SAND2023-05346C

Sandia National Laboratories

A new line list for the N_2 Second Positive System

Elijah R. Jans

76th International Symposium on Molecular Spectroscopy

June 21st, 2023

WB06, Linelists

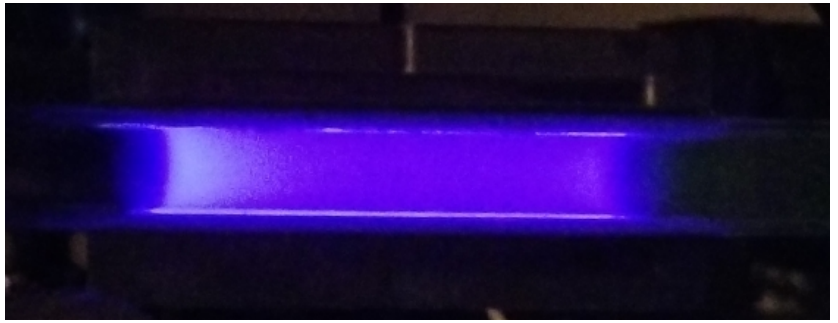
U.S. DEPARTMENT OF ENERGY | NNSA

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

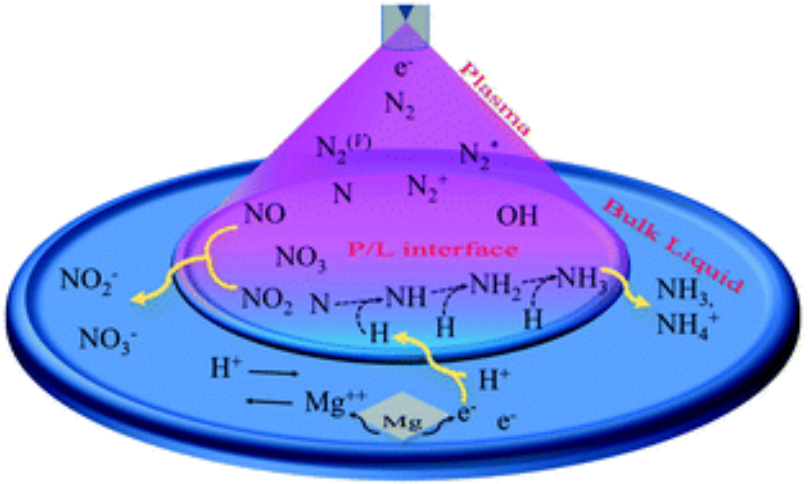
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Importance of N_2 second positive system (SPS)

- The SPS has been widely observed system in nitrogen containing plasmas and used in applications of:
  - Plasma medicine
  - Material processing
  - Plasma catalysis
  - Nitrogen fixation



- SPS has been used for a variety of optical diagnostics such as:
  - Kinetic studies
  - Temperature inference
  - Electric field estimates from ratio of FNS/SPS



Lamichhane et al. Geophys. React. Chem. Eng. 11, (2020)

- Electronic N_2 emission has also been observed in atmosphere of Titan by the Ultraviolet Imaging Spectrograph (UVIS) on Cassini Ajello et al. Geophys. Res. Lett. 34, 24, (2007)

Currently no publicly available linelist for the N_2(C-B) second positive system

N_2 low lying electronic states

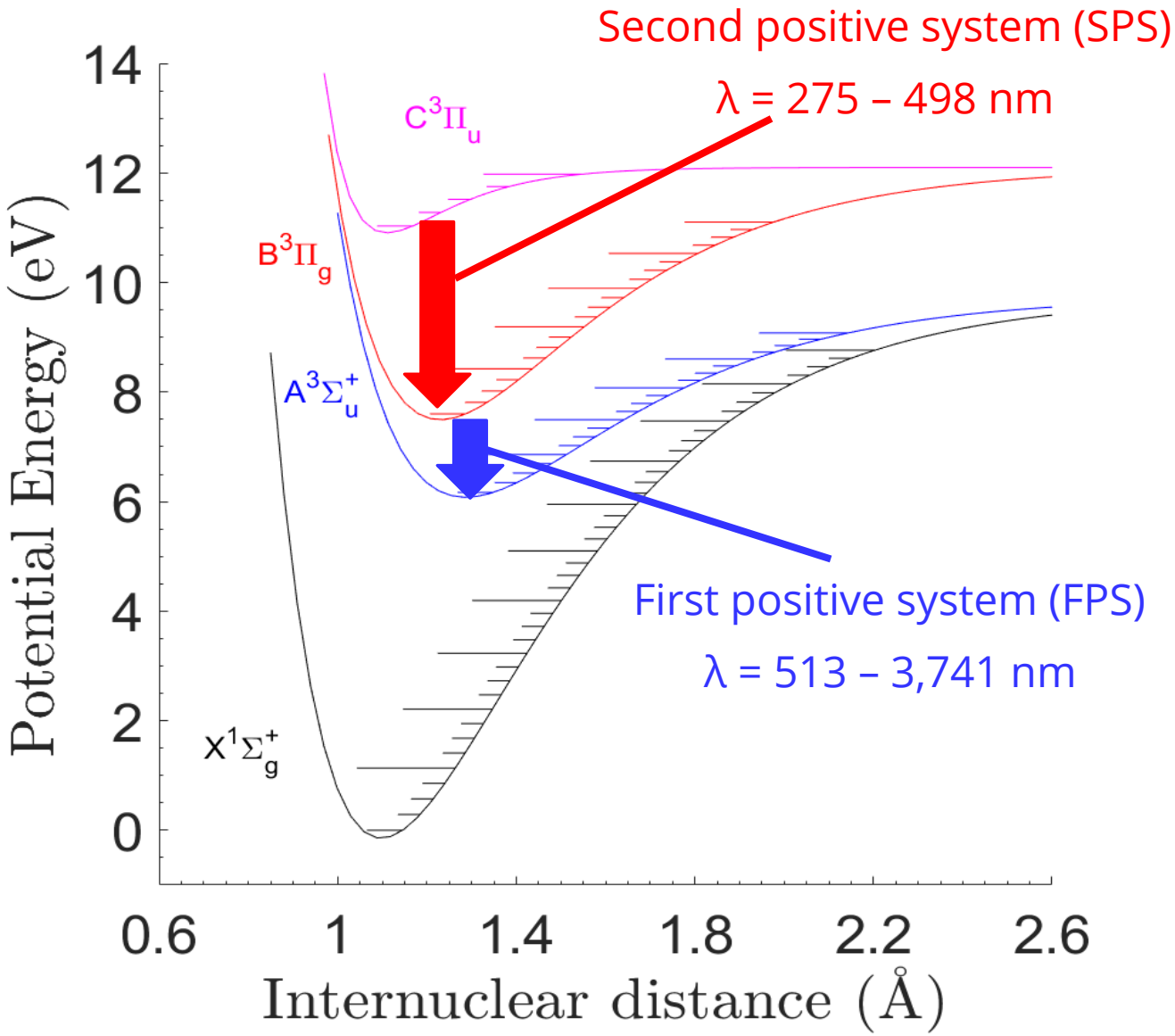
Most common N_2 emission bands are the:

- First Positive System (FPS)
- Second Positive System (SPS)

The FPS has had a comprehensive study by Western et al. JQSRT 219 (2018).

- Currently compiled in the ExoMol database

- The SPS is commonly modeled by the SPECAIR software.



How to calculate new linelist?

What software to use?

- PGOPHER – used by Western et al for excellent results on the FPS

What does PGOPHER need?

- Spectral constants (used for calculating energy states)
  - Bv, Gv, λ, o, p, q
- Electronic-vibrational transition moment

$$\left|R_e^{v'v''}\right|^2 = q_{v'v''}\left(R_e(\bar{r}_{v'v''})\right)^2$$

There have been numerous studies for calculating the spectral constants:

- **For $N_2(B)$** : Western et al., JQSRT 219 (2018)
- **For $N_2(C)$** : Roux and Michaud, JMS 158 (1993)

There have been fewer studies for the electronic-vibrational transition moment:

- Gilmore and Espy, J. Phys. Chem. Ref. Data 21 (1992)
- Laux et al., JQSRT 48 (1992)

Electronic-vibrational transition moment calculations

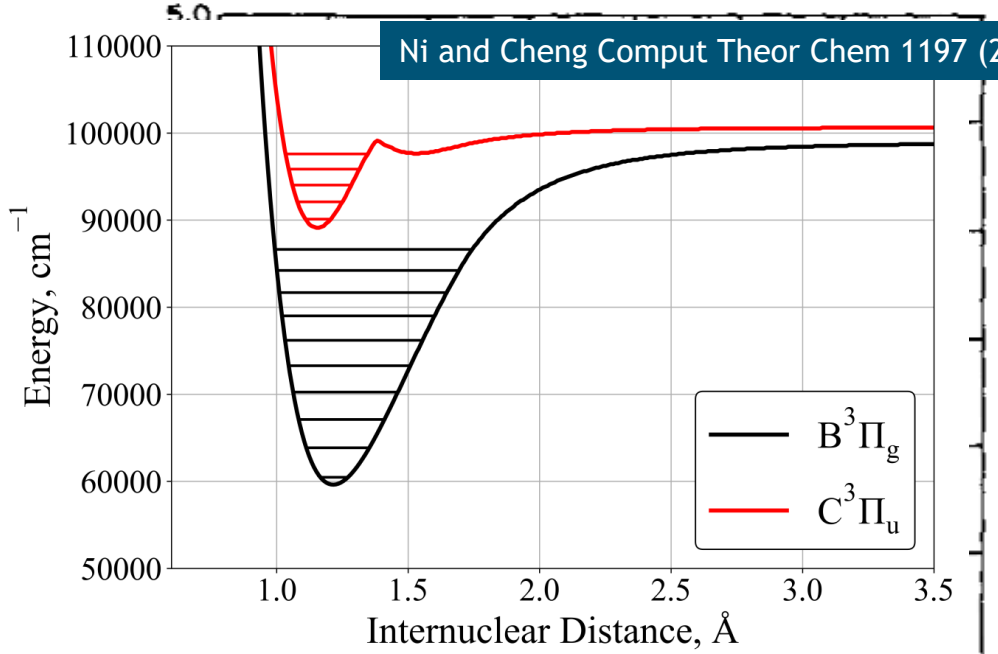
Previous studies only included max vibrational states:

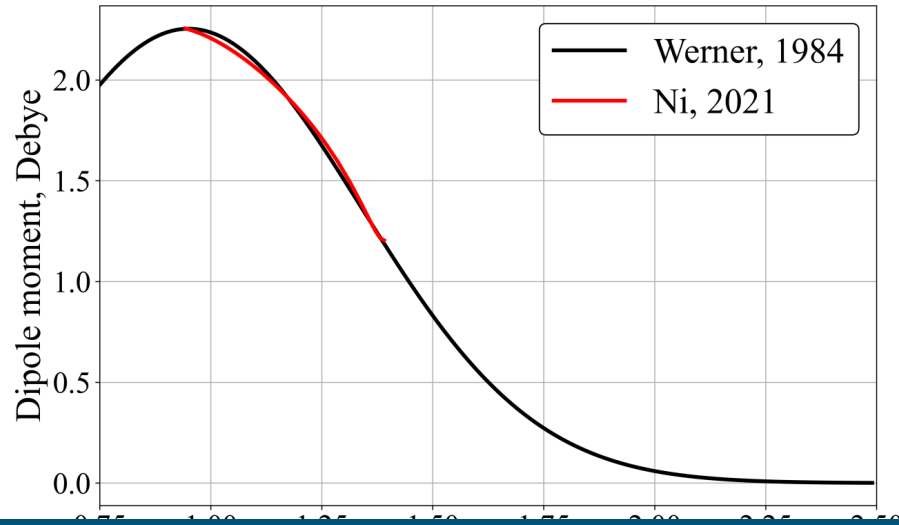
- $N_2(B)$ v = 0 ↔ 21
- $N_2(C)$ v = 0 ↔ 4

We want to extend the calculated electronic-vibrational transition moment up to v = 29 for $N_2(B)$

Previous calculations relied on Werner et al. J. Chem. Phys. 81, 2420–2431 (1984).

Recent potential energy curves (PECs) and transition dipole moment (TDM) have been published by Ni and Cheng Comput Theor Chem 1197 (2021)





Werner et al. J. Chem. Phys. 81, 2420–2431 (1984).

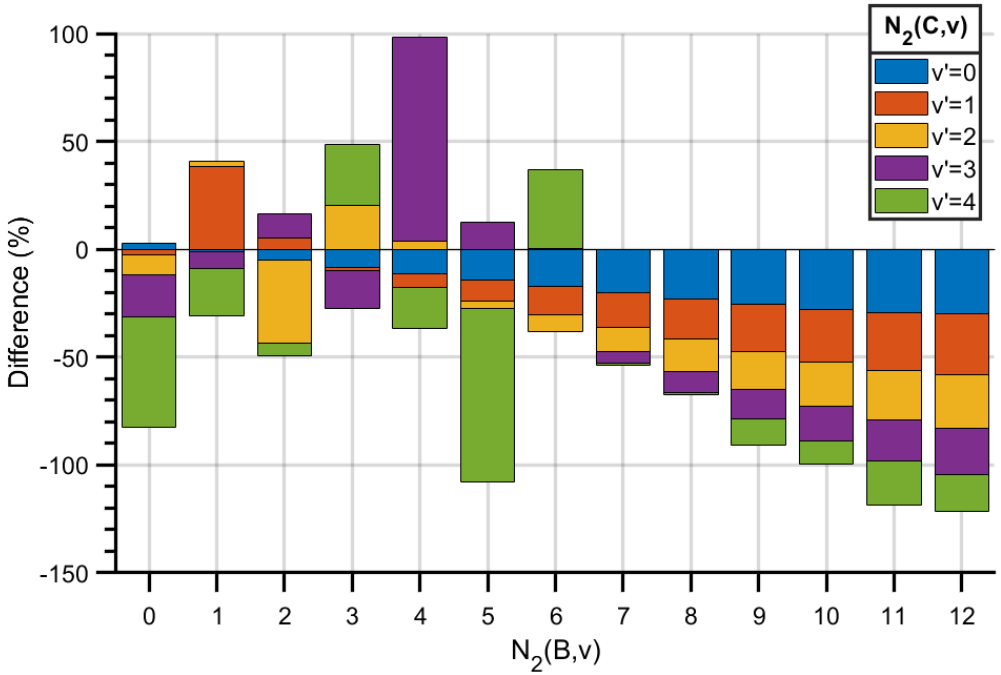
Electronic-vibrational transition moment comparisons

- Using DUO with Ni's *ab initio* calculations new moments were able to be calculated up to N_2(B, v =29)

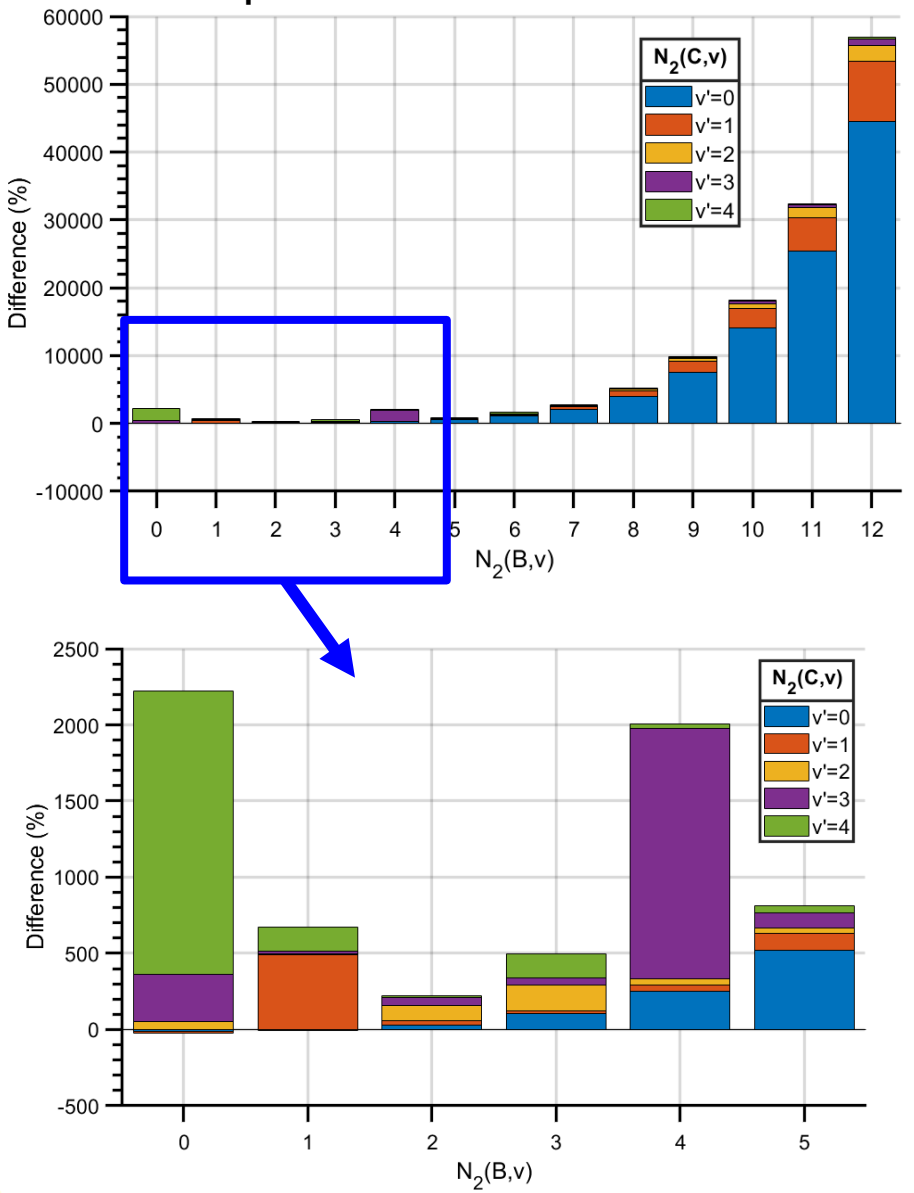
- Comparison with Gilmore et al. and Laux et al.

$$\text{difference (\%)} = \frac{\text{new} - \text{old}}{old} \text{ x } 100\%$$

Comparison with Gilmore et al. 1992

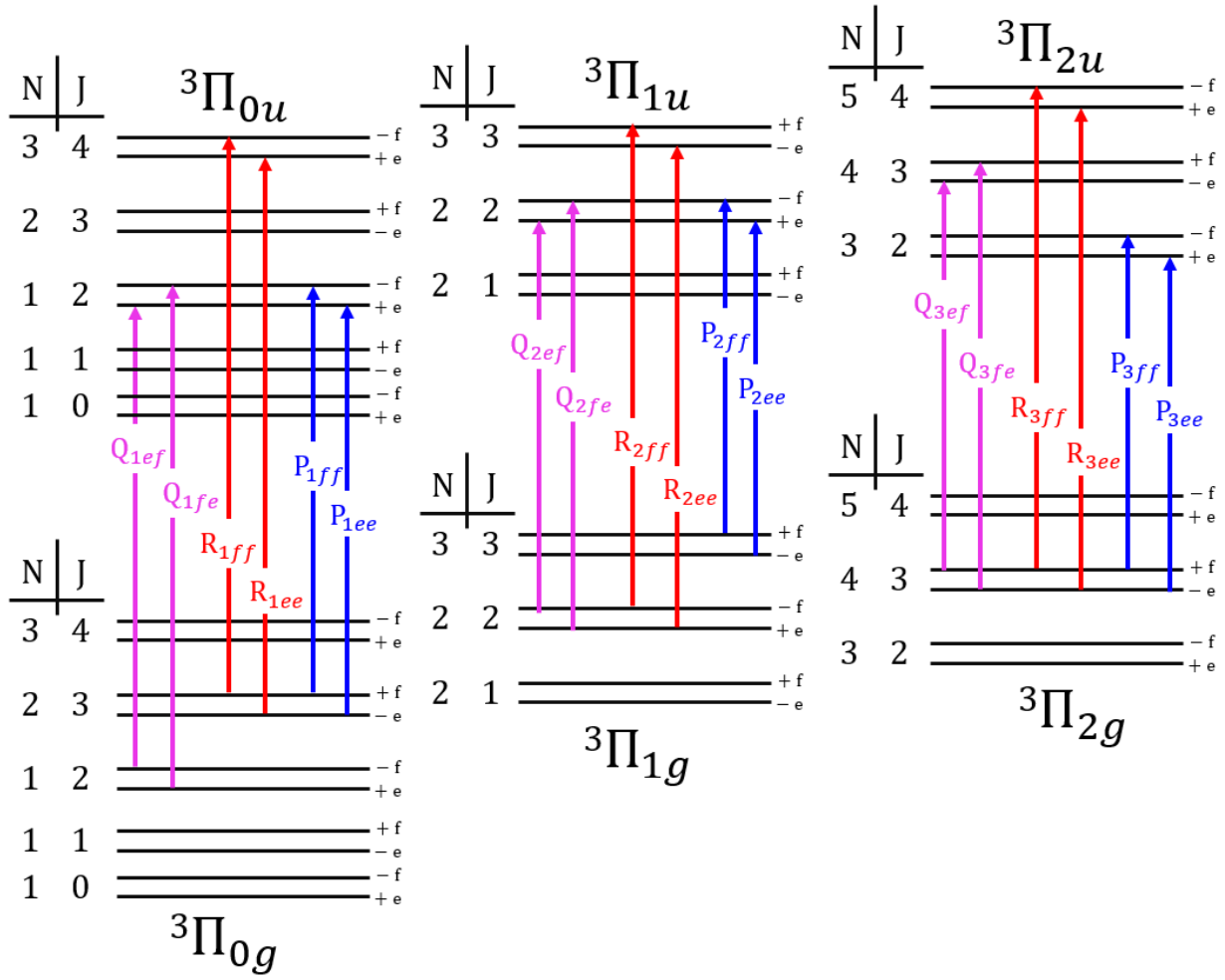


Comparison with Laux et al. 1992



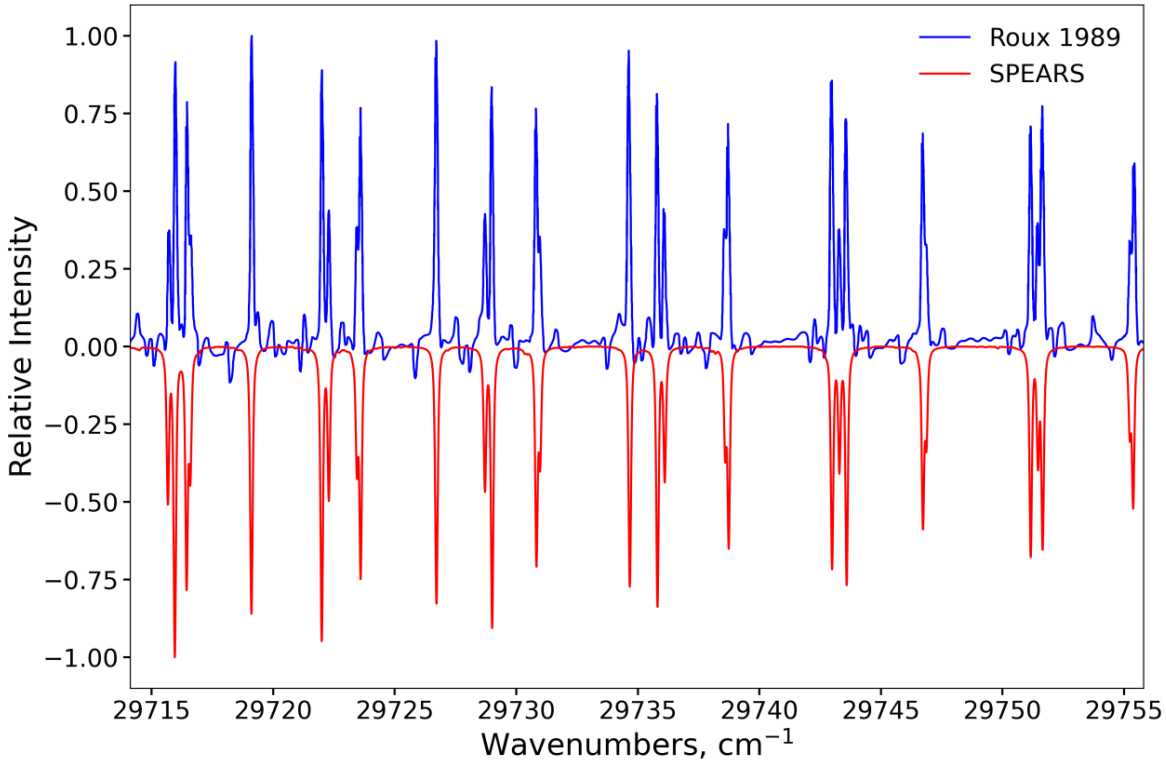
Second positive system spectral information

- The second positive system contains 6 main branches:
  - R_1, R_2, R_3,
  - P_1, P_2, P_3
- With the Q branches only weakly allowed.
- Satellite branches where $\Delta\Omega = \pm 1$ are typically not observed.



Comparison with high-resolution N_2 SPS data

- Comparison of high-resolution Fourier spectroscopy data from Roux 1989 in the $N_2(C, v=0 \rightarrow B, v=0)$ band agrees exceptionally well.

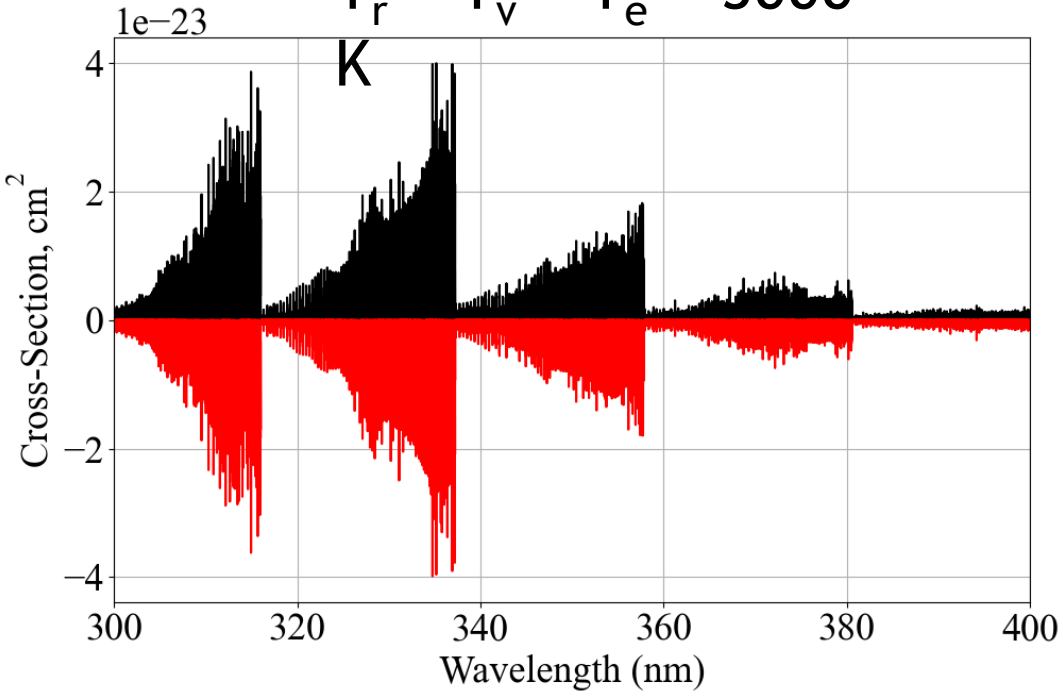


Comparison with SPECAIR

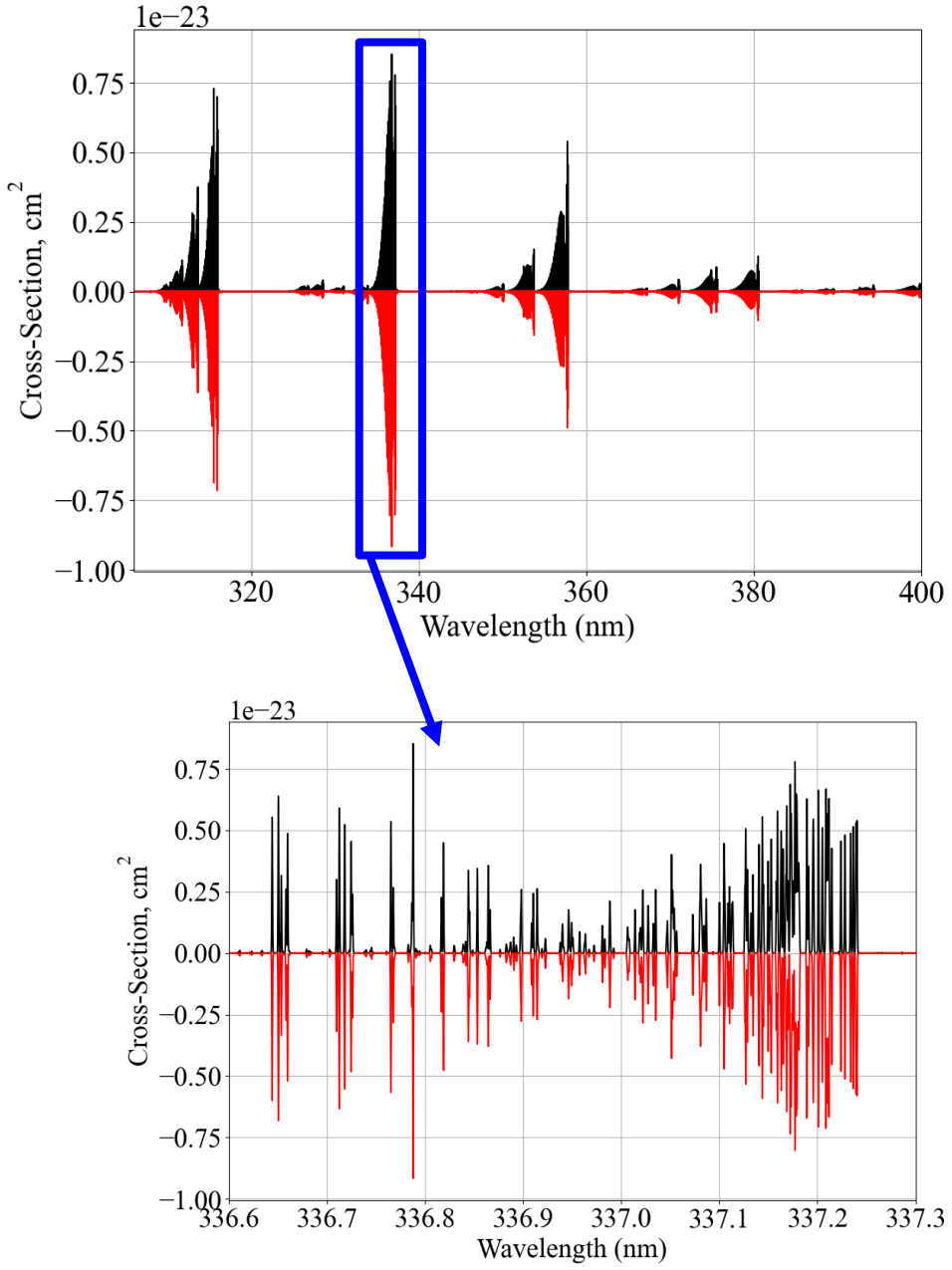
SPECAIR is the industry standard for SPS calculations.

- Typically used in nonequilibrium analysis of SPS spectra.

$T_r = T_v = T_e = 5000$ K



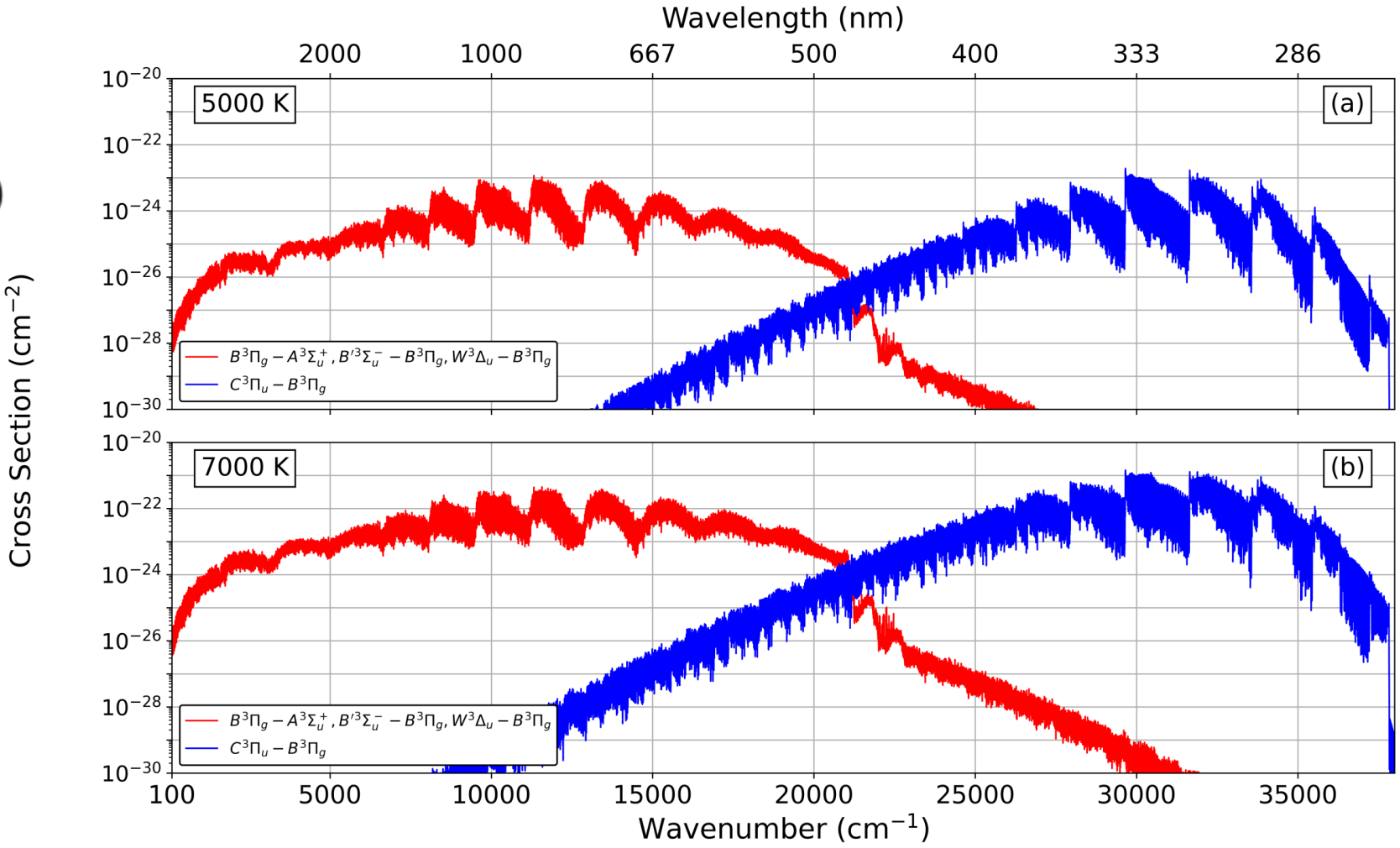
$T_r = 300$K, $T_v = 4000$ K, $T_e = 4000$ K



Broadband cross section calculation for N_2

Broadband cross-section calculation comparison for:

- Western et al., JQSRT 219 (2018)
  - $N_2(B^3\Pi_g - A^3\Sigma_u^+)$
  - $N_2(B'^3\Sigma_u^- - B^3\Pi_g)$
  - $N_2(W^3\Delta_u - B^3\Pi_g)$
- **New $N_2(C^3\Pi_u - B^3\Pi_g)$ linelist**
- **At temperatures:**
  - **5000 K**
  - **7000 K**



Second positive system spectral information

- PGOPHER data has been compiled into ExoMol style database for broader community engagement

Table 1: Extract of the state file for linelist.

i	E	g	J	+/-	e/f	sym	State	spin
1	59266.252923	6	0	+	e	g	B3Pigv=0	F1
2	60971.457769	6	0	+	e	g	B3Pigv=1	F1
3	62647.803530	6	0	+	e	g	B3Pigv=2	F1
4	64295.233138	6	0	+	e	g	B3Pigv=3	F1
5	65913.683586	6	0	+	e	g	B3Pigv=4	F1
6	67503.087164	6	0	+	e	g	B3Pigv=5	F1

- SPS spectra are widely used when not in equilibrium which raises questions on how much more additional data needs to be stored in ExoMol style data.

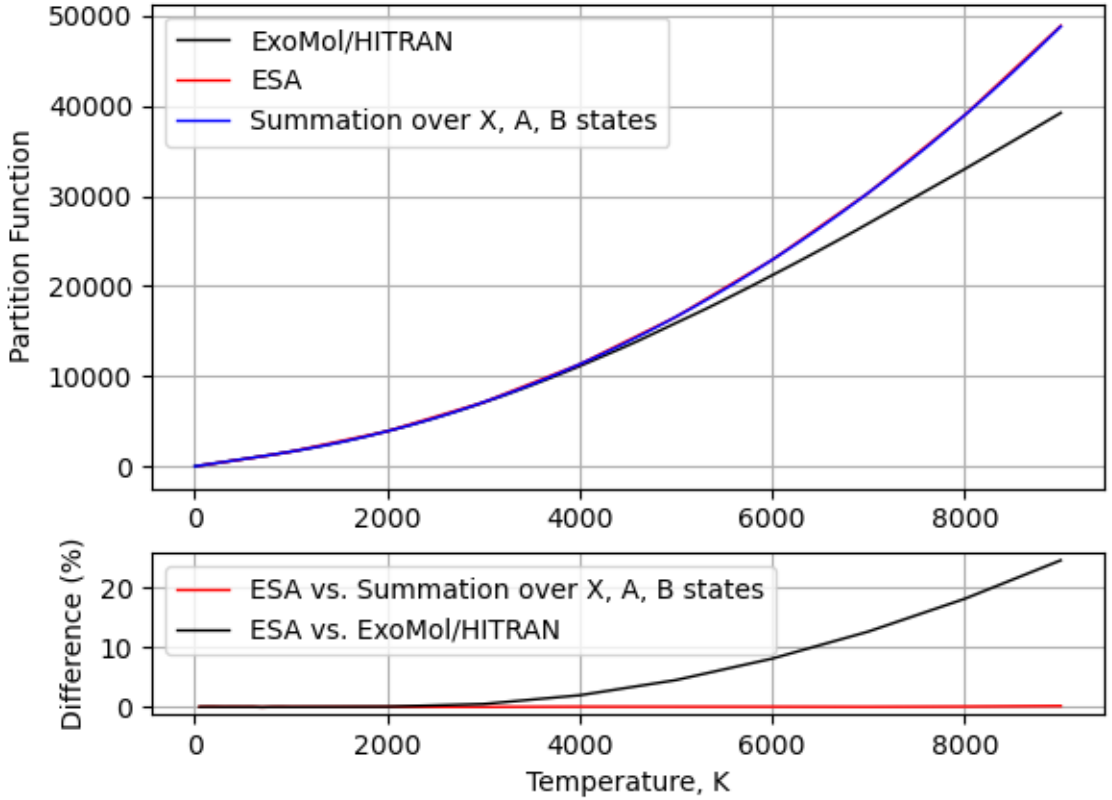
$$I = A_{ul} \cdot h \cdot c \cdot \nu \cdot n_u \cdot Y(\nu)$$

$$\frac{n_i}{n} = \frac{g_i \exp\left(-\frac{e_r}{kT_r}\right) exp\left(-\frac{e_v}{kT_v}\right) exp\left(-\frac{e_e}{kT_e}\right)}{Q_r Q_v Q_e}$$

$$e_r = e_t - e_v - e_e$$

Nitrogen partition function

- It was noticed there is disagreement in the total partition function for high-temperature N_2



Conclusion

- A new N_2 linelist has been developed to model second positive system up to 7000 K.
- A new electronic-vibrational transition moment have been calculated.
- The new linelist extends the vibrational states used
  - N_2(B v = 0 – 29)
- Good comparisons with high resolution spectral data and to SPECAIR software.
- No perturbations of the B or C were considered.

Future Work

- Linelist publication

Acknowledgements

We gratefully acknowledge Sandia National Laboratories and the Laboratory Directed Research and Development (LDRD) program for funding this research