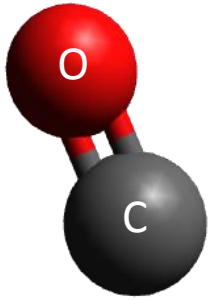
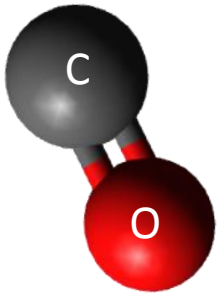
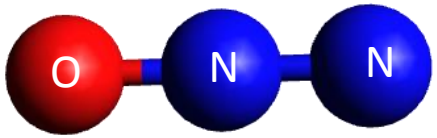
FIRST OBSERVATION OF THE N_2O-OC VAN DER WAALS COMPLEX AND NEW SET OF EXPERIMENTAL MEASUREMENTS ON THE N_2O-CO COMPLEX.

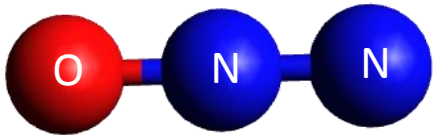
CLÉMENT LAUZIN, A. J. BARCLAY, S. SHEYBANI-DELOUI, NASSER MOAZZEN-AHMADI







N_2O-CO
OC-N_2O



N_2O-OC
CO-N_2O

UCL
Université catholique de Louvain

UNIVERSITY OF CALGARY
RESEARCH

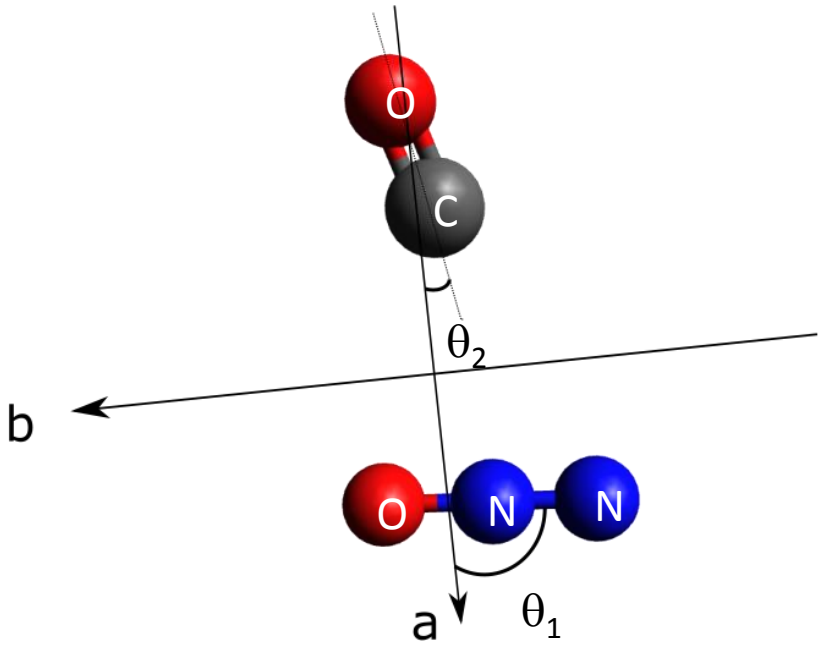
Previous Works (I)

The C-O Stretching Band of the CO-N_2O van der Waals complex
Y. XU, A. R. W. McKellar, JMS **180**,164-169 (1996)

First detection!!
Planar semi-rigid system

R_{dim}=3.878 Å

CO stretch



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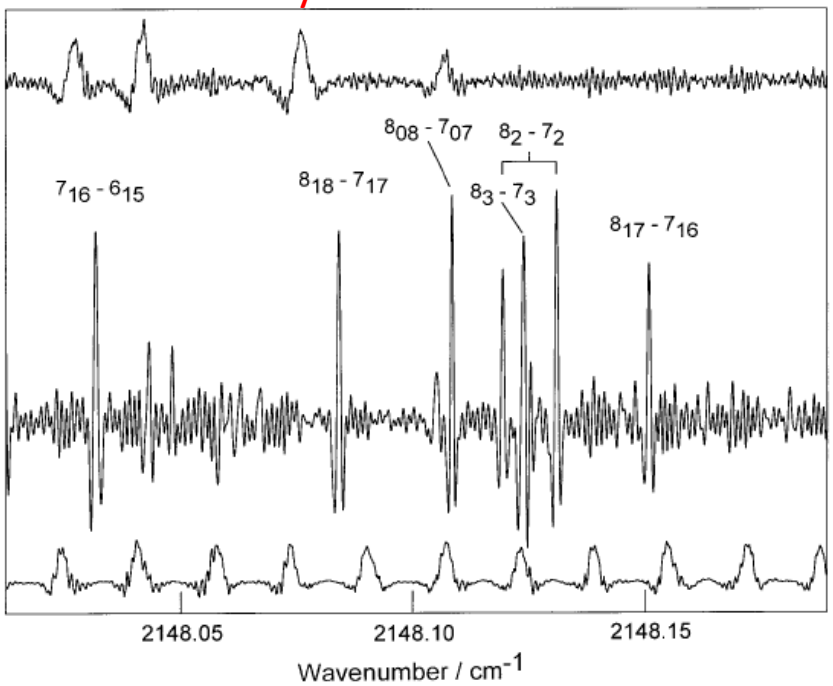
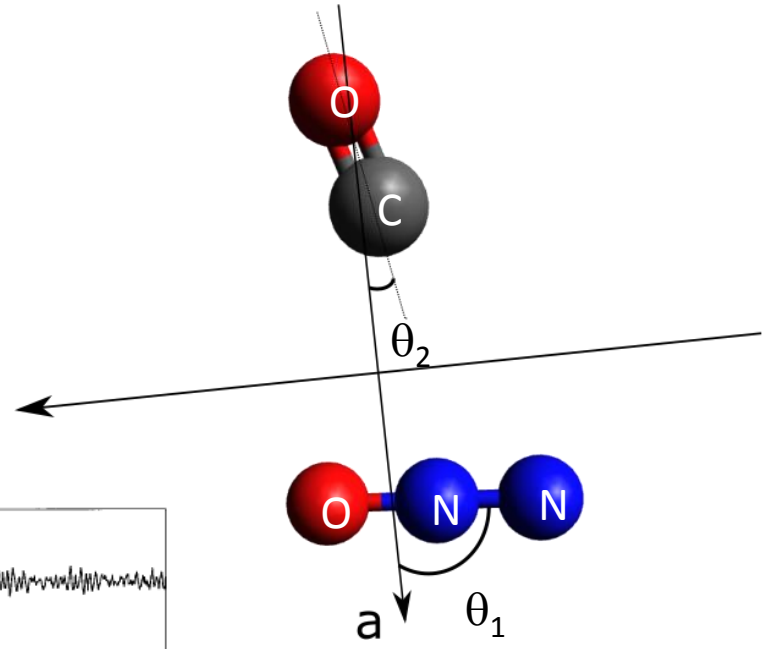
a-type transitions only





Previous Works (II)

8 months later

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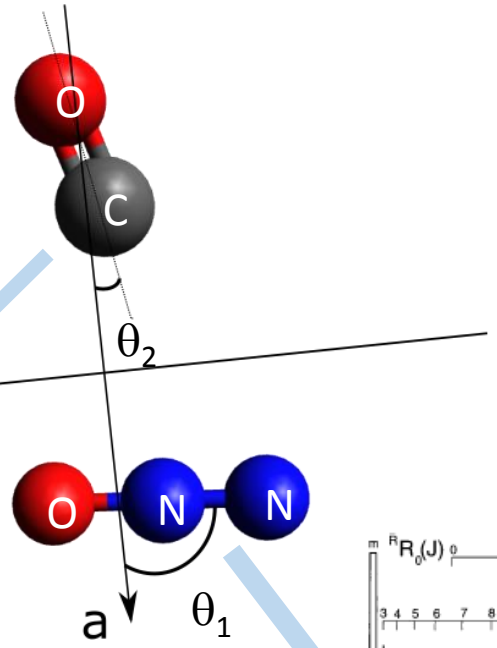
Y. XU, A. R. W. McKellar, JMS **180**,164-169 (1996)

High resolution spectroscopy and structure of CO-N_2O
Hai-Bo Qian and Brian Howard, JMS **184**,156-161 (1997)

First detection!!
Planar semi-rigid system

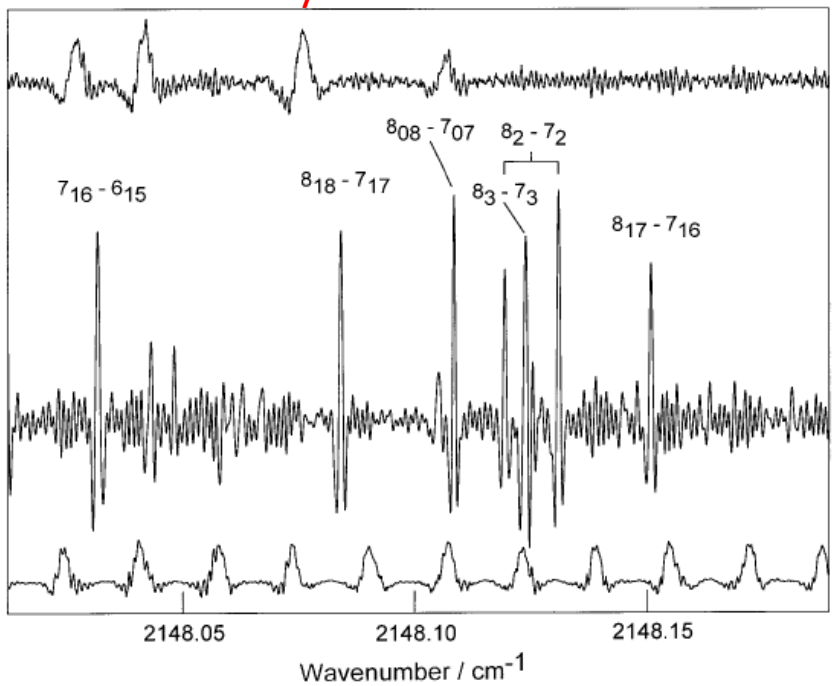
R_{dim}=3.878 Å

Rdim=3.87
θ_2=20° ± 5°
θ_1=80° ± 5°



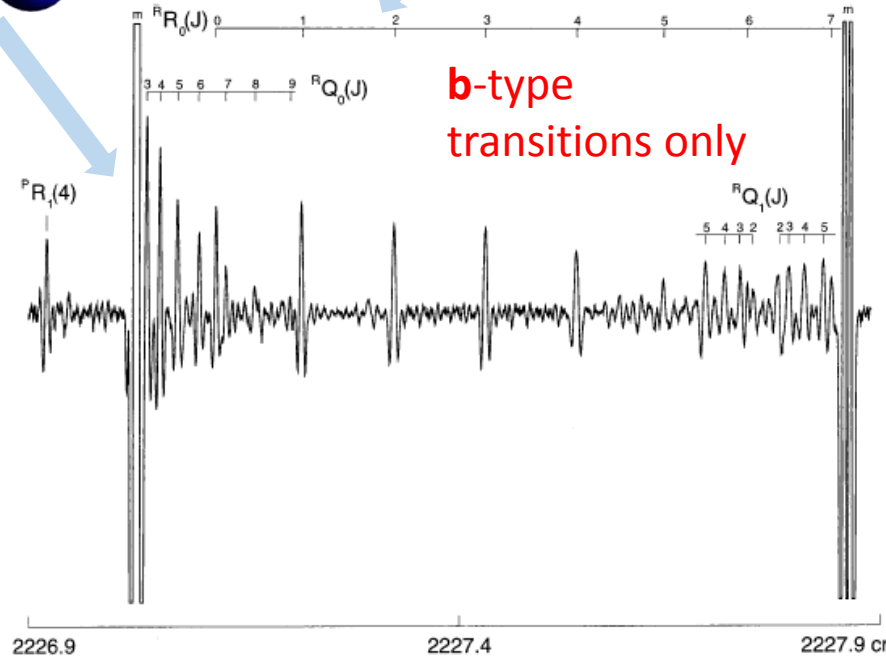
CO stretch

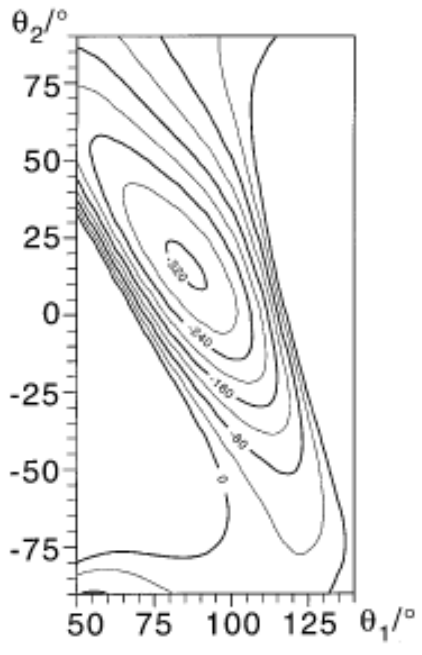
a-type transitions only



NN stretch

b-type transitions only





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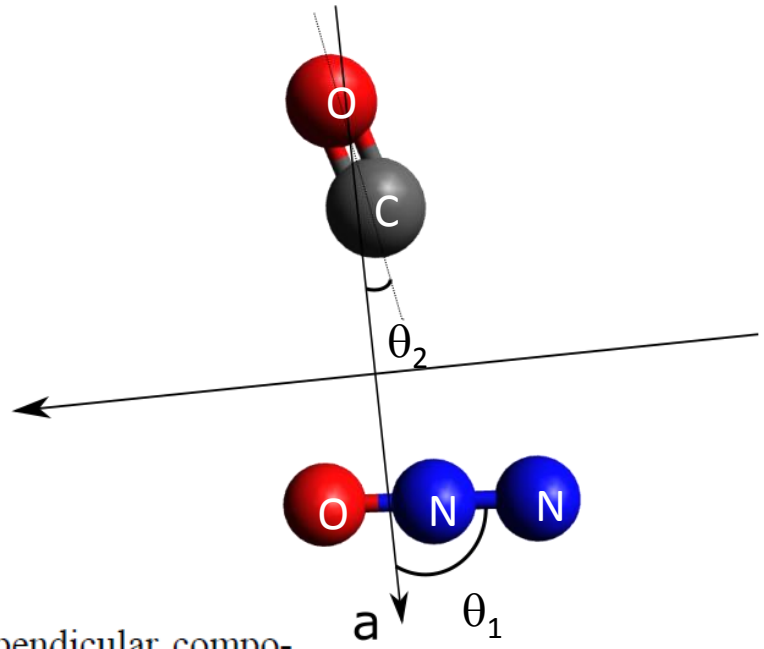
First detection!!
Planar semi-rigid system

R_{dim}=3.878 Å

a-type
transitions only

$$\frac{\mu_{b_{CO}}}{\mu_{a_{CO}}} = \frac{\mu_{CO} sin(\theta_2)}{\mu_{CO} cos(\theta_2)} = tan(\theta_2)$$



we estimated that any perpendicular component was at least 10 times weaker than the parallel component.

Rdim=3.87
θ_2=20° ± 5°
θ_1=80° ± 5°

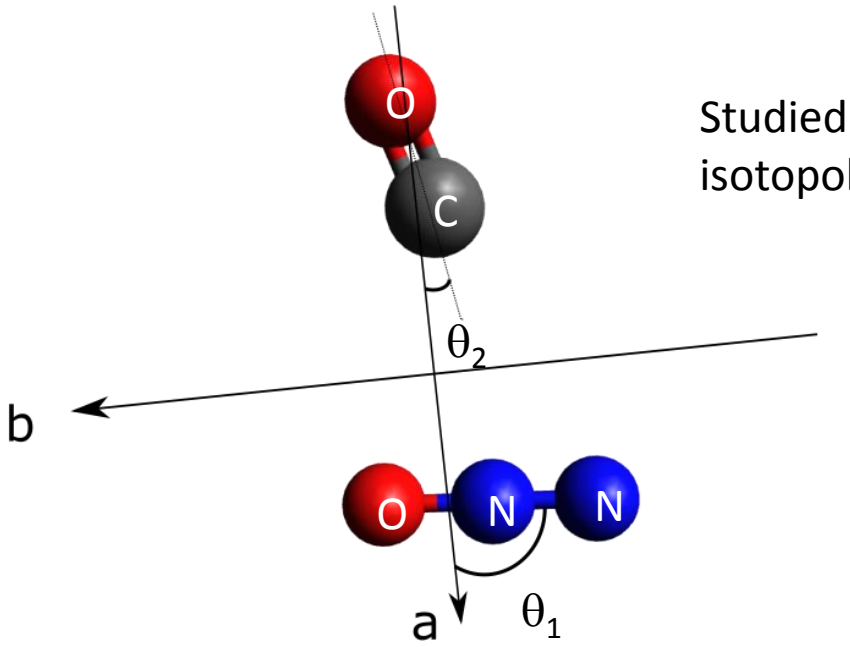
b-type
transitions only

$$\frac{\mu_{b_{N_2O}}}{\mu_{a_{N_2O}}} = \frac{\mu_{N_2O} sin(\theta_1)}{\mu_{N_2O} cos(\theta_1)} = tan(\theta_1)$$

θ(°)	tan(θ) Transition dipole moment ratio	Intensity ratio between the two types of transitions **a**,**b**
20	0.36	7.5 (0.13)
15	0.27	14 (0.073)
10	0.18	31 (0.032)

Previous Works (III)

Rotational Spectroscopic investigation of the weak interaction between CO and N_2O
M. NgarÎ, Y. Xu, W. Jäger, **JMS** 197,244-253 (1999)



Studied the microwave spectrum of five different isotopologues.

Structural parameters of the CO-N_2O complex

Parameters	Effective	Pseudo-substitution
R_{dim}	3.863	3.879
θ_1	80.8	88.7
θ_2	10.8	15.7

Previous Works (IV)

Ab initio molecular orbital studies of the vibrational spectra of some van der Waals complexes. Part 3: Complexes of carbon monoxide with carbon dioxide, nitrous oxide, carbonyl sulphide and carbon disulphide
M. Venayagamoorthy, T. Ford, J. Mol. Struc. **717**, 111-119 (2005)

MP2/6-311 +G(d)
Geometry optimization (VERYTIGHT)
Harmonic evaluation of the frequencies

Important conclusions and predictions:

1. In agreement with M. Ngari, Y. Xu and W. Jaeger about the structure of N_2O-CO

2. Evaluation of the intermolecular frequencies of N_2O-CO

3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N_2O-OC)

4. Calculation of the intermolecular frequencies of N_2O-OC.

Previous Works

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   Try to observe the missing lines on the fundamental bands

2. Evaluation of the intermolecular frequencies of N_2O-CO

   Try to observe combination bands

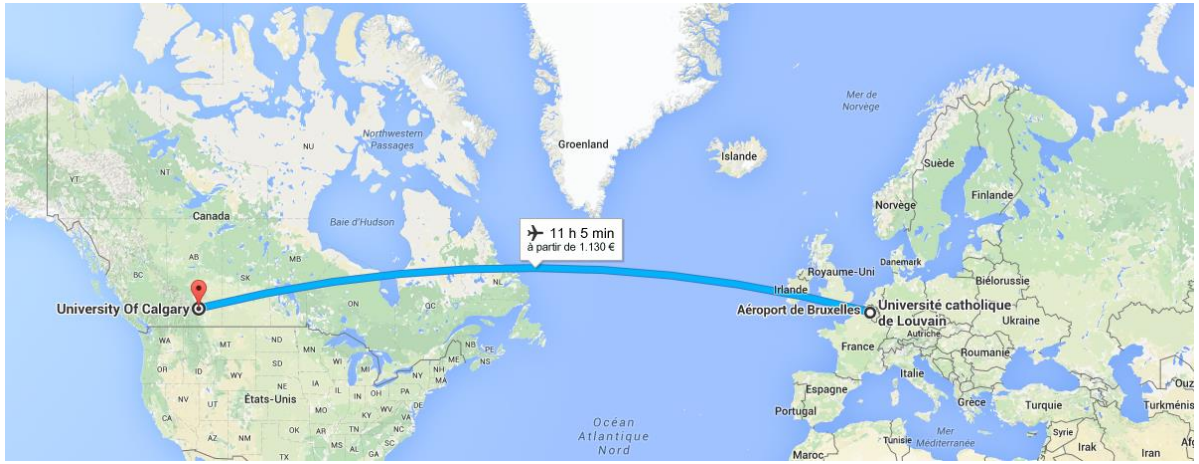
3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N_2O-OC)

   ????????

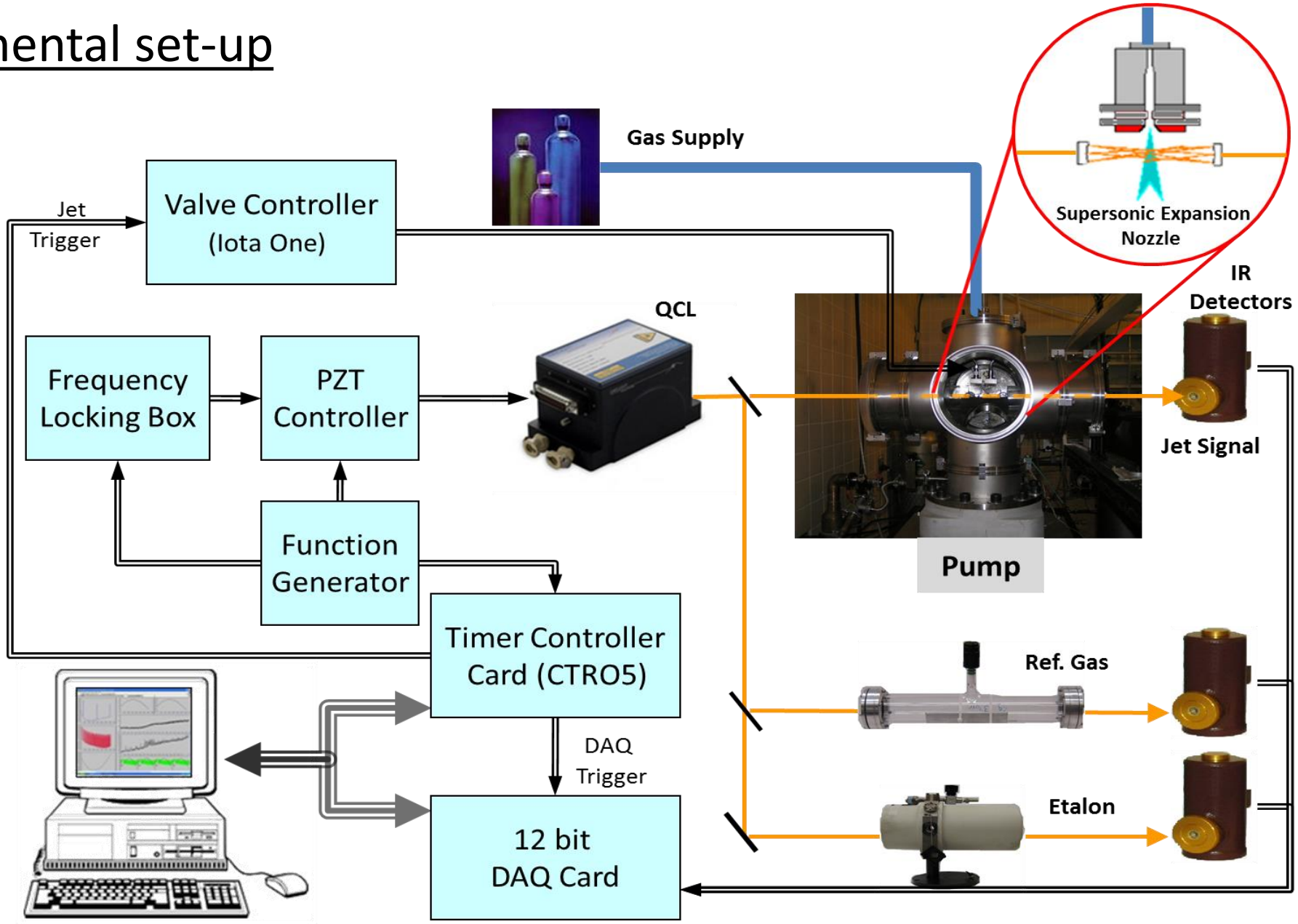
4. Calculation of the intermolecular frequencies of N_2O-OC.

   ??????

Experimental roadmap

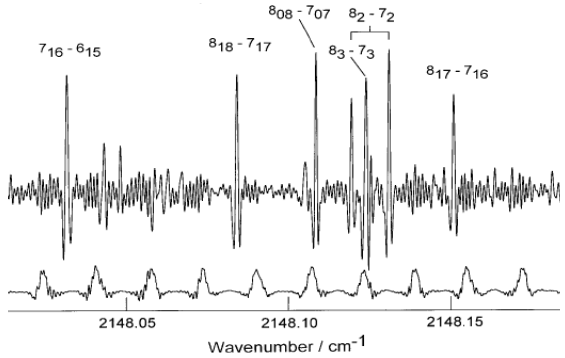


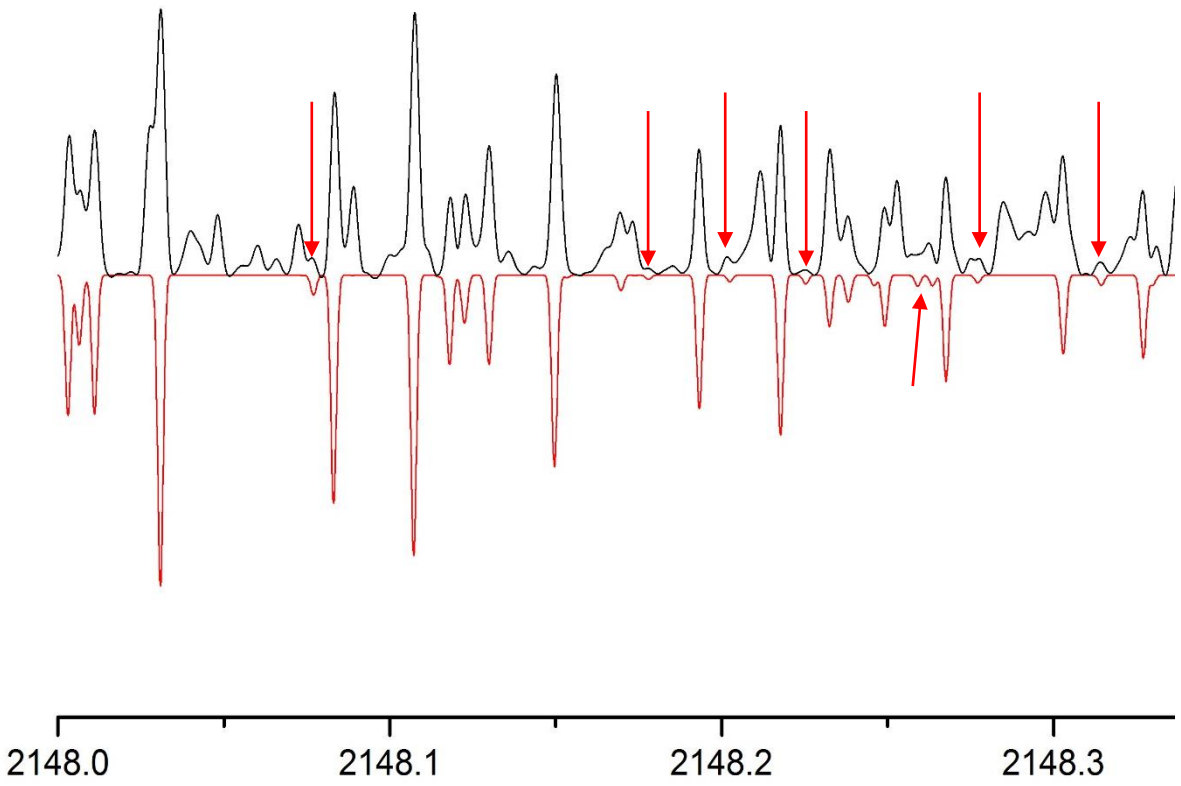
Experimental set-up



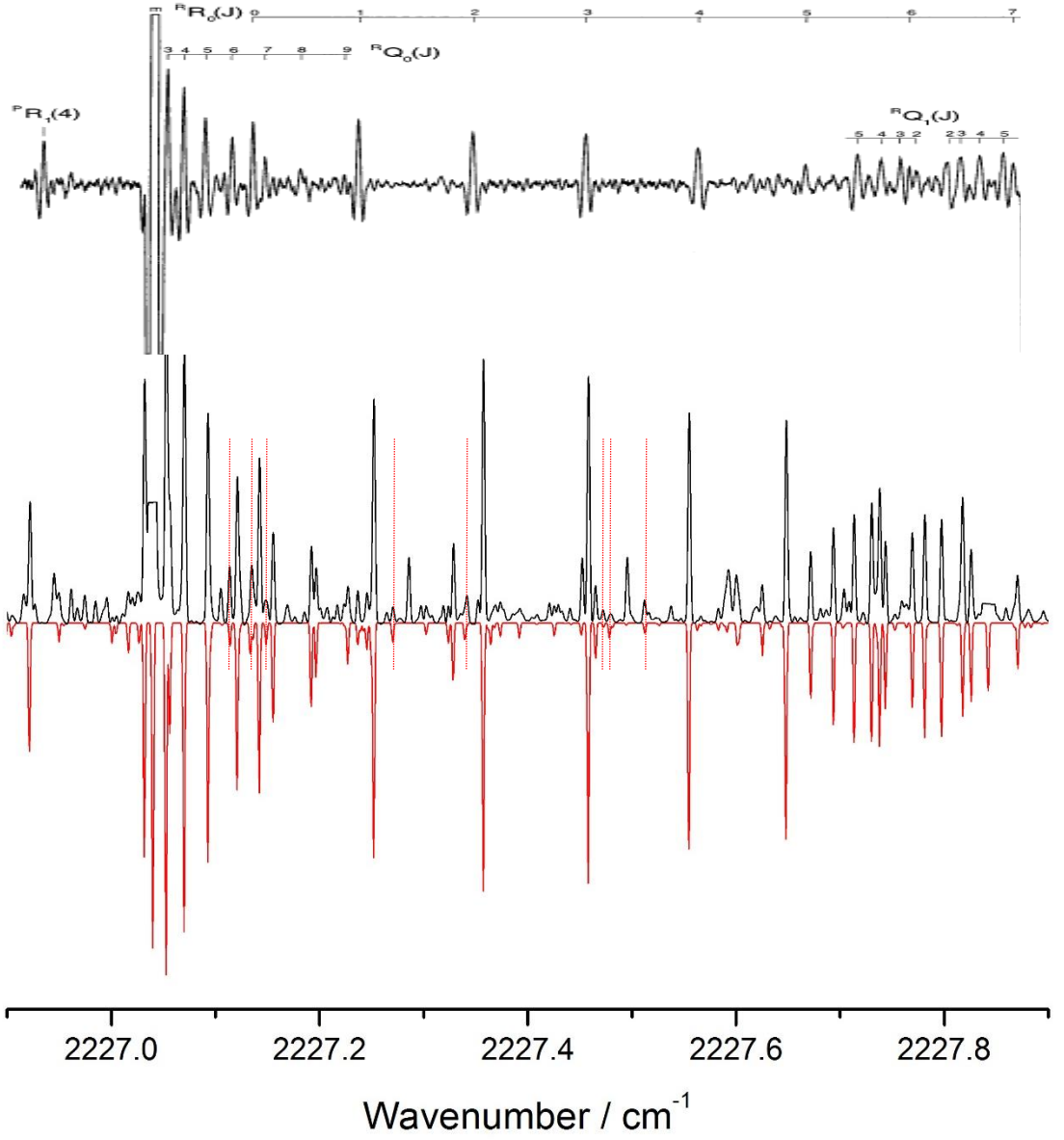
1. Trying to observe the missing lines on the fundamental bands

Y. Xu, A. R. W. McKellar, JMS **180**,164-169 (1996)



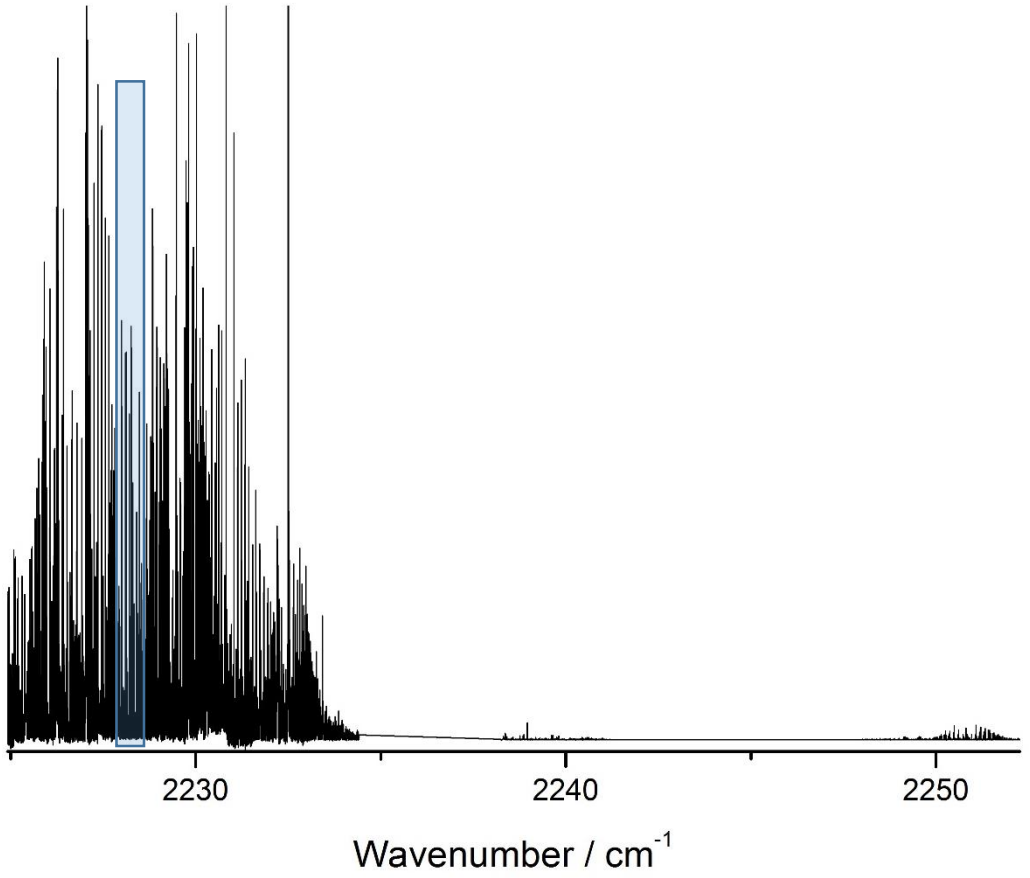


Hai-Bo Qian and Brian Howard, JMS **184**,156-161 (1997)



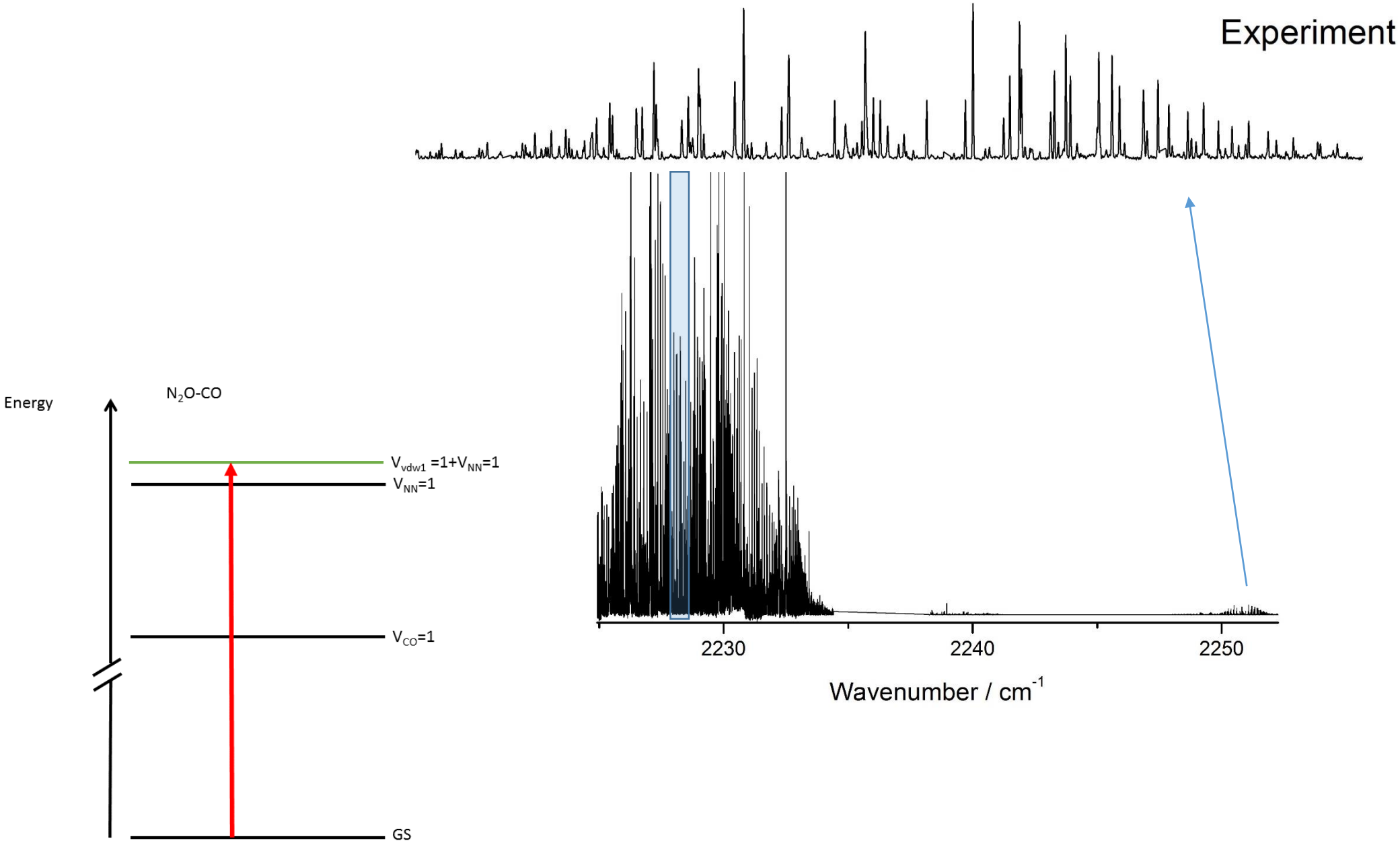
2. Trying to observe combination bands of N_2O-CO

a) N_2O v_3 stretch region



2. Measurement of the combination bands of N_2O-CO

a) N_2O v_3 stretch region



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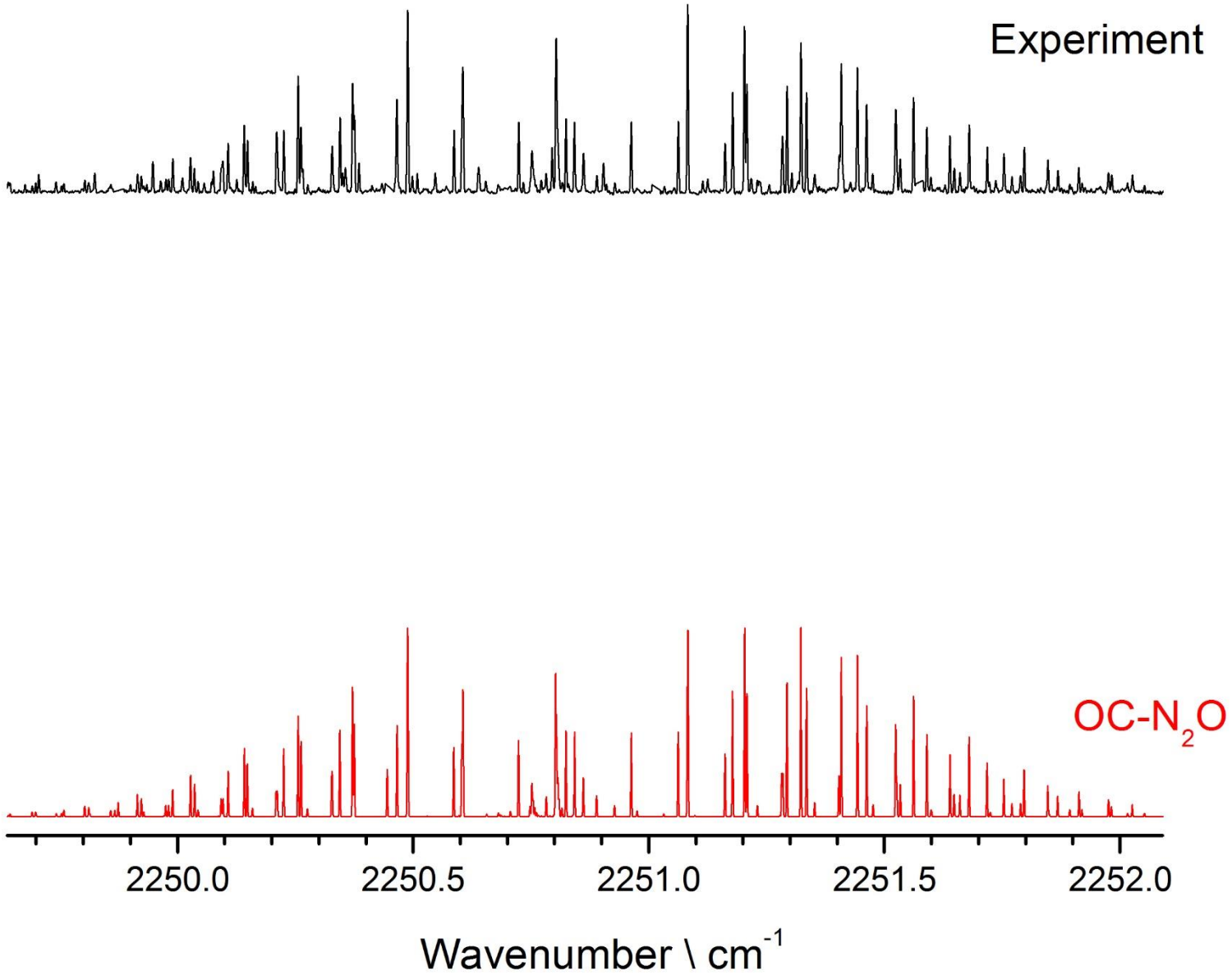
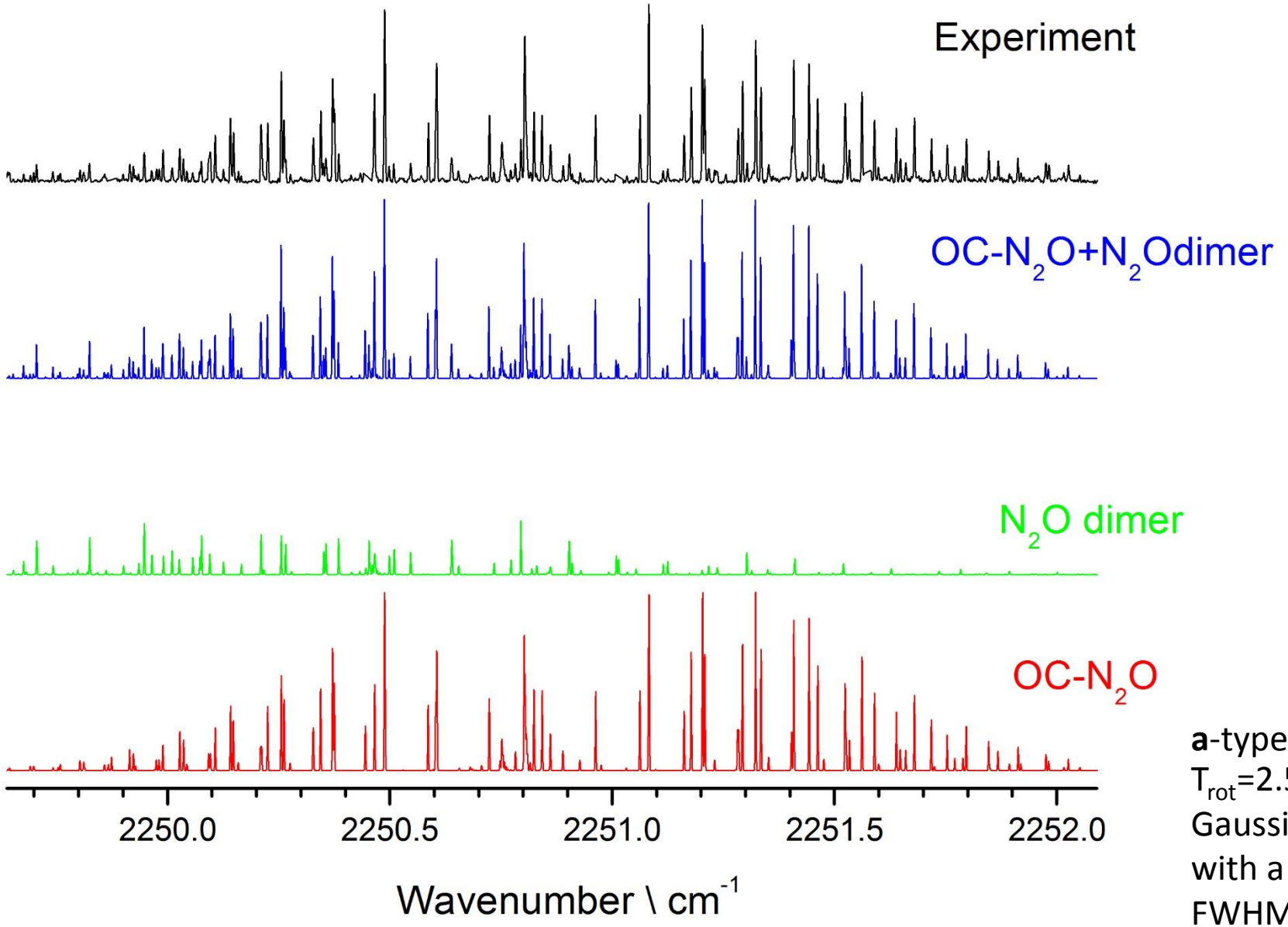


a-type transitions

2. Measurement of the combination bands of N_2O-CO

a) N_2O v_3 stretch region

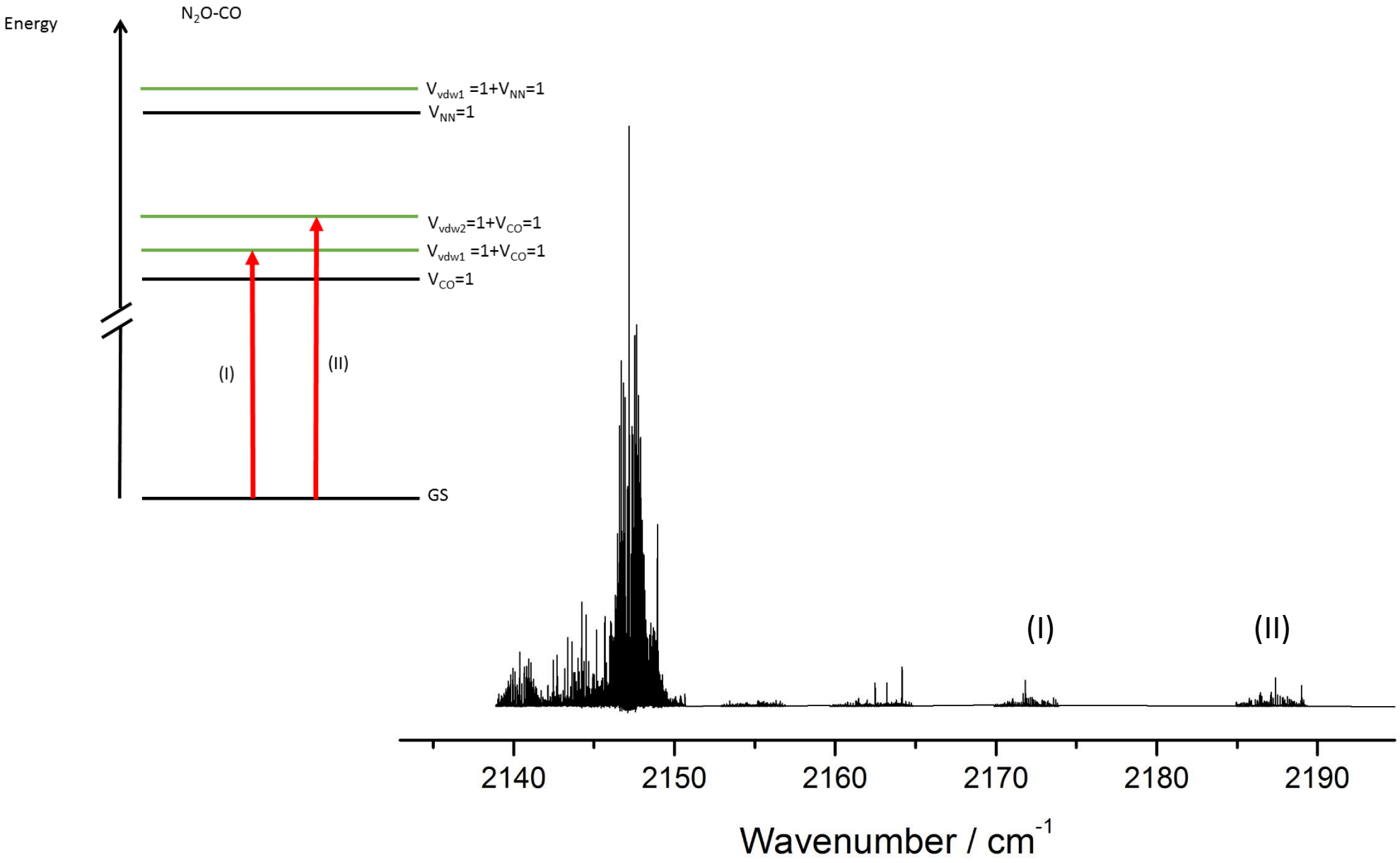
$$\tilde{\nu}_0 - \tilde{\nu}_{(V_{NN}=1)} = 24.181\ cm^{-1}$$



a-type transitions
T_{rot}=2.5 K
Gaussian line profile with a
FWHM =0.002 cm^{-1}

2. Measurement of the combination bands of N_2O-CO

b) CO stetch region



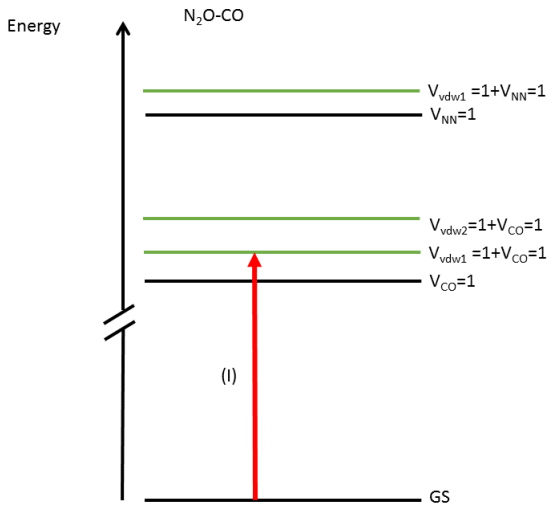
2. Measurement of the combination bands of N_2O-CO

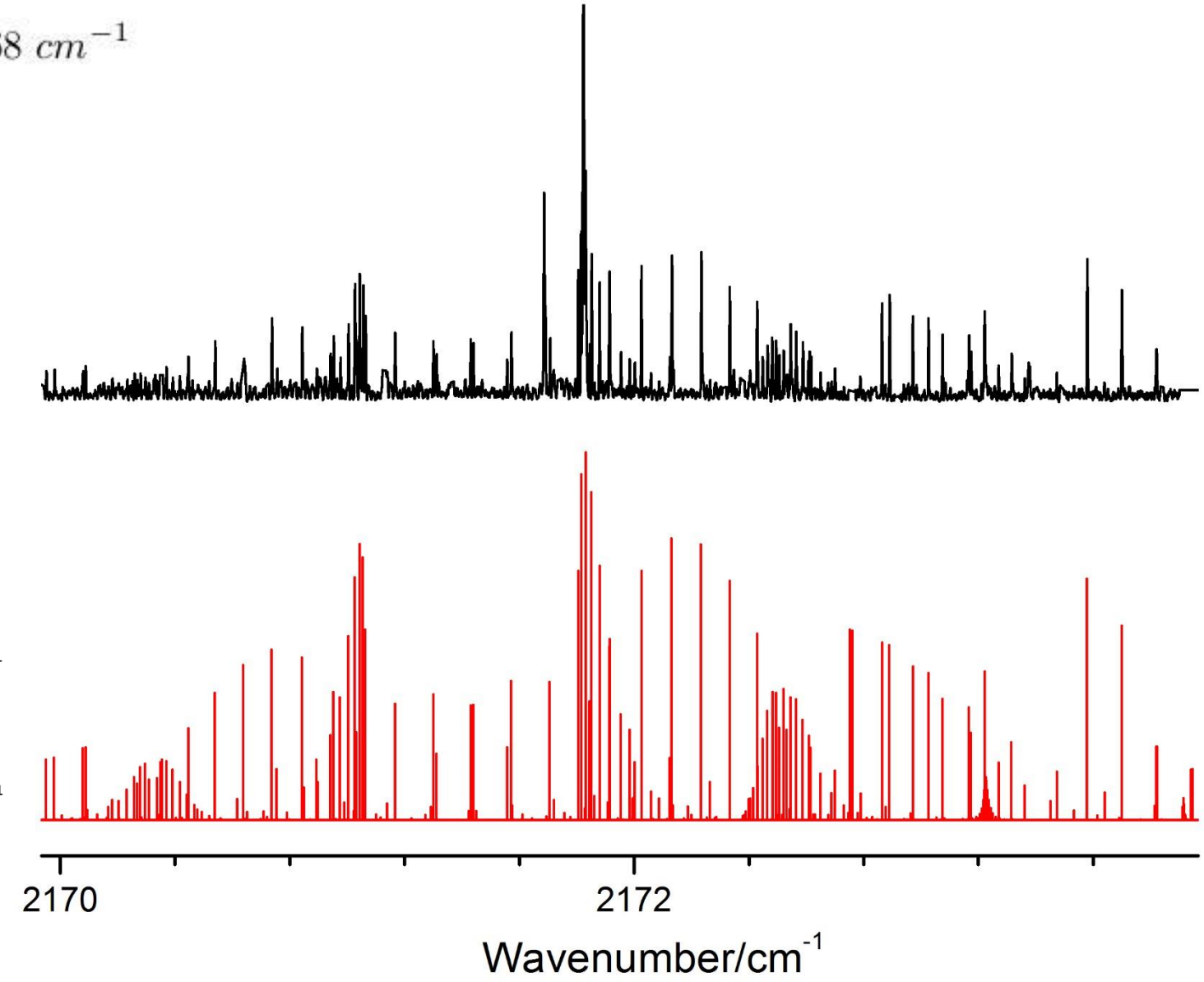
b) CO stetch region

(I)

b-type transitions

$$\tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 24.2568\ cm^{-1}$$





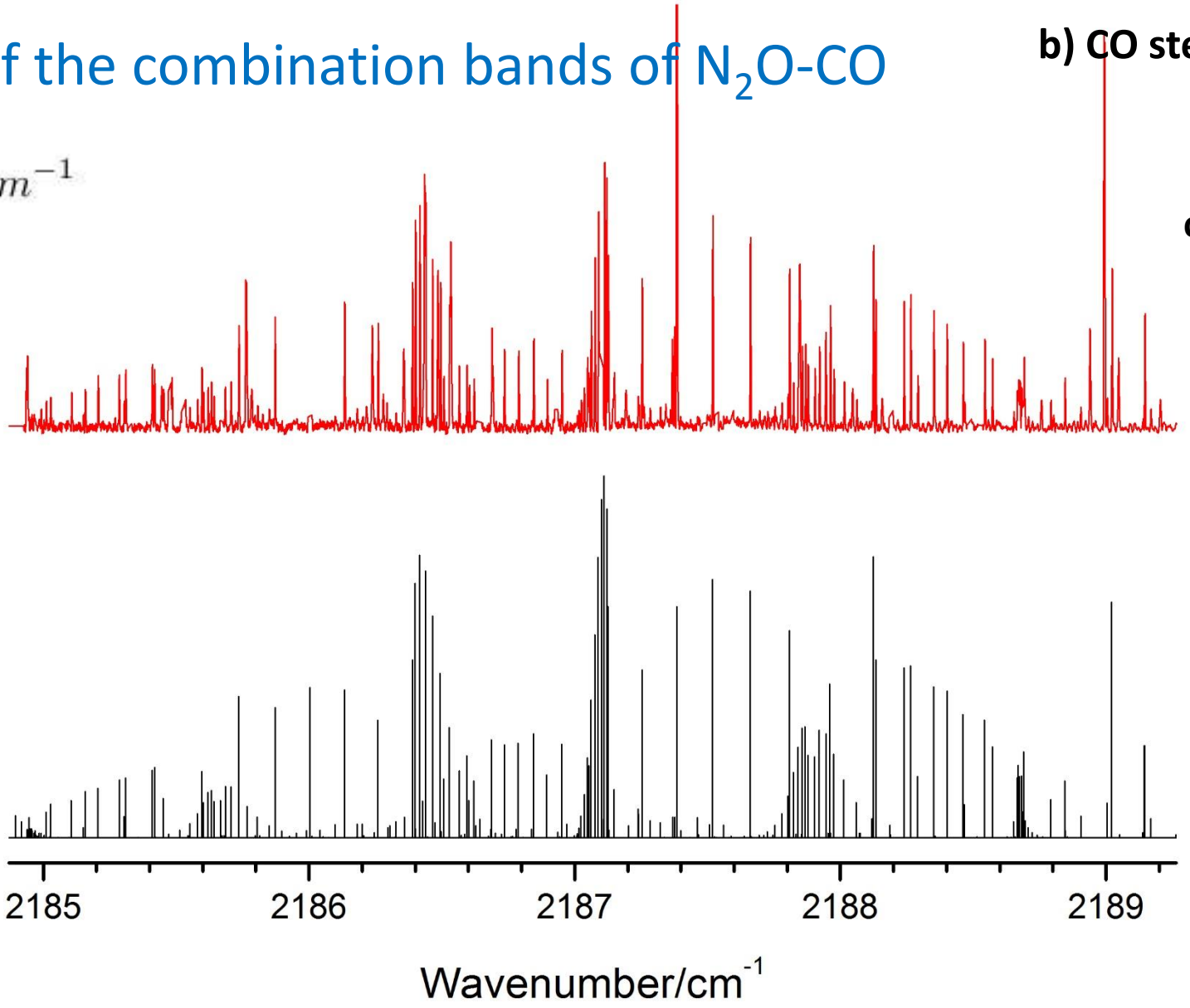
2. Measurement of the combination bands of N_2O-CO

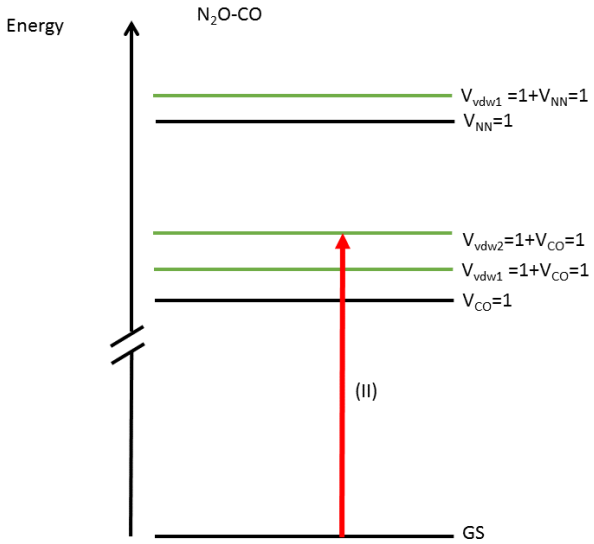
$$\tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 39.571\ cm^{-1}$$

b) CO stetch region

(II)

c-type transitions





- Vibrational assignment:

  comparison with ab initio prediction and similarities with previous work on CO_2-CO
  A. Barclay, S. Sheybani-Deloui,K.H Michaelain, A. R. W. McKellar, N. Moazzen-Ahmadi
  Chem. Phys. Lett.,**651**, 62-65, (2016)

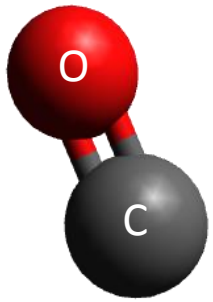
Intermolecular vibration	This work / cm^{-1}	Selection rules	*ab-initio* Venayagamoorthy *et al.*	OC-CO_2	*ab-initio* Venayagamoorthy *et al.*
CO bend or geared motion + NN stretch	24.180	**a**-type	(29.13)	(24.343)	(24.3)
CO bend or geared motion + CO stretch	24.256	**b**-type	(29.13)	24.343	(24.3)
Out of plane rock + CO stretch	39.571	**c**-type	(48.51)	43.958	(42.81)

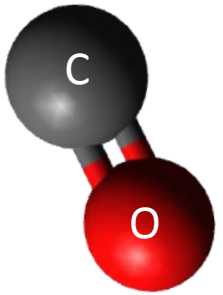
- Summary

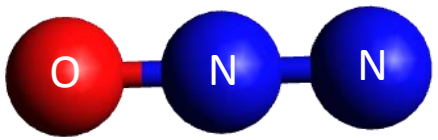
  More than 300 assigned lines fitted with a residuals of 0.0004 cm^{-1} (12 MHz)--------Agreement for the structure intermolecular potential energy surface seem to be quite harmonic (relatively good agreement with ab initio values)

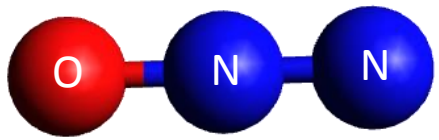
3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N_2O-OC)

Predicted to be the same structure with the CO flipped by 180°.



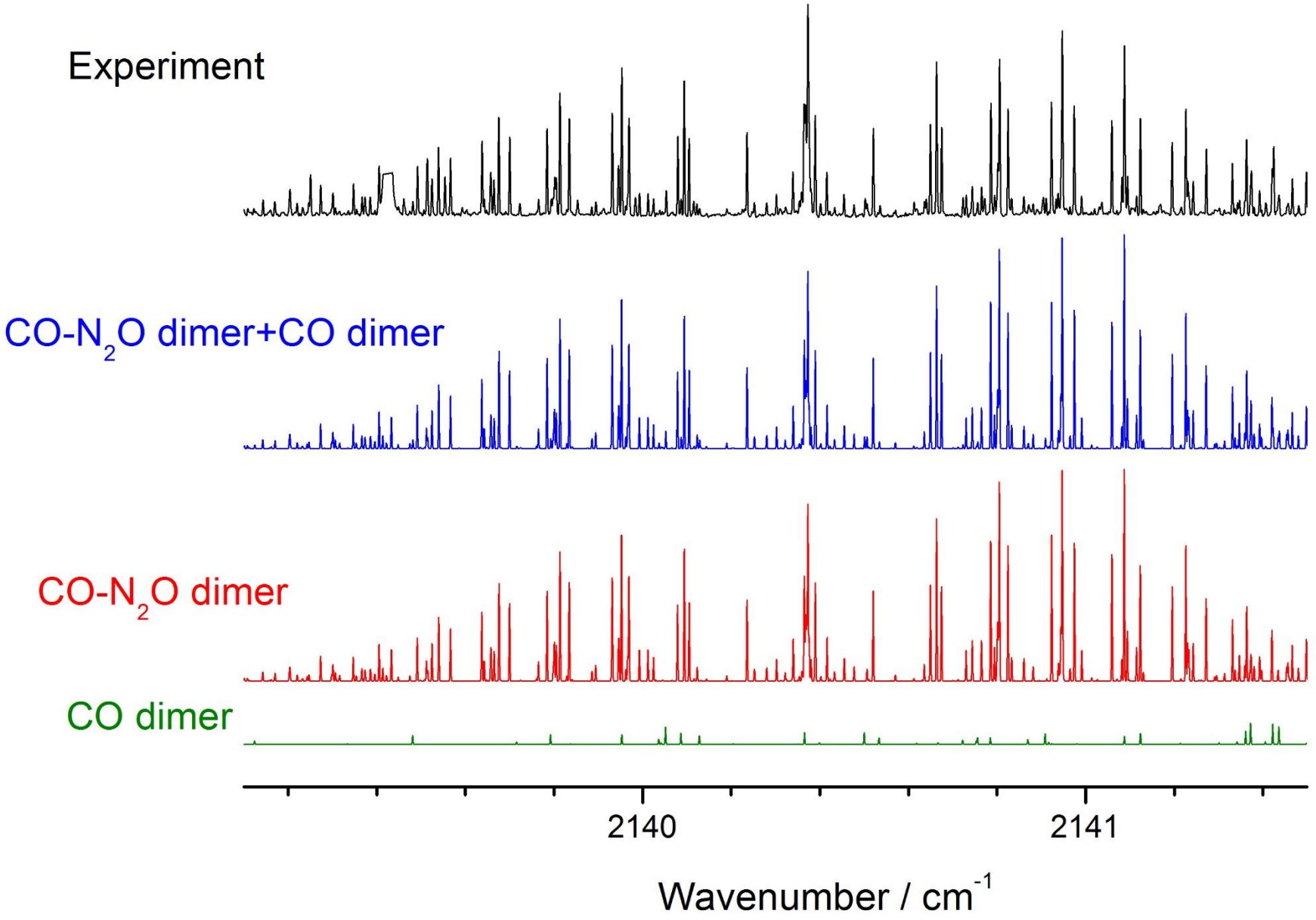






3. Prediction of the existence of a second isomer, O-bounded

CO stretch region



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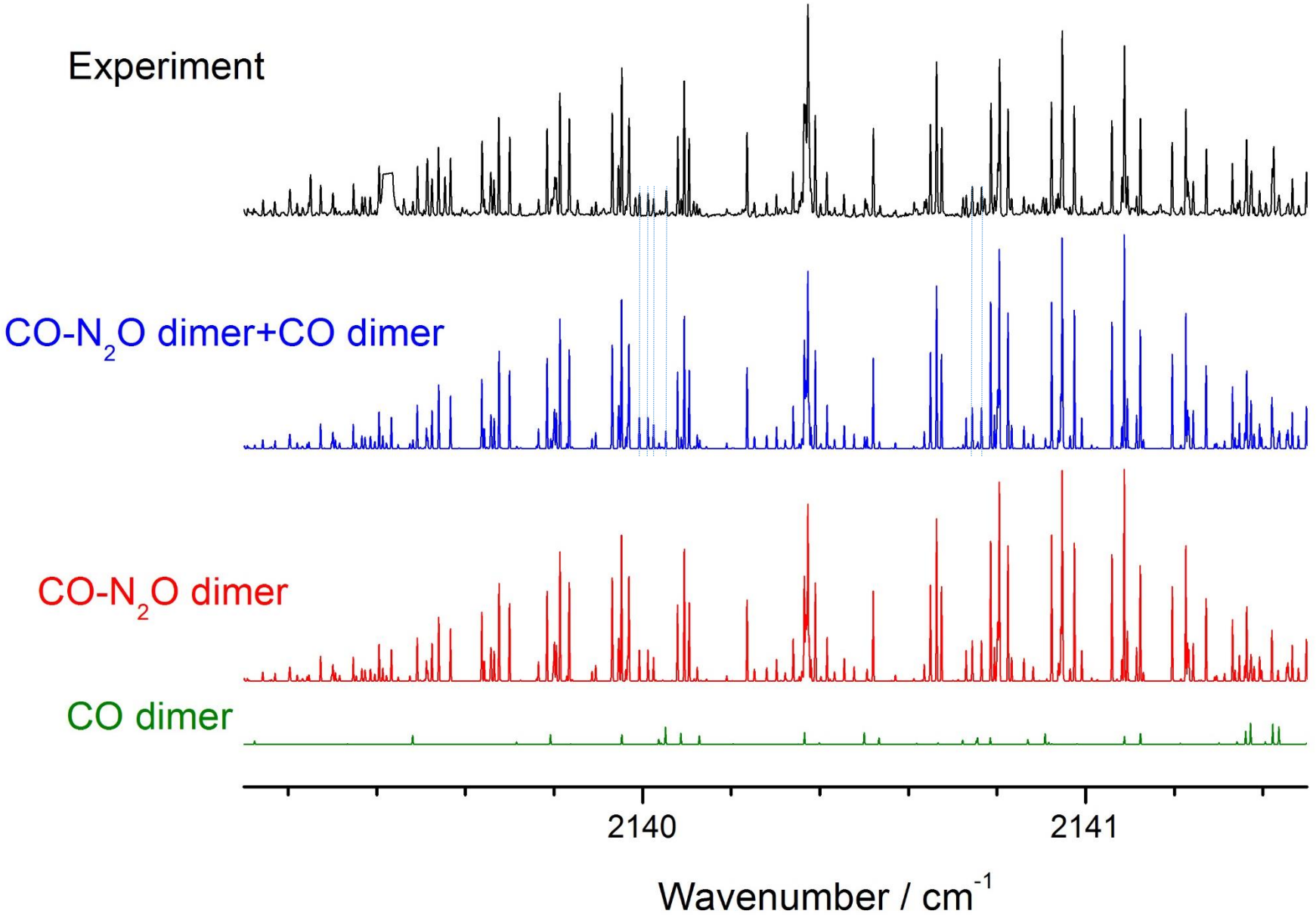


CO stretch region

Example of b type transitions

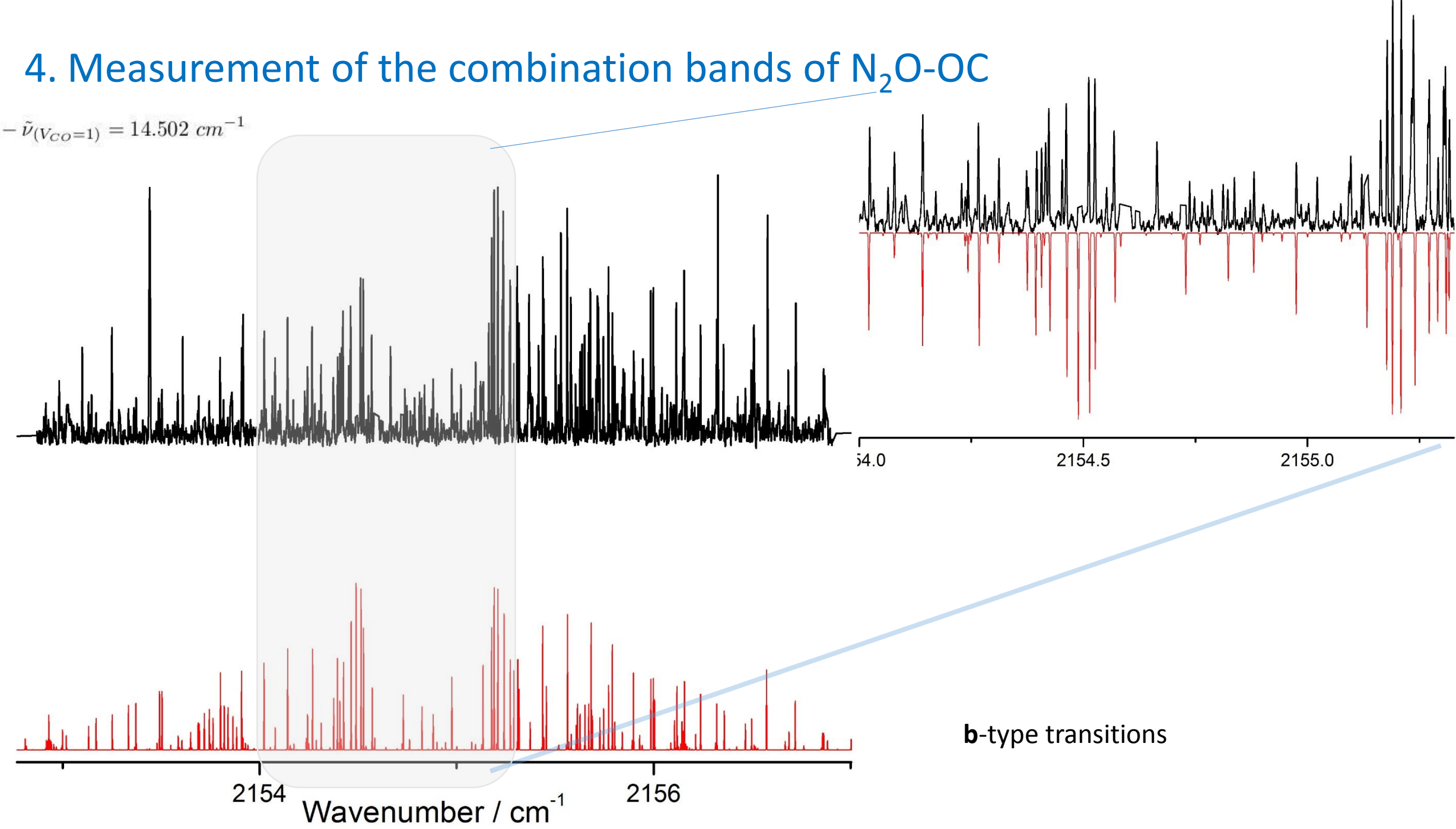
Also detected and assigned in the N_2O range.

From the a-type/b-type ratio. θ_2 is larger than for N_2O-CO. 22°±5 rather than 10-15°.

θ_1 is the same as in isomer 1. Rdim is smaller 3.51 Å instead of 3.87 Å for N_2O-CO.

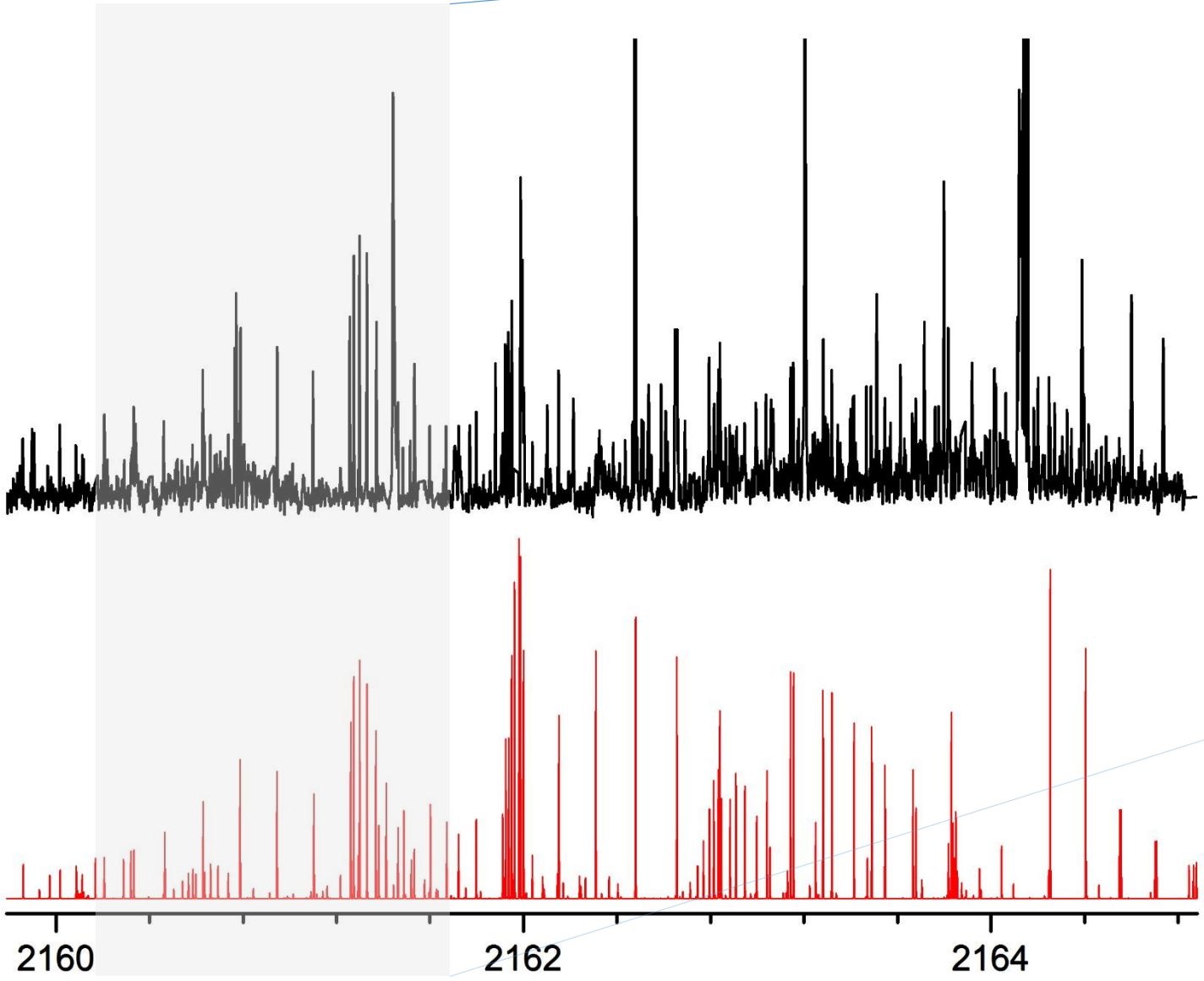
4. Measurement of the combination bands of N_2O-OC

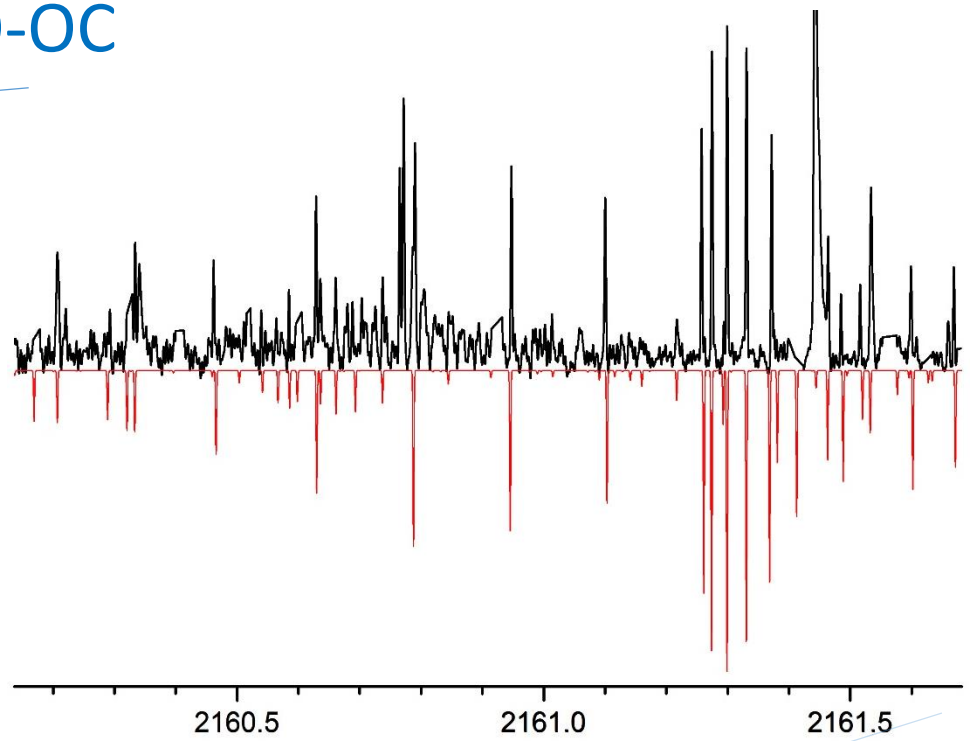
$\tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 14.502\ cm^{-1}$



b-type transitions

4. Measurement of the combination bands of N_2O-OC





$$\tilde{\nu}_0 - \tilde{\nu}_{(V_{CO}=1)} = 21.219\ cm^{-1}$$

c-type transitions

Conclusions

The second isomer exists!!!!

θ_2 is larger in N_2O-OC than in N_2O-CO and R_{dim} is smaller than for N_2O-CO.

We measured the intermolecular frequencies

Intermolecular vibration	This work / cm^{-1}	Selection rules	Ab-initio Venayagamoorthy *et al.* /cm^{-1}	$CO\text{-}CO_2$	Ab-initio Venayagamoorthy *et al.* /cm^{-1}
CO bend or geared motion CO stretch region	14.502	a-type	(23.85)	14.19	15.45
Out of plane rock CO stretch region	21.219	c-type	(44.46)	22.68	36.32

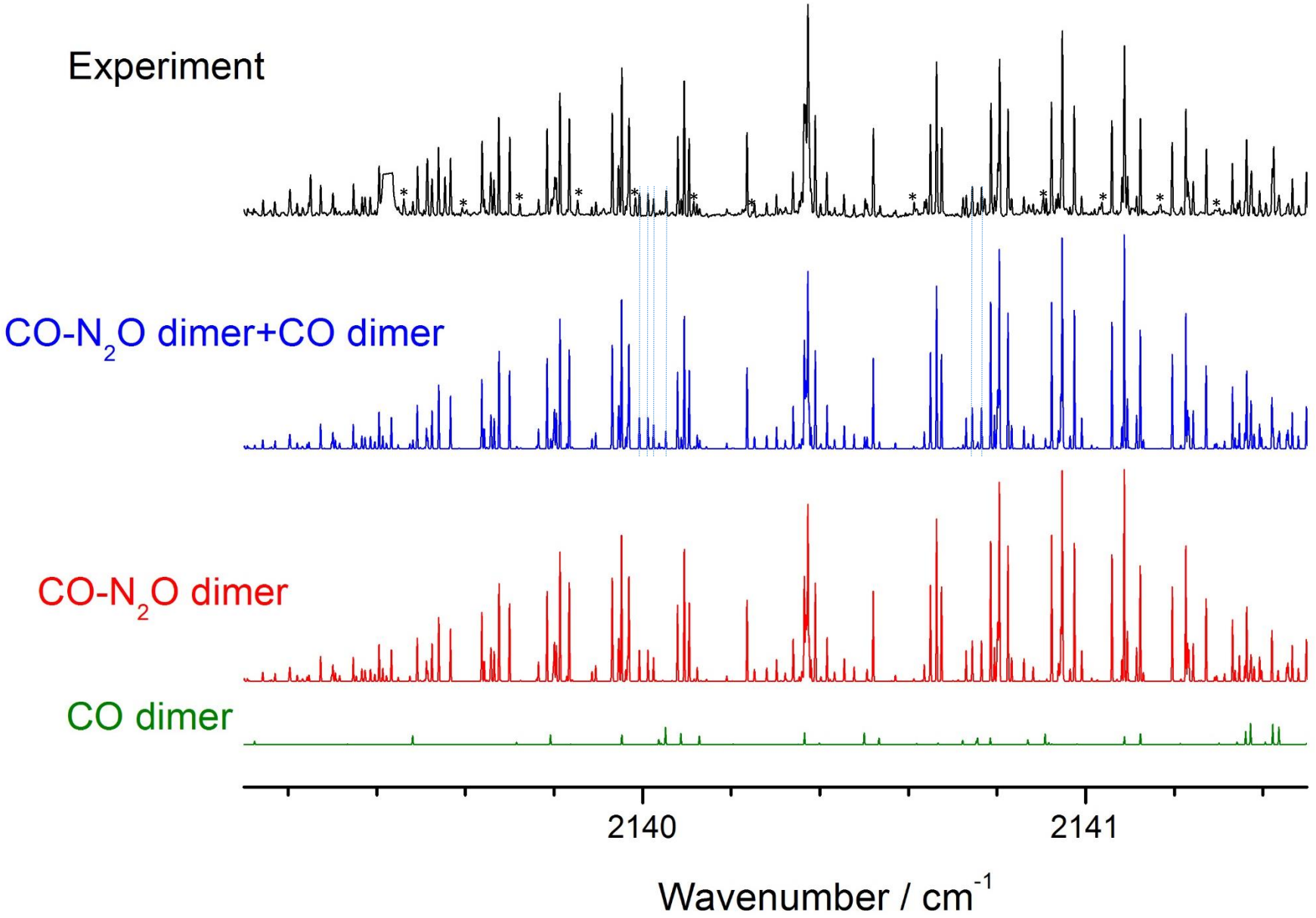
c-type Coriolis interaction

Not a good agreement between ab initio predictions and experimental measurements until now…..

Similarity between CO_2 and N_2O gets stronger!

Thank you for your attention!!!!!

3. Prediction of the existence of a second isomer O-bounded (Isomer 2, N_2O-OC)



* He-CO-N_2O ?

Example of b type transitions

From the a-type/b-type ratio.
θ_2 seem to be larger than for isomer 1.
~20° rather than 10-15°

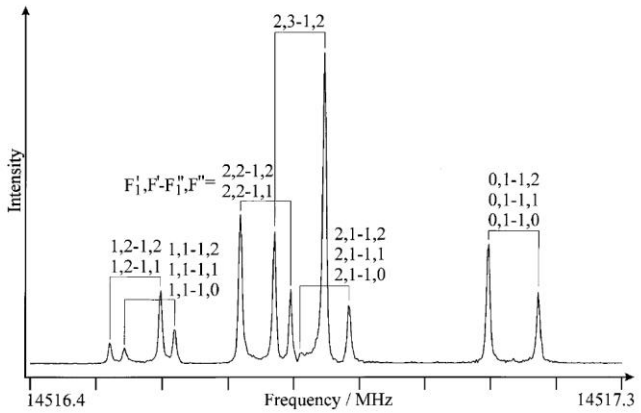


FIG. 2. Observed rotational spectrum of the rotational transition $J, K_a, K_c = 1, 1, 1–0, 0, 0$ of $^{12}C^{16}O–^{14}N^{14}NO$, showing the nuclear quadrupole hyperfine components due to two quadrupolar ^{14}N nuclei. The spectrum was recorded using 50 averaging cycles with 60 ns sampling interval. Each component is split into a doublet due to the Doppler effect (see Section II, Experimental Details). The variations in intensity of the Doppler components is a result of the particular excitation conditions, such as off-resonance of the excitation frequency from the transition frequency and excitation pulse length, and of the adjustment and width of the MW cavity mode.

TABLE 5

Structural Parameters of the CO–N_2O Complex

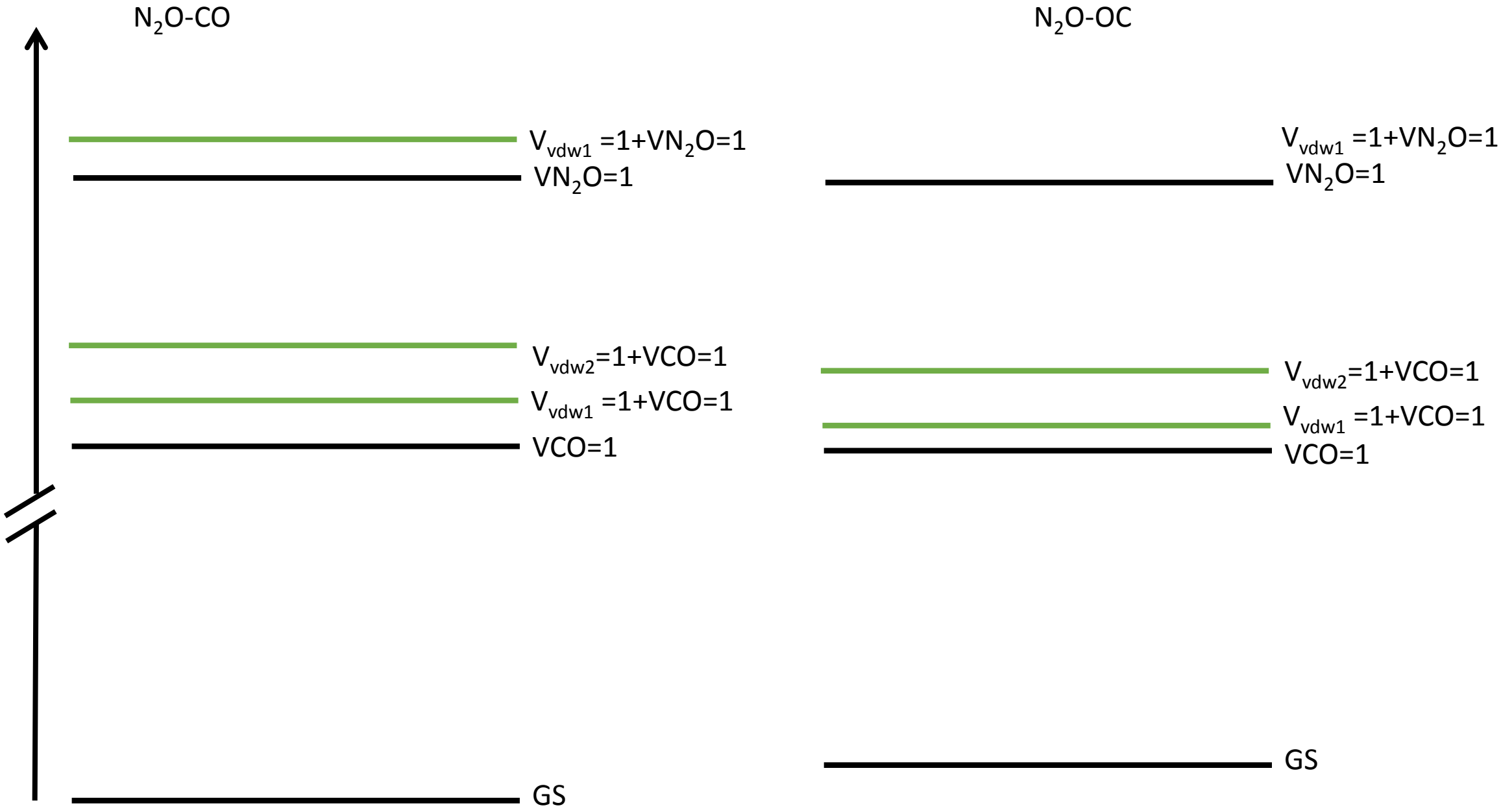
Parameters	Effective	Pseudo-substitution[a]	Equilibrium[b]
r_{CO}[c]	1.1310 Å	1.1310 Å	1.1310 Å
r_{NO}[d]	1.1923 Å	1.1923 Å	1.1923 Å
r_{NN}[d]	1.1278 Å	1.1278 Å	1.1278 Å
R_{cm}	3.863 Å	3.879 Å	3.87 Å
θ_1	80.8°	88.7°	86°
θ_2	10.8°	15.7°	15°

[a]See text for the definition.
[b]Ref. 13.
[c]Fixed at the value from Ref. 25.
[d]Fixed at the values from Ref. 26.

structural parameters as outlined in Ref. (*13*). This moment-of-inertia tensor can then be diagonalized to obtain the principal moments that are related to the effective rotational constants of the complex. Since several isotopomers were investigated, the three structural parameters were fit to the rotational constants of all the isotopomers. Here, the bond lengths of N_2O and CO were fixed at the respective monomer values (*26*, *25*). The effective structural parameters thus obtained are listed in Table 5. It is also possible to obtain a "pseudosubstitution" structure by fitting to the differences of the inertial moments between the normal isotopomer and the substituted isotopomers. The pseudo-substitution parameters are also listed in Table 5.

atom–atom Lennard–Jones potentials (*28*). They found that the potential minimum is at $R_{cm} = 3.87$ Å, $\theta_1 = 86°$, and $\theta_2 = 15°$. These values are very close to the pseudosubstitution structural parameters obtained from the present study, suggesting that the pseudosubstitution procedure was reasonably effective in removing the van der Waals vibrational effects.

Rotational Spectroscopic investigation of the weak interaction between CO and N_2O
M. NgarÍ, Y. Xu, W. Jäger, **JMS** 197,244-253 (1999)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N2O-OC
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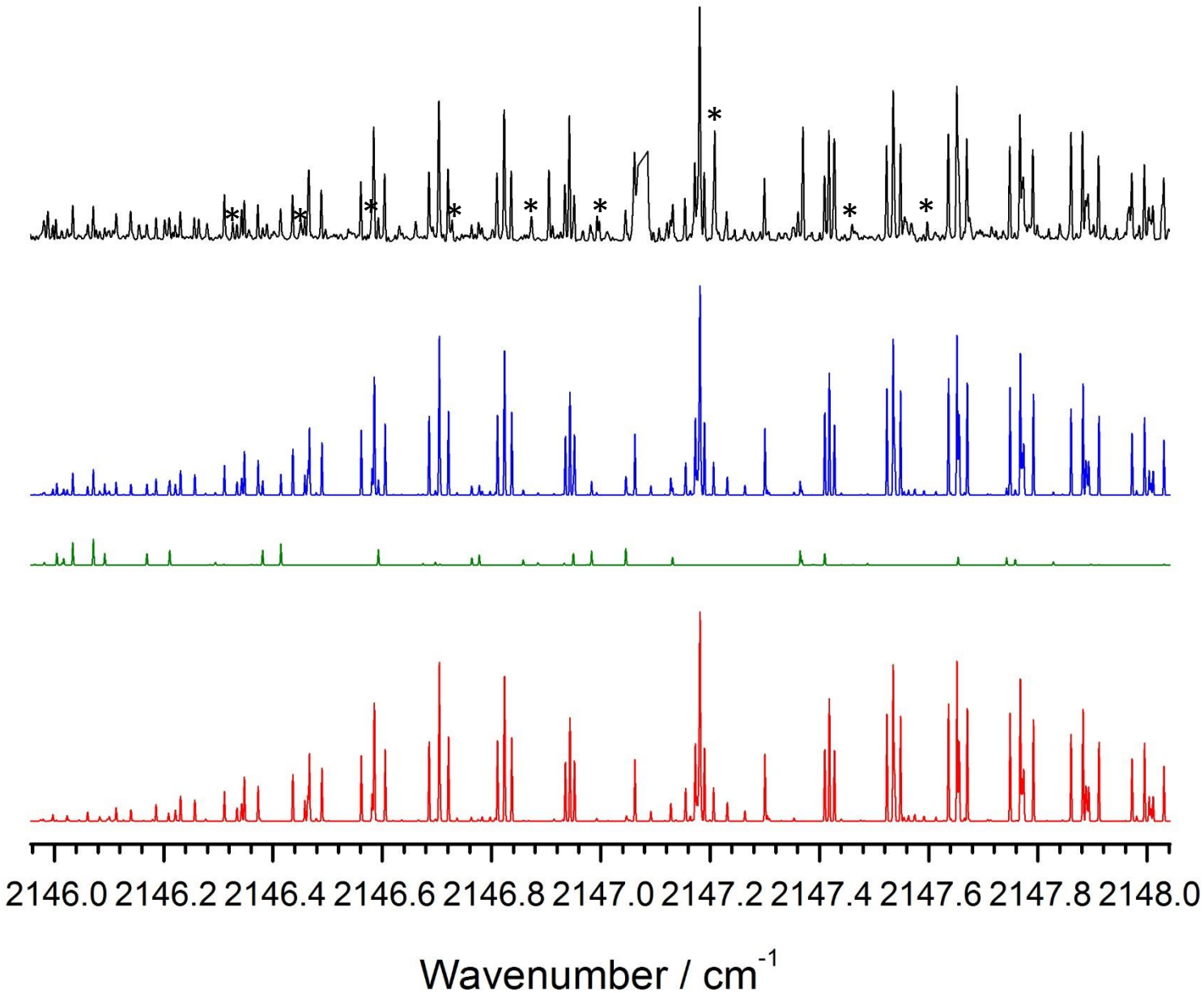
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Wavenumber / cm-1