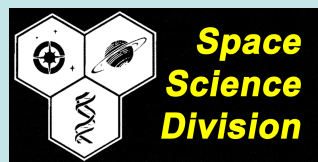




Combining *Ab Initio* Theory with Experiment to Obtain Highly Accurate Line Lists: CO₂ and SO₂

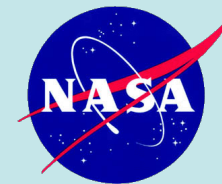
Timothy J. Lee, Xinchuan Huang, and David W. Schwenke

Space Science and Astrobiology Division
NASA Ames Research Center, Moffett Field, CA, USA





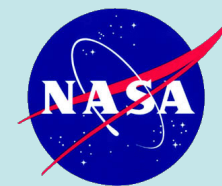
Some Recent & Current Projects



- *High-resolution rovibrational spectroscopy: NH_3 , CO_2 , CH_3OH , CH_3CN , SO_2 , CH_3OCH_3 (X. Huang, D. W. Schwenke, and others)*
- *Highly accurate quartic force fields => spectroscopic data for small astrochemistry molecules and their isotopologues: C_3H_3^+ , HC_2N , C_3H^+ , N_2OH^+ , HOCO isomers, etc. (X. Huang, N. Inostroza Pino, R. Fortenberry, and others)*
- *Comparison of basis set extrapolation vs. use of explicitly correlated R12 (or F12) methods at the CCSD(T) level of theory (E. Valeev and X. Huang)*
- *Global warming studies, specifically the radiative efficiency of various fluorinated compounds used in industry (P. Bera, J. Francisco, S. Kokkila)*
- *Determination of the mechanism for the UV-induced oxidation of pyrimidine/water ice mixtures into uracil (P. Bera, S. Sandford, M. Nuevo, S. Milam)*
- *Studies of ionic complexes between small astrochemistry molecules and their growth into larger ringed organic molecules (P. Bera and M. Head-Gordon)*
- *On the use of Morse-Cosine coordinates for variational calculations of rovibrational levels and spectroscopic constants with QFFs (R. Fortenberry, X. Huang, W. Thiel)*



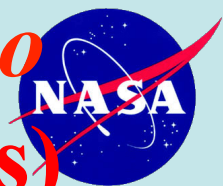
Outline



-
- Brief summary of the theoretical approach for computing highly accurate *ab initio* potential energy surfaces (PESs)
 - Brief summary of the empirical refinement procedure to improve the PES
 - Illustrative applications to:
 - CO₂
 - SO₂
 - Conclusions



Approach for Accurate *Ab Initio* Potential Energy Surfaces (PESs)

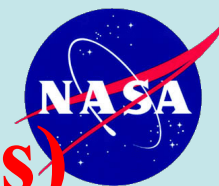


- Determine “reference” geometry (5Z basis set; include core-correlation)
- Set up grid of points for a PES about the reference geometry
- Calculate CCSD(T) energies for the TZ, QZ, and 5Z basis sets
- Compute ic-ACPF energies (or different higher-order method); TZ or QZ basis
- Compute core-correlation correction with CCSD(T) and QZ basis set
- Compute scalar relativity effects at CCSD(T)/TZ level
- Compute correction for diffuse functions or include explicitly
- If desired, compute DBOC and non-adiabatic corrections
- Extrapolate CCSD(T) TZ/QZ/5Z energies to basis set limit
- Include higher-order correlation, core-correlation, scalar relativity, diffuse function corrections (+DBOC)
- Fit the “local” part of the PES to high precision
- Combine with the long range part of the PES that allows dissociation
- Run many tests on the PES to eliminate holes and improve fit (more points; low weight “bridge” points; etc.)

X. Huang, D. W. Schwenke, and T. J. Lee, JCP **129**, 214304 (2008); Huang, Schwenke, and Lee, JCP **134**, 044320 (2011); Huang, Schwenke, and Lee, JCP **134**, 044321 (2011); X. Huang, D. W. Schwenke, S. Tashkun, and T. J. Lee, J. Chem. Phys., **136**, 124311 (2012).



Empirical Refinement of Potential Energy Surfaces (PESs)

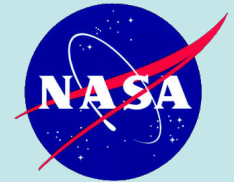


- Acquire and examine the available high-resolution rovibrational data for the molecule of interest and assess its precision (quality)
- Try to include as many J values as possible (this improves the J dependence of our extrapolations); weight the data according to its assessed precision
- Refinement performed on PES parameters using energy levels that are derived from observed rovibrational transitions to within a cutoff (0.02 cm^{-1} or better)
- Do not include in the refinement procedure any energy levels that have been obtained strictly through rovibrational models (i.e., a rovibrational model constructed from observed transitions and then extrapolated)
- Invariably, the energy levels from these models are not precise enough and degrade the empirical refinement
- Perform many refinements, tests, look for outliers, etc. in order to make the refined PES as robust as possible and useful for extrapolating beyond the experimental data included.
- Once completed, work with experimentalists on assigning new spectra, and once these have been assigned, go back to step 1.

H. Partridge, and D. W. Schwenke, JCP **106**, 4618 (1997); X. Huang, D. W. Schwenke, and T. J. Lee, JCP **129**, 214304 (2008); Huang, Schwenke, and Lee, JCP **134**, 044320 (2011); Huang, Schwenke, and Lee, JCP **134**, 044321 (2011); X. Huang, D. W. Schwenke, S. Tashkun, and T. J. Lee, J. Chem. Phys., **136**, 124311 (2012).



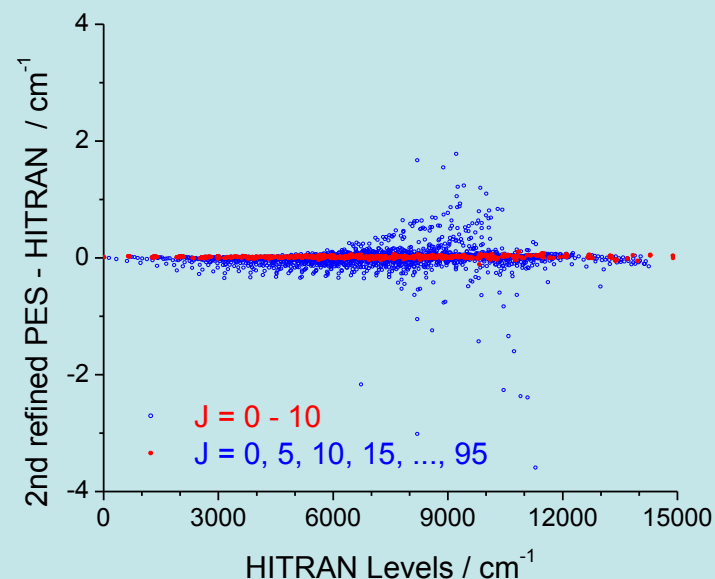
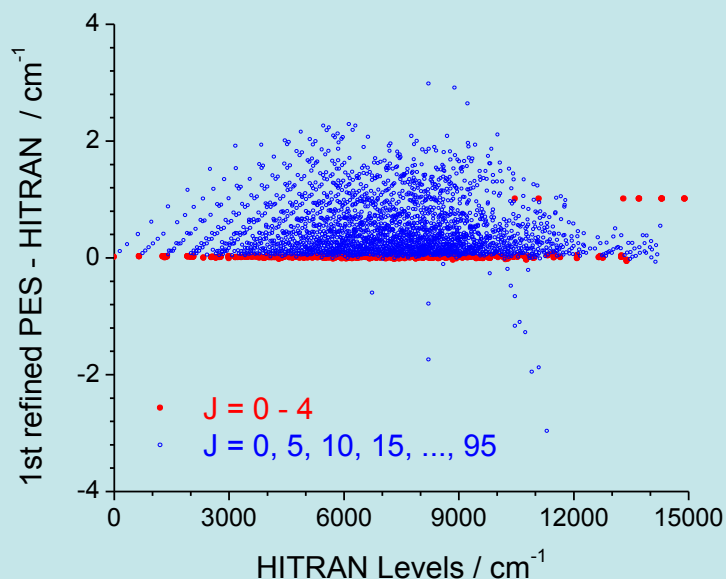
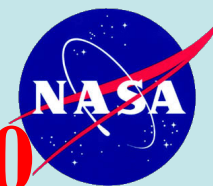
CO₂ : Motivation



- Venus Express is an ESA mission with NASA participation
- Venus Express completed its Primary Mission Sept 2007, and Extended Mission no. 1 Dec 2009
- Extended Mission no. 2 extends to Dec 2014 subject to validation in mid-2012
- Two of the goals of Venus Express are to study the atmospheric dynamics of Venus, and to study the atmospheric composition and chemistry
- CO₂ is the principle component of the Venusian atmosphere
- But the spectroscopy of CO₂ is not well characterized under the high temperature (750 K) and high pressure (100 bar) conditions present on Venus
- The current state of knowledge severely limits the analysis of data from the PFS and SOIR instruments
- Our goals:
 - to use state-of-the art *ab initio* calculations to construct a global PES for CO₂ and to use the best high-resolution experimental data to refine the PES (similar to NH₃ and H₂O)
 - To compute an accurate dipole moment surface (DMS) and to generate a highly accurate line list for CO₂ up to 20,000 cm⁻¹ above zero-point
 - To determine line shape parameters relevant to the conditions on Venus
 - To repeat this for the other isotopologues of CO₂



Global PES for CO₂: Initial Empirical Refinement of Ames-0

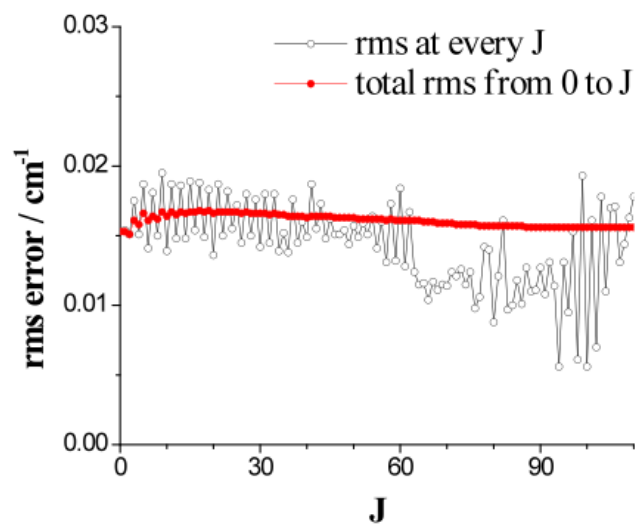
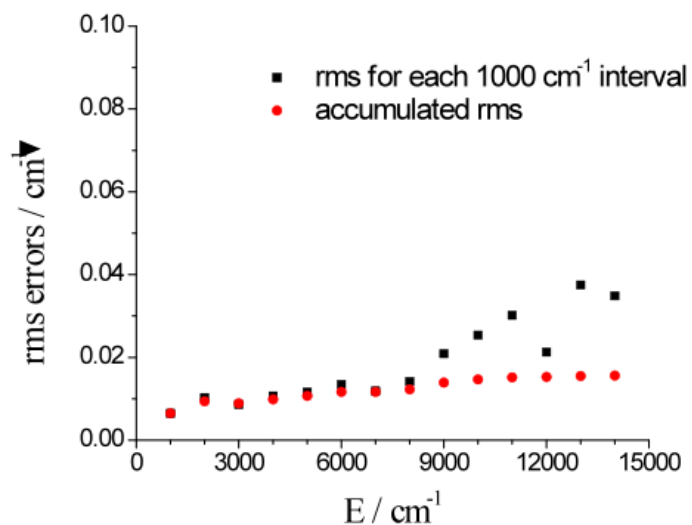
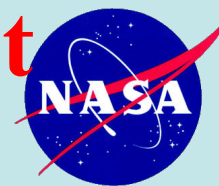


- Initial attempts to refine the PES used $J=0-4$ and then $J=0-10$ data from HITRAN2008; the increased J data significantly reduced the J dependent errors.
- As was done with NH₃, only up through the quartic constants were allowed to vary (22), and the maximum change was less than 2% in all cases.
- Use of higher J values (>40) was a disaster; the problem is that many of the HITRAN2008 energy levels are from models and not experimentally observed.
- Enter our collaborator Dr. Sergey Tashkun, who has compiled a set of 8142 experimentally determined energy levels for ¹²C¹⁶O₂.

X. Huang, D. W. Schwenke, S. Tashkun, and T. J. Lee, J. Chem. Phys., **136**, 124311 (2012).



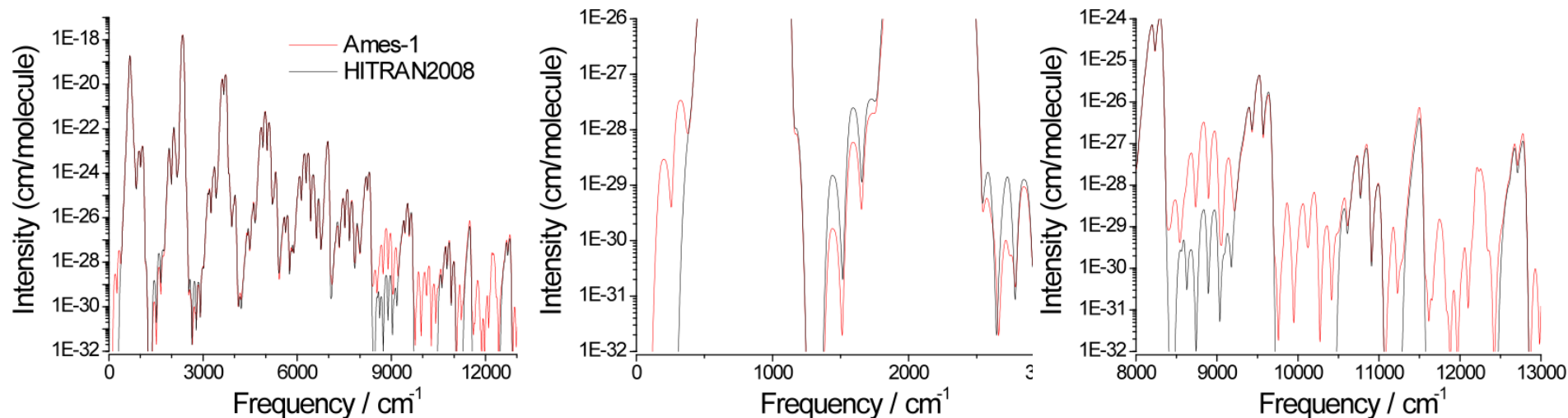
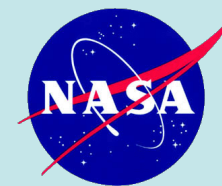
Global PES for CO₂: Refinement using only Expt (Ames-1)



- Refinement included all $J=0,1,2,10,25,40,55,70,85$ IR rovibrational levels (471); 3 levels above 20,000 cm⁻¹ and one $J=85$ level given smaller weight.
- We started with the previous $J=0-4$ refined PES: the change in all 22 coefficients was less than 0.7%.
- The RMS error is reduced from 0.085 cm⁻¹ on the $J=0-4$ PES to 0.0197 cm⁻¹ for Ames-1 for the 467 equally weighted energy levels.
- RMS errors range from 0.01 to 0.015 cm⁻¹ up to 8000 cm⁻¹, rising to 0.04 cm⁻¹ at 14,000 cm⁻¹ (J up to 117), with accumulated RMS of 0.0156 cm⁻¹ (6873 levels).



Initial IR Line List for $^{12}\text{C}^{16}\text{O}_2$ at 296K

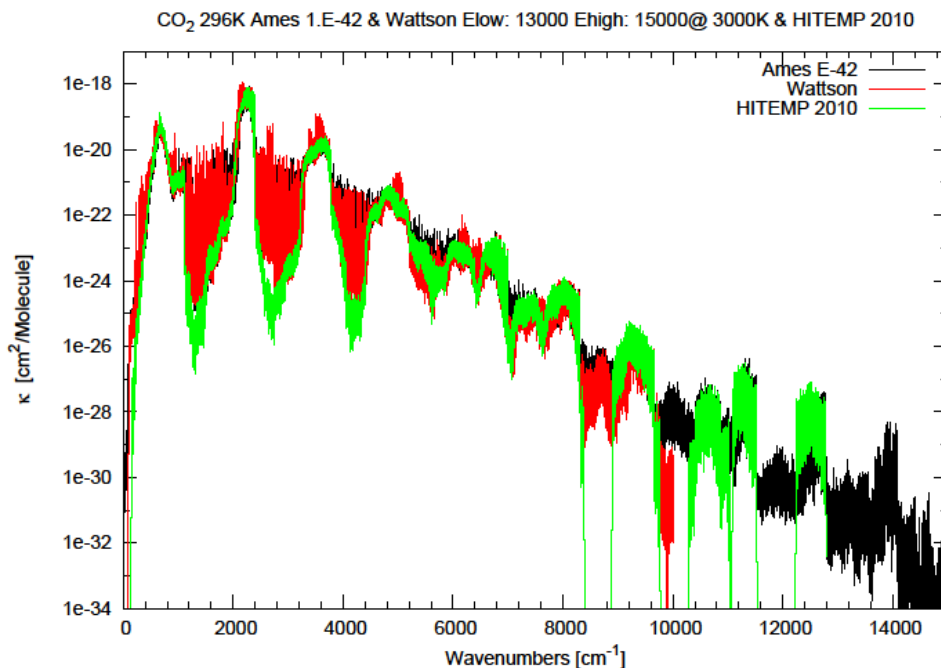
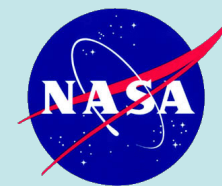


- Computed spectra at 296K using Ames-1 PES and Ames-0 DMS.
- For energies between 500 cm^{-1} and about 8400 cm^{-1} , agreement for IR intensities is reasonable.
- Some of the differences ($<500\text{ cm}^{-1}$ and around $10,000\text{ cm}^{-1}$ and $12,000\text{ cm}^{-1}$) are most likely due to a lack of experimental data in these regions.
- Some of the differences, such as around 1500 cm^{-1} , are probably due to deficiencies with the Ames-0 DMS; differences in other regions are not yet clear.
- Comparison with HITEMP, HOT-CO₂, and CDSO leads to similar conclusions.

X. Huang, D. W. Schwenke, S. Tashkun, and T. J. Lee, *J. Chem. Phys.*, **136**, 124311 (2012).



$^{12}\text{C}^{16}\text{O}_2$: Ames296 vs. HITEMP and Wattson

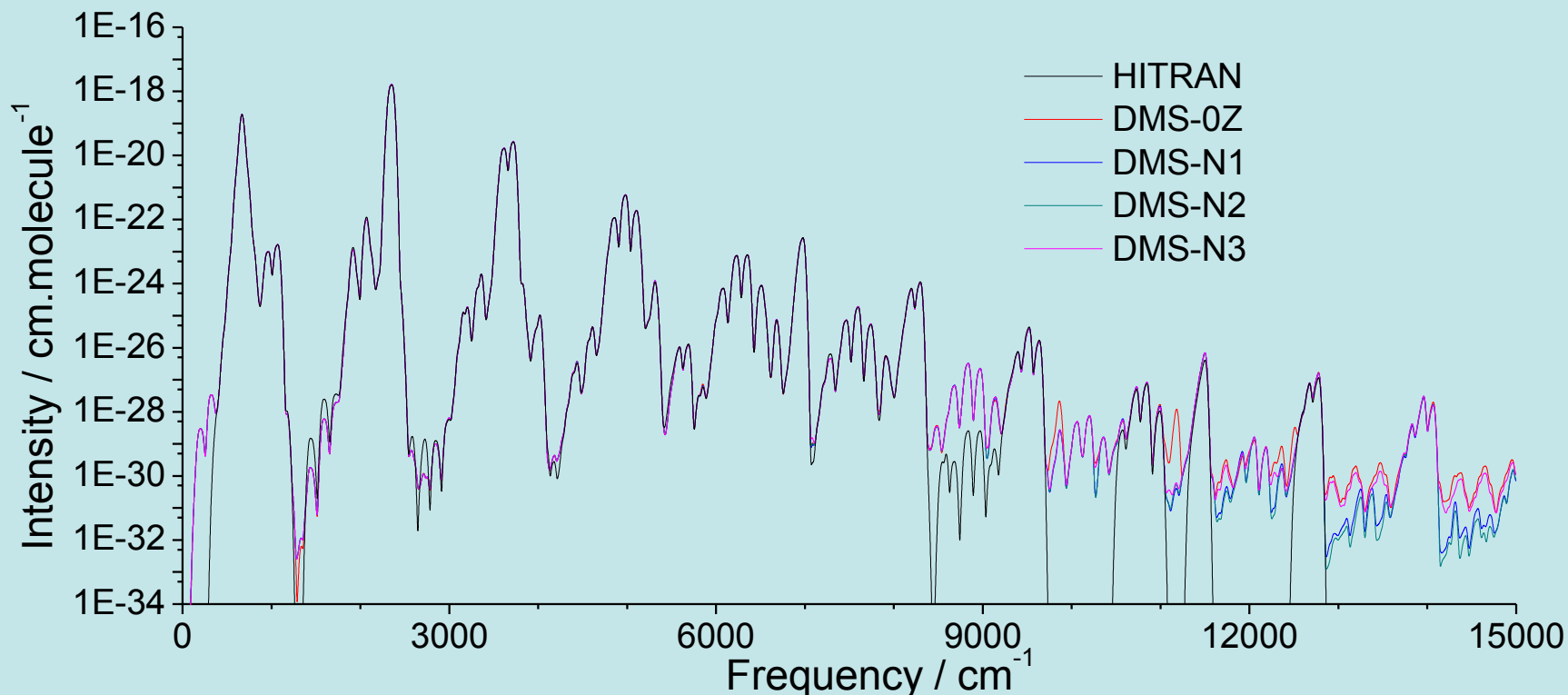


Computed by Richard
Freedman; unpublished.

- Computed spectra at 3000K using Ames-1 PES and Ames-0 DMS.
- Regions where HITEMP is incomplete and we are complete, but...
- Regions where our intensities do not agree
- Similar comparisons with CDSD show that our Ames-0 DMS is lacking

X. Huang, D. W. Schwenke, S. Tashkun, and T. J. Lee, *J. Chem. Phys.*, **136**, 124311 (2012).

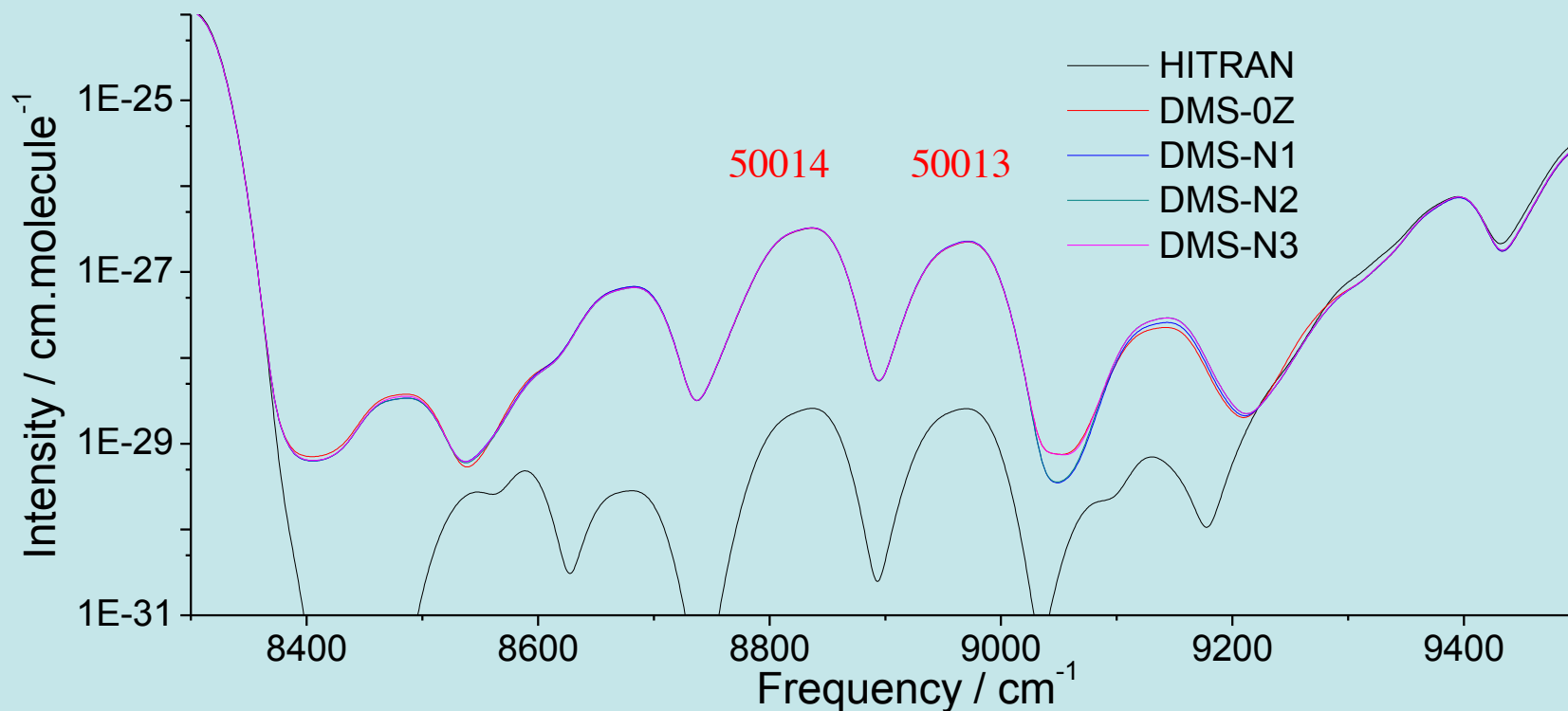
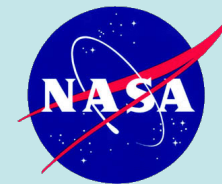
$^{12}\text{C}^{16}\text{O}_2$: New DMSs



- Computed spectra at 296K using the Ames-1 PES and new DMSs.
- DMS-N2 (or DMS-N1) are preferred; tests show that DMS-N3 is over determined
- There are significant changes above 11,500 cm⁻¹.
- Changes around 2000 cm⁻¹ are not large – minor differences in this region.



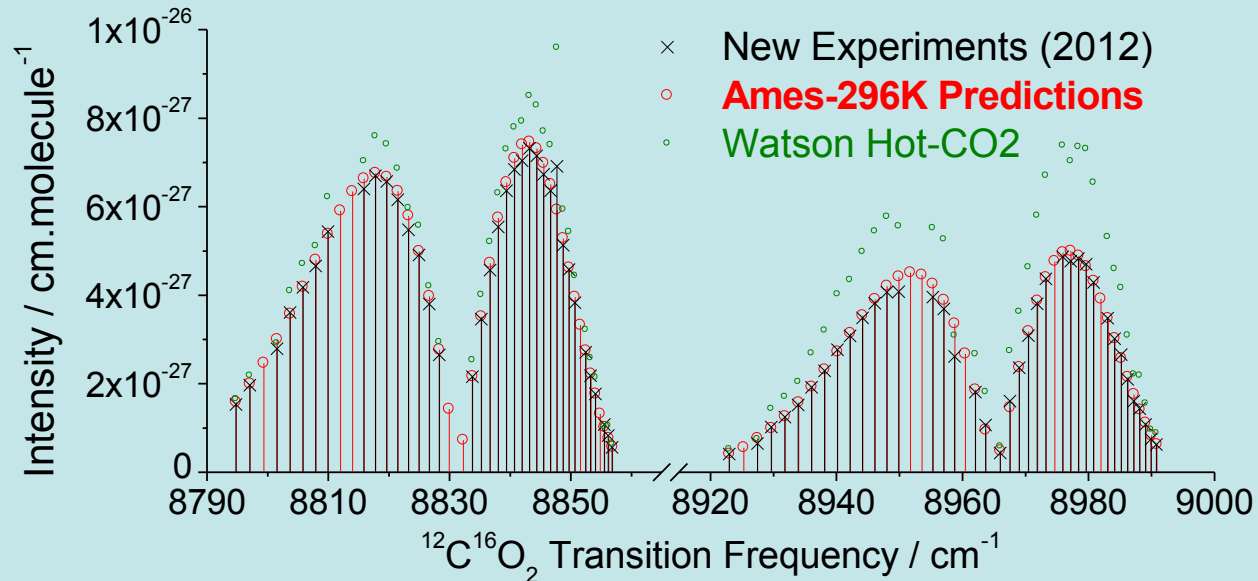
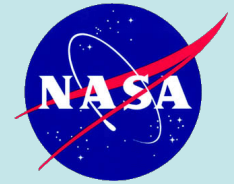
$^{12}\text{C}^{16}\text{O}_2$; New DMSs: 9000 cm^{-1} region



- Computed spectra at 296K using the Ames-1 PES and new DMSs.
- Still significant disagreement (two orders of magnitude) with HITRAN
- Which is correct?



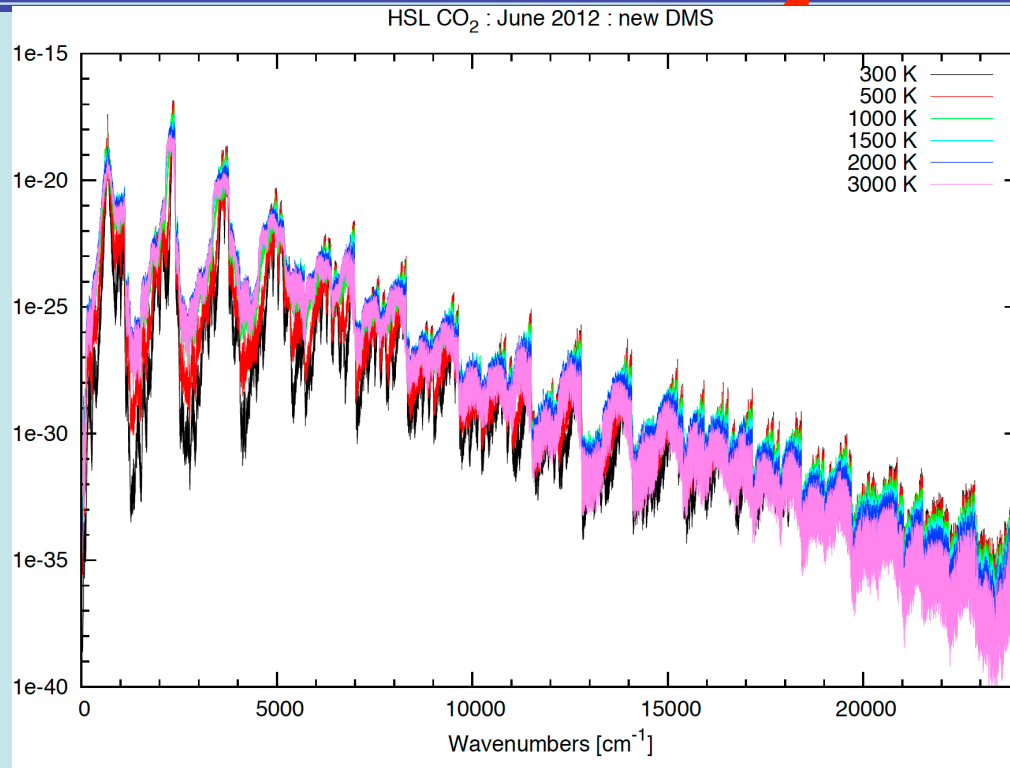
$^{12}\text{C}^{16}\text{O}_2$; New DMSs: 9000 cm^{-1} region



- Agreement between Ames-296K and the new experiments is excellent!
- HITRAN intensities 1/100th the Ames-296K/Expt values; do not appear
- The Ames-296K values are more accurate than the Wattson Hot-CO2 values also.
- The Ames-296K list is more complete than the new experiments.
- New experiments by T.M. Petrova, A.M. Solodov, A.A. Solodov, O.M. Lyulin, S.A. Tashkun, and V. I. Perevalov; Presented at The XVII Symposium on High Resolution Molecular Spectroscopy in July, 2012.

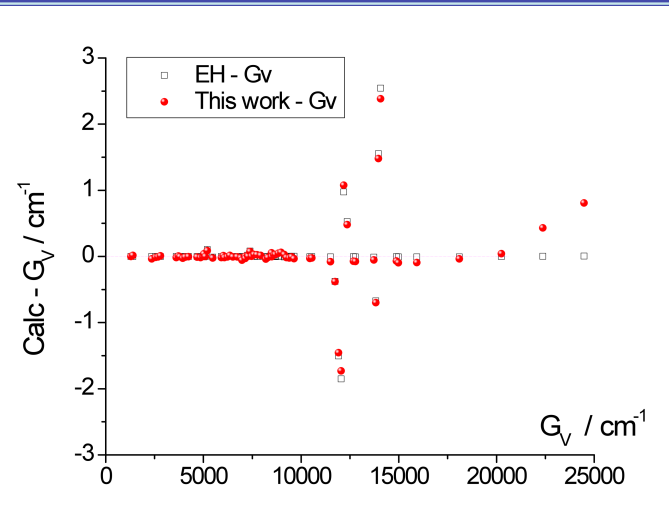
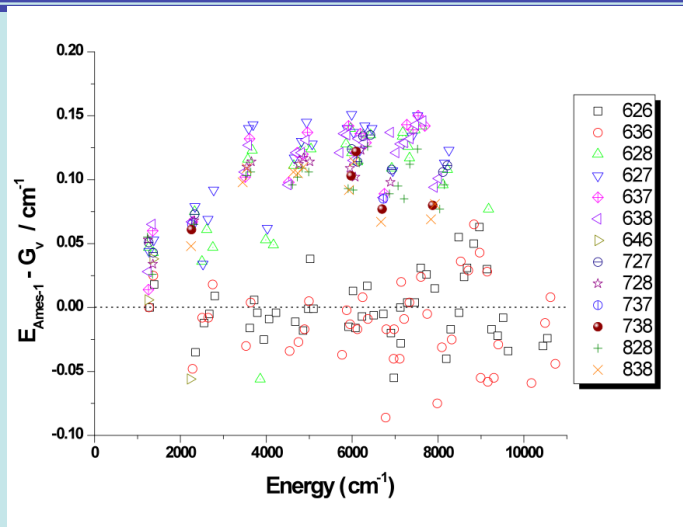


High Temperature Spectra for $^{12}\text{C}^{16}\text{O}_2$



- Based on published PES, but a new DMS (DMS-N2); using a 296K line list adapted to the temperatures shown.
- Covering J up to 170; E up to $30,000\text{ cm}^{-1}$; transitions $> 1\text{E-}42$
- We are confident in reliability of spectra up to $22,000\text{ cm}^{-1}$.
- A manuscript describing this new line list is in preparation.

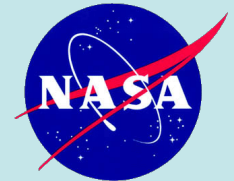
Isotopologues of CO₂



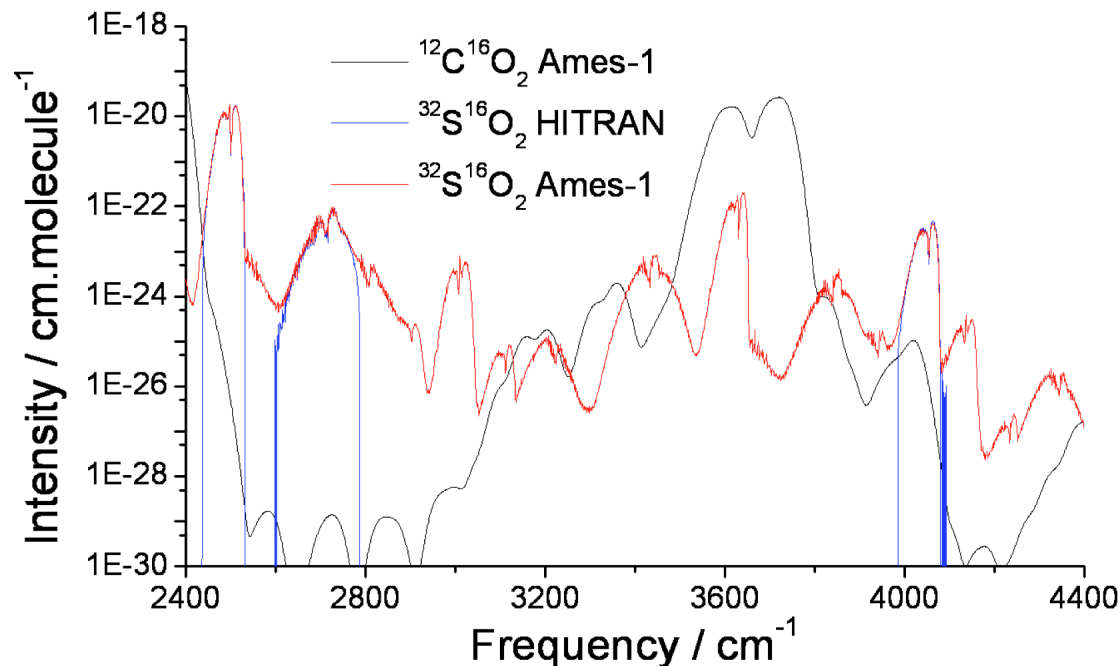
- The Ames-1 PES has been used to compute the J=0 band origins for 13 major isotopologues of CO₂, including: ¹²C¹⁶O₂, ¹³C¹⁶O₂, ¹²C¹⁸O₂, ¹²C¹⁷O₂, ¹³C¹⁸O₂, ¹³C¹⁷O₂, ¹⁴C¹⁶O₂, ¹⁶O¹²C¹⁸O, ¹⁶O¹²C¹⁷O, ¹⁶O¹³C¹⁸O, ¹⁶O¹³C¹⁷O, ¹⁷O¹²C¹⁸O, and ¹⁷O¹³C¹⁸O.
- The RMS error is less than 0.13 cm⁻¹ for all isotopologues
- For all known G_v values of these isotopologues (minus outliers), the RMS error from Ames-1 is 0.08 cm⁻¹, with E_{max} = 25,865 cm⁻¹
- G_v outliers were confirmed by comparison of Ames-1 values with those obtained from an Effective Hamiltonian model (Tashkun, to be published).



SO₂ : Motivation



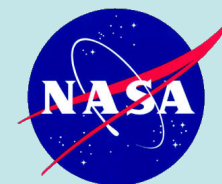
- SO₂ has been identified as a “2nd-class weed” by the HIFI community
- As such, its lines will obscure those from other (more interesting) molecules in various astrophysical environments.
- It is also an important minor constituent in some planetary atmospheres, such as Venus.



- There are regions where there is no CO₂ absorption, and there is SO₂ absorption but it is missing in HITRAN.
- This is the spectral region covered by the high resolution SOIR instrument on Venus Express



From Ames-0 to Ames-1: Details



489 selected geometries
 CCSD(T)/(aug-)cc-pV(X+d)Z basis, X=T,Q,5
 CCSD(T)/aug-cc-pcwVXZ, X=T,Q
[CCSD\(T\)/aug-cc-pV\(Q+d\)Z dipoles](#)
 core/scalar relativistic effects

219 unique coeffs, $i, j, k \leq 8$, $i+j+k \leq 12$, $i \leq j$
 Higher weights on ~ 400 points $< 30,000 \text{ cm}^{-1}$

Initial Ames-0: CCSD(T)/cc-pVQZ-DK

For $0 - 30,000 \text{ cm}^{-1}$,
 PES $\Delta(\text{avg}) = 0.21 \text{ cm}^{-1}$, $\sigma_{\text{RMS}} = 0.31 \text{ cm}^{-1}$

DMS $\delta(\text{avg}) = 1.2\text{E-}5 \text{ D}$, $\sigma_{\text{RMS}} = 1.96\text{E-}5 \text{ D}$
 DMS $\delta\%(\text{avg}) = 0.02\%$

E = Long-range terms (Morse-type) + Short-range terms * damping function

$$V_{\text{Long}} = \sum_{i=1}^2 D_{e1} (1 - e^{-\beta \cdot \Delta r_i})^2 + \sum_{i=1}^2 D_{e2} (1 - e^{-\beta \cdot \Delta r_i})^4 + e^{-0.2 \cdot (\Delta r_1^2 + \Delta r_2^2)} \cdot (A_{e1} \Delta \alpha_1^2 + A_{e2} \Delta \alpha_1^4)$$

$$V_{\text{Short}} = f_{\text{damp}} \sum_{n=1}^{969} C_{ijk}^n P[(\Delta r_1)^i (\Delta r_2)^j] (\Delta \alpha_1)^k, \quad f_{\text{damp}} = e^{-\text{damp}1 \sum_{i=1}^2 (\Delta r_i)^2 - \text{damp}2 \sum_{i=1}^2 (\Delta r_i)^4 - \text{damp}3 \cdot (\Delta \alpha_1)^2 - \text{damp}4 \cdot (\Delta \alpha_1)^4}$$

$D_{e1} = 233,156 \text{ cm}^{-1}$, $D_{e2} = 5,250 \text{ cm}^{-1}$, $A_{e1} = 56,000 \text{ cm}^{-1}$, $A_{e2} = 50,000 \text{ cm}^{-1}$
 $\beta = 1.152733 \text{ \AA}^{-1}$, $\Delta r_i = r_i - 1.43108 \text{ \AA}$, $\Delta \alpha_1 = \cos \alpha(\angle \text{OSO}) - \cos(119.3209^\circ)$

Refined with 465 selected HITRAN levels
 5/43/183/158/57 levels at J=0/4/20/50/70 with
 weights: 2.5/1.0/1.5/2.0/3.0.

80/73/49/47/43/30/22/74/28/ levels from GS/
 $\sqrt{3}/2\sqrt{3}/\sqrt{2}/\sqrt{2}+\sqrt{3}/2\sqrt{2}/\sqrt{1}/\sqrt{1}+\sqrt{2}$
 Plus 19 high res band origins.

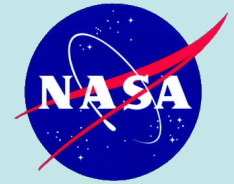
In short, a HITRAN-based refinement

On the Final Refined Ames-1 PES

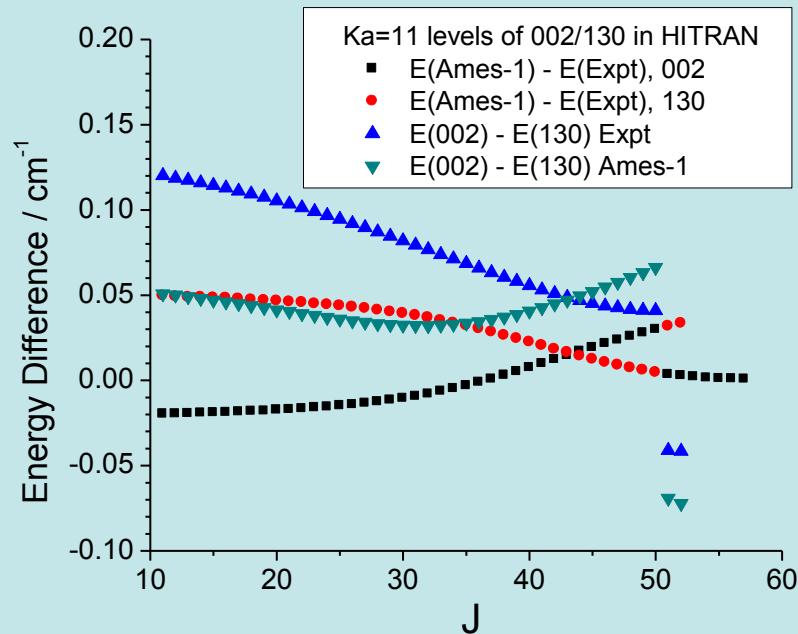
$\sigma_{\text{RMS}} = 0.024 \text{ cm}^{-1}$ (weighted)
0.010 cm^{-1} (unweighted)



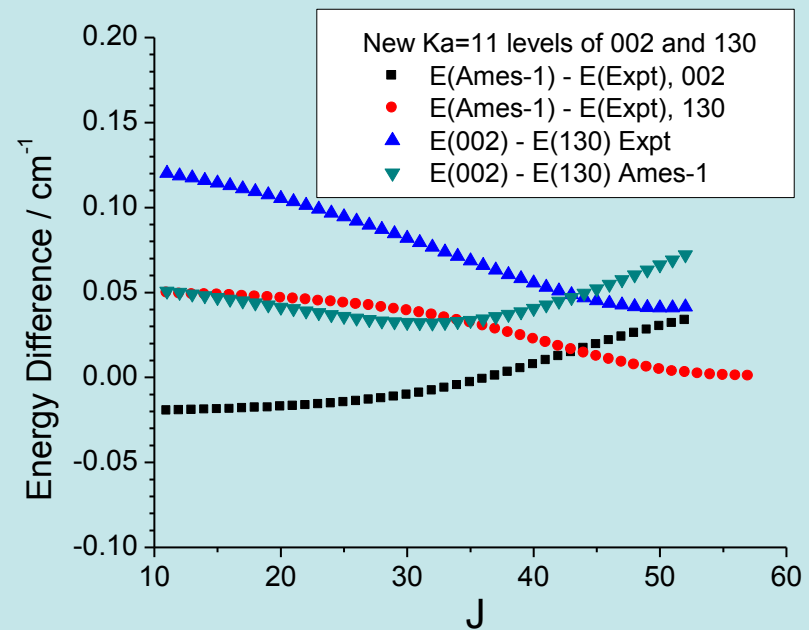
SO₂ : Relabeling a few 2v₃/v₁+3v₂ Ka=11 levels



Based on existing HITRAN assignments



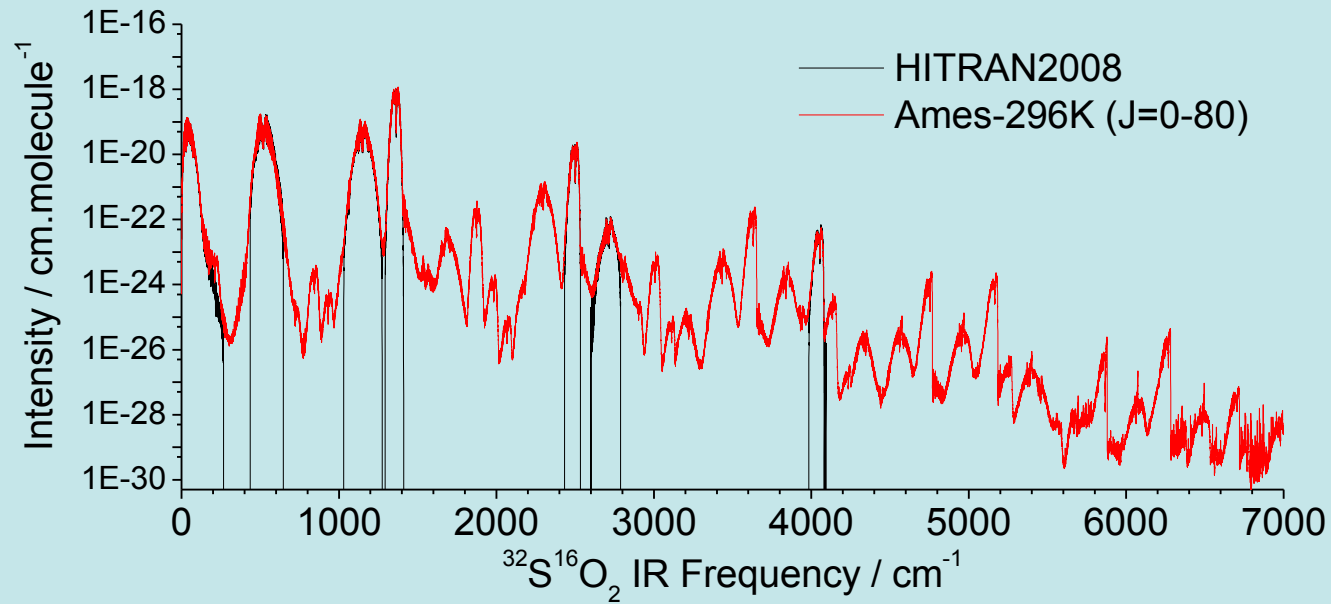
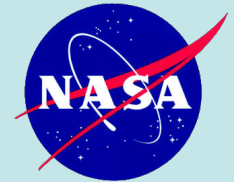
After relabeling 9 HITRAN levels
and 21 transitions



- 9 HITRAN levels and 21 transitions have been relabeled
- 2v₃: J=51-57 → v₁+3v₂: J=51-57
- v₁+3v₂: J=51-52 → 2v₃: J=51-52



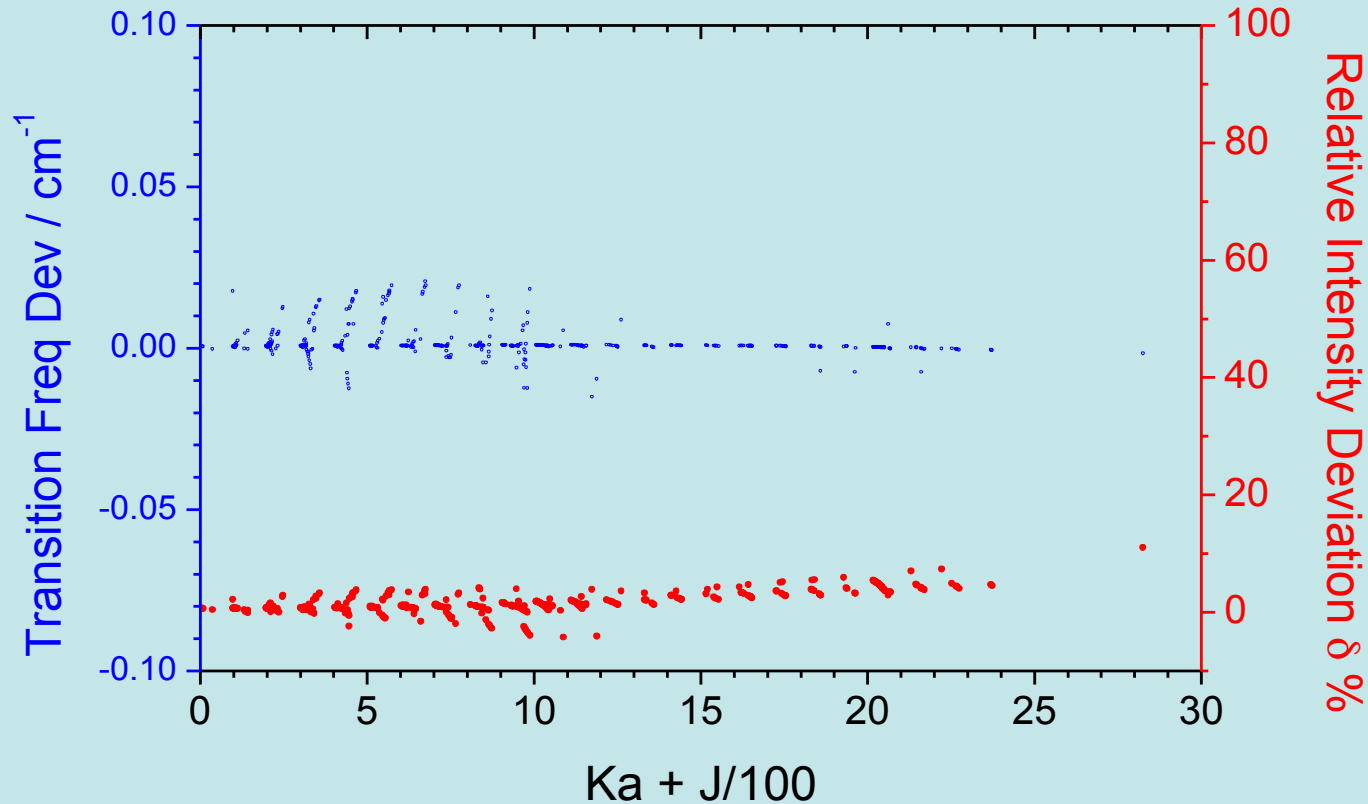
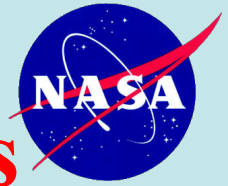
SO₂ : Line Lists



- ³²S¹⁶O₂ Line list above. Results for ³⁴S¹⁶O₂ look very good as well.
- Clearly, there are a lot of gaps in HITRAN for ³²S¹⁶O₂ (and for ³⁴S¹⁶O₂, the situation is not improved).
- But there is work to be done...



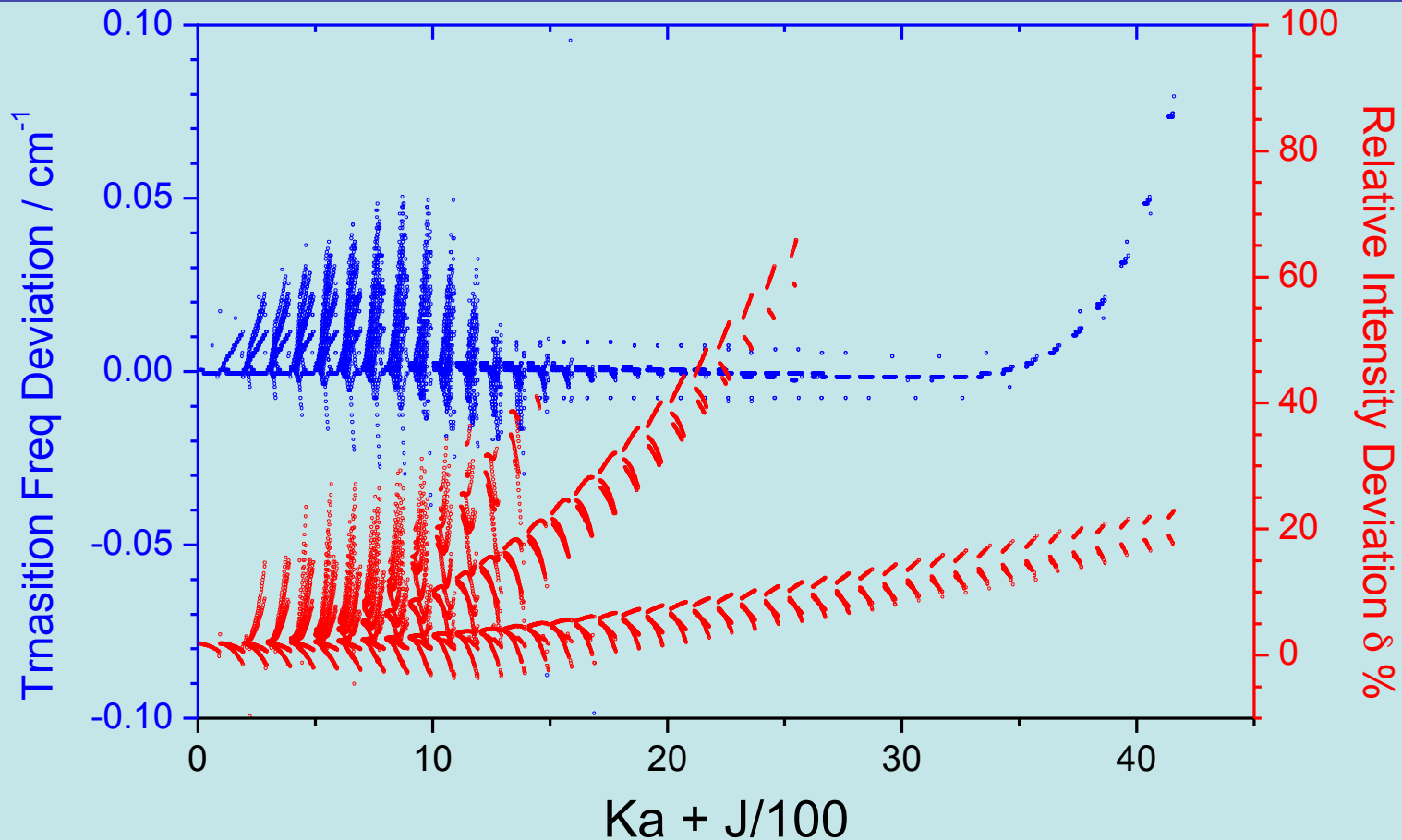
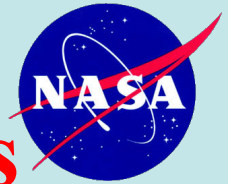
Comparison to Fitted CDMS: Purely rotational GS transitions



- Ames-296K vs. CDMS at 300K: 518 transitions from CDMS fitted set
- Symmetric residual: $\delta(I)\% = 50\% * (I_{\text{Ames}}/I_{\text{obs}} - I_{\text{obs}}/I_{\text{Ames}})$
- Range for $\Delta_{\text{freq}} = -0.0155 - 0.0203 \text{ cm}^{-1}$; for $\delta(I)\% = -4.5\% - 10.7\%$



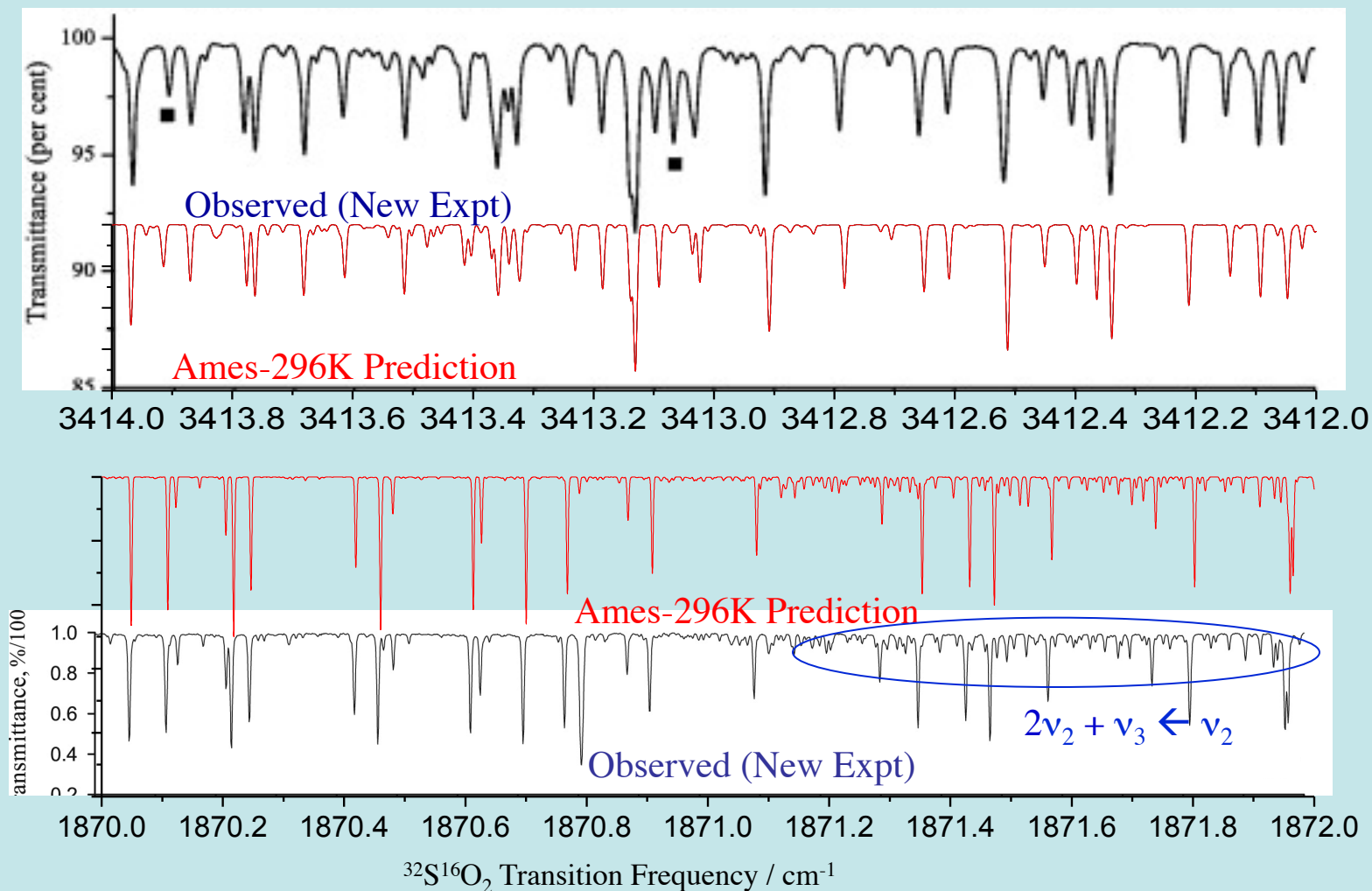
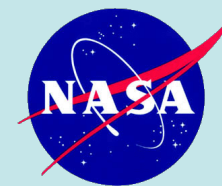
Comparison to Full CDMS: Purely rotational GS transitions



- Clearly there are problems with the extrapolated transitions, especially for intensities.
- A new and improved DMS shows the same behavior.
- We are working to resolve these differences.



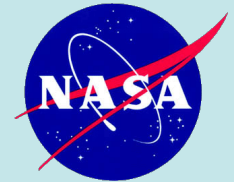
Accuracy for $^{32}\text{S}^{16}\text{O}_2$: $0.01\text{-}0.02\text{ cm}^{-1}$



- Agreement with experiment is very good (both 2 cm^{-1} windows)
- Experiment from: Ulenikov et al. JQSRT 112, 486 (2011).



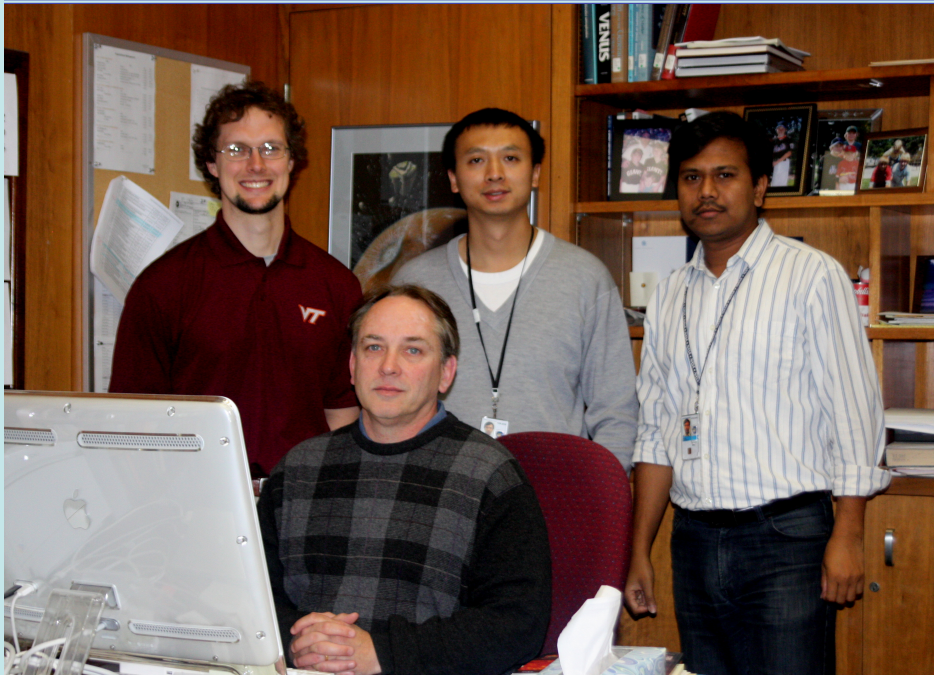
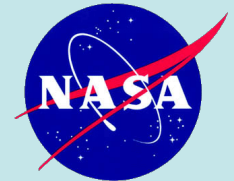
Conclusions & Future Work



- State-of-the art for accurate line lists involves a combination of *ab initio* theory and high-resolution laboratory experiment.
- Overall RMS error of 0.0156 cm^{-1} for 6873 rovibrational energy levels of $^{12}\text{C}^{16}\text{O}_2$ with J up to 117 for the Ames-1 PES.
- New CO_2 line list with DMS-N2; J up to 170 and $22,000 \text{ cm}^{-1}$; suitable for simulation of high-resolution high-temperature spectra (in preparation).
- Next, need to investigate pressure broadening due to the high pressures on Venus
- For $^{32}\text{S}^{16}\text{O}_2$, the weighted σ_{RMS} is 0.023 cm^{-1} (in preparation); more to come.
- Much more to do on SO_2 (e.g., not yet suitable for high temperatures).
- It is essential to use quality control in determining which experimental data is reliable and thus can be used in the refinement step. (energy levels obtained from spectroscopic models should be excluded in the refinement procedure)
- Determining high-quality molecular rovibrational line lists an iterative procedure.
- DMSs need to be evaluated with their own (larger) grid of points.



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