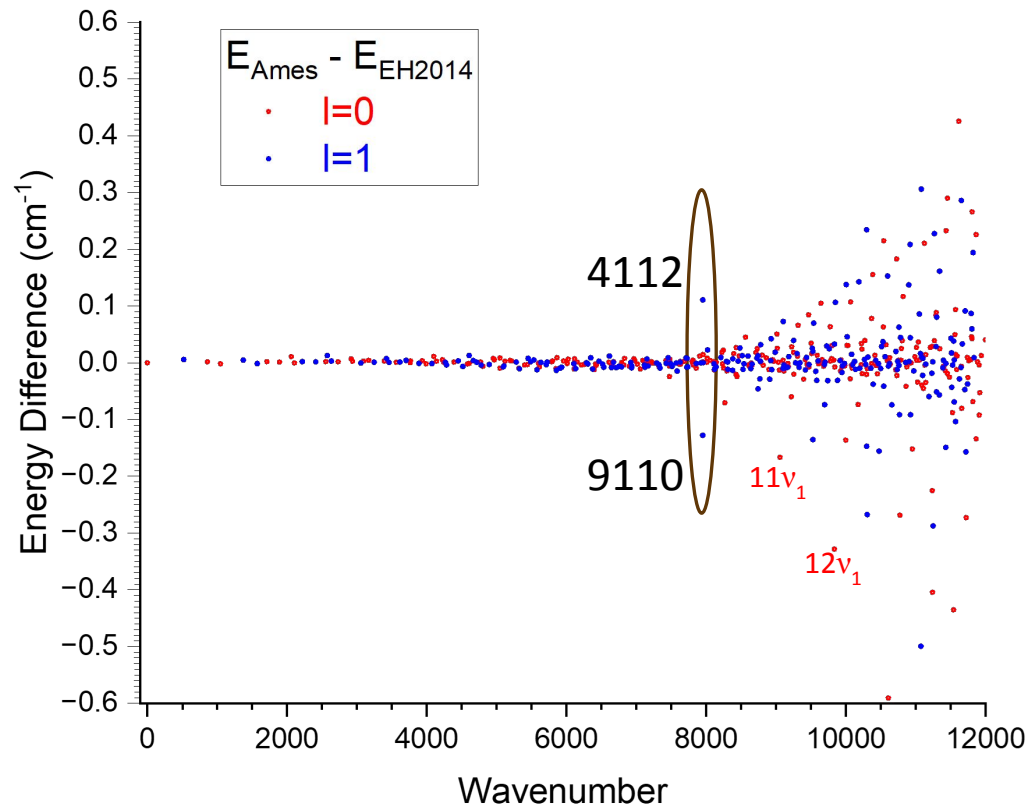
Smallest σ_{RMS} error we ever achieved



Global EH model of minor isotopologues
need more experimental data



OCS: Compare to 2014 experiment & EH model



We found EH(2014) has 0.1 cm^{-1} deviations at 8000 cm^{-1} , and $2-3 \text{ cm}^{-1}$ deviations at 1006 and 0206 states, etc..



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- Use reliable EH model fits or selected reliable data from global EH model



N₂O: Experimental-based Energy Levels

ISO	HITRAN	RITZ	OBS_Lines	EH	NOSL (EH)	MARVEL	SISAM (EH)
446	(6915)	19892	√	J=0-125	311676	17561	√
456	1769	8606	√	J=0-125			√
546	1952	9341	√	J=0-125			√
448	1894		2912	J=0-125			√
447	828		969	J=0-125			√
556		5225	√	J=0-125			√
458							107
548							105

N₂O ISO#2-8: RITZ/Obs/Toth + EH + HITRAN

- Global EH models need more experimental data

✓ Step 1: reliable experimental data

RITZ levels: 456, 546, and 556

Obs (Toth list included): 448, 447

Toth list: 458, 548

✓ Step 2: Selected data from Global EH models

EH model: 456, 546, 448, 447, 556

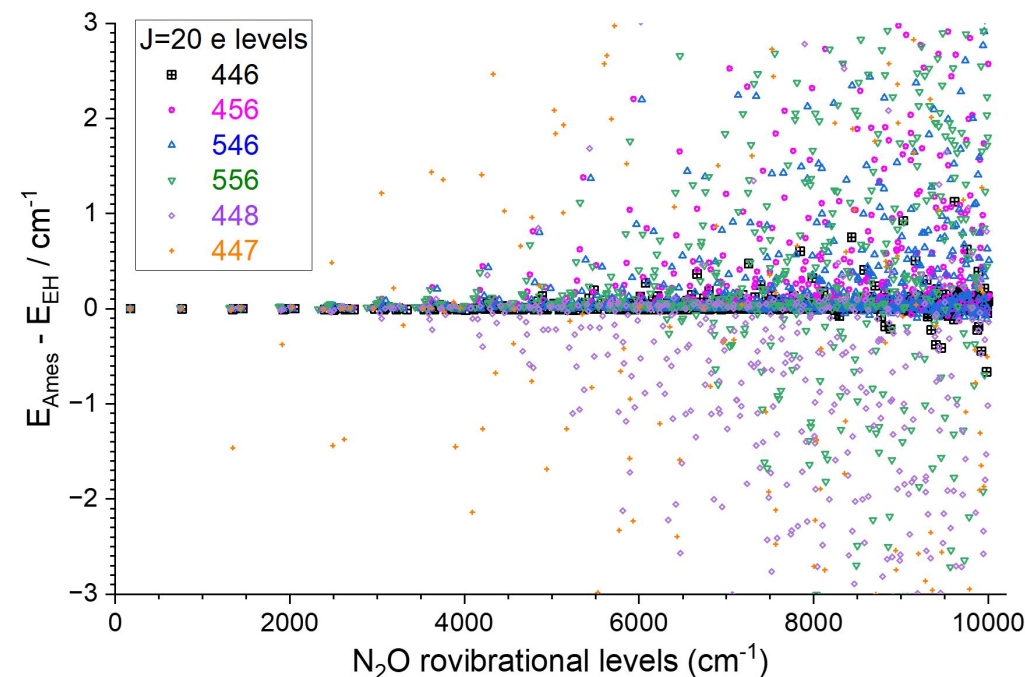
use E_{EH} if $|E_{EH} - E_{expt}| \leq 0.0066 \text{ cm}^{-1}$

or it is a GS, v_1 , v_2 , and v_3 level

✓ Step 3: reliable HITRAN levels

HITRAN: 456, 546, 448, 447

447 1111 data ignored; 447 2201 levels $E=E_{ames} - 0.025 \text{ cm}^{-1}$*



Global EH model of minor isotopologues
need more experimental data



N₂O : Upgraded ABG-IMRHT with uncertainty

"**A**mes-**B**1b PES + DMS **C**10K + **I**AO (NOSL & EH) + **M**ARVEL + **R**ITZ + **H**ITRAN + **T**oth"

✓ Uncertainty estimate for line position ω , and energy levels E' , and E'' :

$$u_{\omega} = \max(u_{E'}, u_{E''}), \text{ pure rotational } u_{\omega} = \max(0.04 \cdot u_E, 0.0001 \text{ cm}^{-1})$$

446 levels	Minor isotopologue levels
default for NOSL energies: 0.001 cm^{-1} if $< 7500 \text{ cm}^{-1}$, 0.005 cm^{-1} if $7500 - 10,000 \text{ cm}^{-1}$, 0.02 cm^{-1} if $> 10,000 \text{ cm}^{-1}$. Additional RITZ/MARVEL based adjustments : 0.01 cm^{-1} Unmatched levels: $0.05 \text{ cm}^{-1} - 0.10 \text{ cm}^{-1} - 0.50 \text{ cm}^{-1}$	HITRAN/RITZ/Obs/Toth/EH energies adopted: 0.001 cm^{-1} if $E < 7500 \text{ cm}^{-1}$, 0.005 cm^{-1} if $7500 < E < 10,000 \text{ cm}^{-1}$, 0.02 cm^{-1} if $E > 10,000 \text{ cm}^{-1}$. (or refer to the u in original databases, if reliable) Unmatched levels: $0.05 \text{ cm}^{-1} - 0.10 \text{ cm}^{-1} - 0.50 \text{ cm}^{-1}$

✓ Source index for E' and E'' energies

	0	1	2	4	
446	Ames	NOSL	MARVEL	RITZ	
minor iso	Ames	RITZ/Obs/Toth	HITRAN	EH	

✓ Uncertainty estimate for line intensity:

2-5% for strong bands ($>10^{-25}$); 5-15% for moderate bands (10^{-25} - 10^{-28}); 15-30% for weakest bands (below 10^{-28})



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 - reliability of global EH model – use isotopologue consistency
- Use reliable EH model fits or selected reliable data from global EH model
 - reliable range of EH models, simple correction for extrapolations



Summary & Future work

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From “experimental is experimental” to

- BTRHE consistency may help improve Expt/MARVEL data quality
- make reliable predictions at missing Js or extrapolations

From “simple match and adopt” to “Use reliable (global) EH model levels first”

- not all experimental data (collections) or (global) EH models are reliable
- refine PES wrt global EH + 1-to-1 match for high temperature line lists
- manual check is possible for low energy (if PES is accurate enough)

From directly using MARVEL data to

- direct MARVELization is not the best way to use MARVEL data
- Recommend consistent 0th-2nd order adjustments on $E_{\text{BTRHE/Calc}}$ or $E_{\text{Global EH}}$
- Recommend iterative improvement of MARVEL + highly accurate PES (refinement)

Future work:

- Explore new methods based on the advantages of BTRHE line lists

Funding from: NASA APRA, XRP, Venus Express SIP, and the NASA/SETI Co-operative Agreements
Collaborates with experimentalists to evaluate the performance of different methods