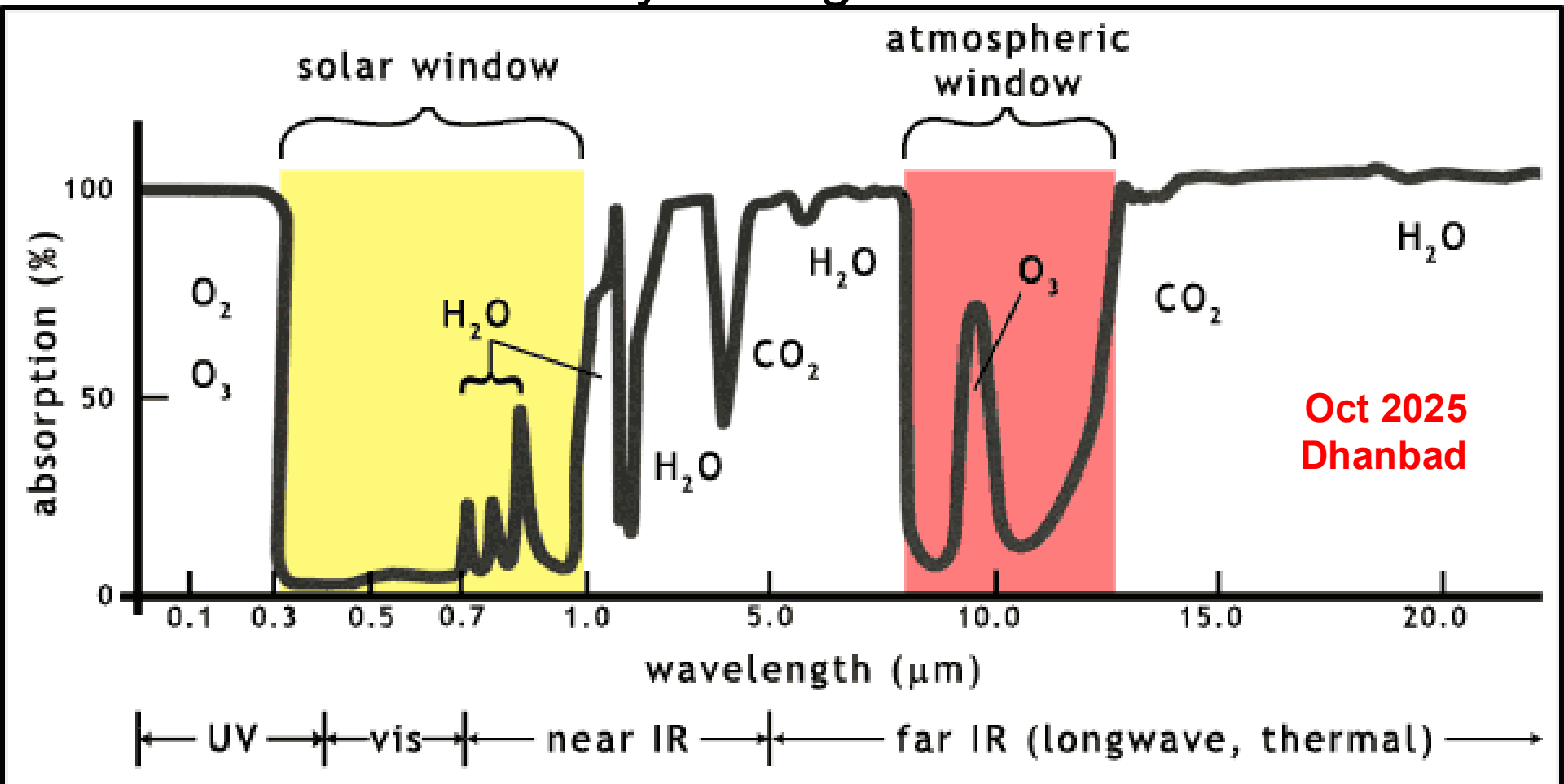
Rovibronic Molecular Spectroscopy

Jonathan Tennyson

University College London



Oct 2025
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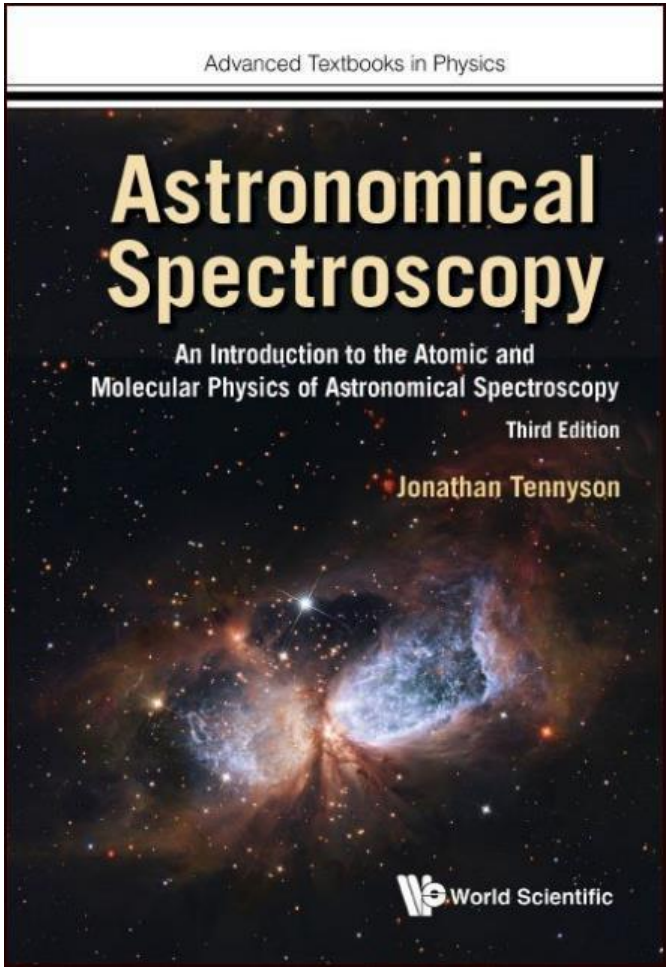

About the first edition
"The best book for anyone who is embarking on research in astronomical spectroscopy"
Contemporary Physics (2006)

About the third edition:
"*Makes an ideal companion … for observational aspects of spectroscopy*"
The Observatory Magazine (2019)

3rd edition published 2019

www.worldscientific.com/worldscibooks/10.1142/q0207

ExoMol

Hot line lists; Published in MNRAS

I. BeH, MgH, CaH
II. SiO
III. HCN/HNC
IV. CH_4
V. NaCl, KCl
VI.PN
VII. PH_3
VIII. H_2CO
IX. AlO
X. NaH
XI. HNO_3
XII. CS
XIII. CaO
XIV. SO_2
XV. HOOH
XVI. H_2S
XVII. SO_3
XVIII. VO

XIX. $H_2{}^{18}O$, $H_2{}^{17}O$
XX. H_3^+
XXI. NO
XXII. SiH_4
XXIII. PO, PS
XXIV. SiH
XXV. SiS
XXVI. SN, SH
XXVII. AlH
XXVIII. C_2H_4
XXIX. CH_3Cl
XXX. $H_2{}^{16}O$
XXXI. C_2
XXXII. TiO
XXXIII. MgO
XXXIV. PH
XXXV. NH_3
XXXVI SH (UV)

XXXVII HCCH
XXXVIII SiO_2
XXXIX CO_2
XL. H_3O^+
XLI. NaOH, KaOH
XLII. NO (UV)
XLIII. SiO (UV)
XLIV. NaO
XLV. MgH (UV), CaH (UV)
XLVI. SiN
XLVII. CaOH
XLVIII AlCl
XLVIIII H_2CS
L. H_3^+, H_2D^+, D_2H^+, D_3^+
Li. LiOH
LII. CH^+
LIII. YO
LIV. VO (hyperfine)
LV. AlH

LVI. SO
LVII. CH_4
LVIII. OCS
LIX. N_2O
LX. $^{15}NH_3$
LXI. OH
LXII. C_3
LXIII. HDO
LXIV. PN
LXV. NiH
LXVI. CO_2
LXVII. O_2

In progress
CH, KH, CS_2, HCO^+, NO^+, OH^+, BH, etc

2024 data releases:
J. Tennyson *et al.*, JQSRT **326**, 109083(2024)

ExoMol

Hot line lists; Published in MNRAS
Line lists important for fusion

I. BeH, MgH, CaH
II. SiO
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L. H_3^+, H_2D^+, D_2H^+, D_3^+
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In progress
CH, KH, CS_2, HCO^+, NO^+, OH^+, BH, NH, etc

2024 data releases:
J. Tennyson *et al.*, JQSRT **326**, 109083(2024)

Molecule degrees of freedom

Nuclear motion

Molecule with N atoms has 3N degrees of freedom

3 are translation (not interesting)

3 are rotation (2 if molecule linear)

3N-6 are vibration (3N-5 if linear)

Electronic motion

Like atoms but more complicated (lower symmetry)

Electronic spectra:

- Lie largely in ultra-violet except open shell systems eg TiO, VO etc
- Involve changes in electronic state
- And vibrational state (Any, Franck-Condon approx.)
- And rotational state (ΔJ = -1, (0),1)
- Most important for fusion studies. Why?

Table 13.1 Selection rules for spectra of diatomic molecules undergoing allowed electric dipole transitions.

Rotations	$\Delta J = \pm 1$	for $\Lambda = 0 - 0$,
	$\Delta J = 0, \pm 1$	not $J = 0 - 0$, for other $\Delta\Lambda$.
Vibrations	Δv any.	
Spin	$\Delta S = 0$.	
Orbital	$\Delta\Lambda = 0, \pm 1$.	
Σ states	$\Sigma^+ \leftrightarrow \Sigma^+$,	
	$\Sigma^- \leftrightarrow \Sigma^-$.	
Symmetry	$g \leftrightarrow u$	Homonuclear molecules only.

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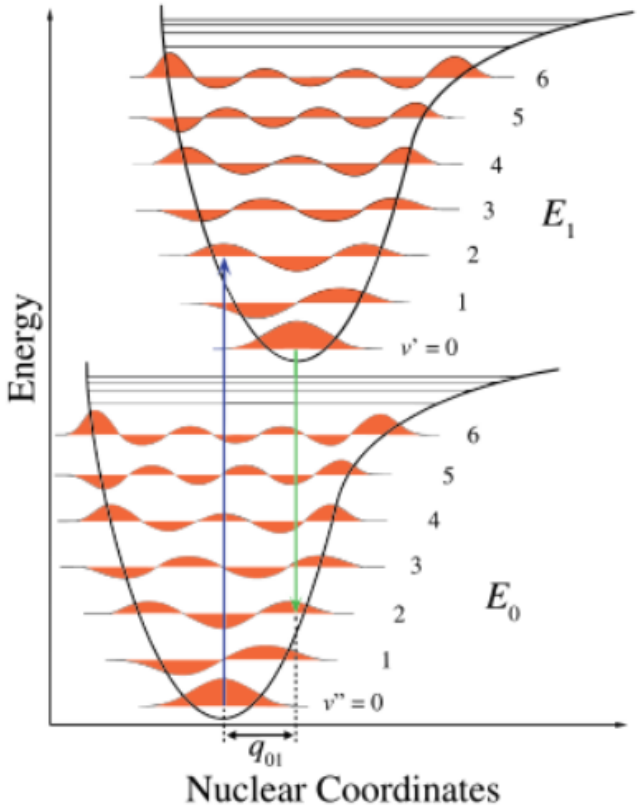
Σ states	$\Sigma^+ \leftrightarrow \Sigma^+$,	
	$\Sigma^- \leftrightarrow \Sigma^-$.	
Symmetry	$g \leftrightarrow u$	Homonuclear molecules only.

Franck-Condon approximation

For an electronic transitions:
Intensity of a vibrational band v' – v" given by a Franck-Condon factor:

$$| \langle v'' | v' \rangle |^2$$

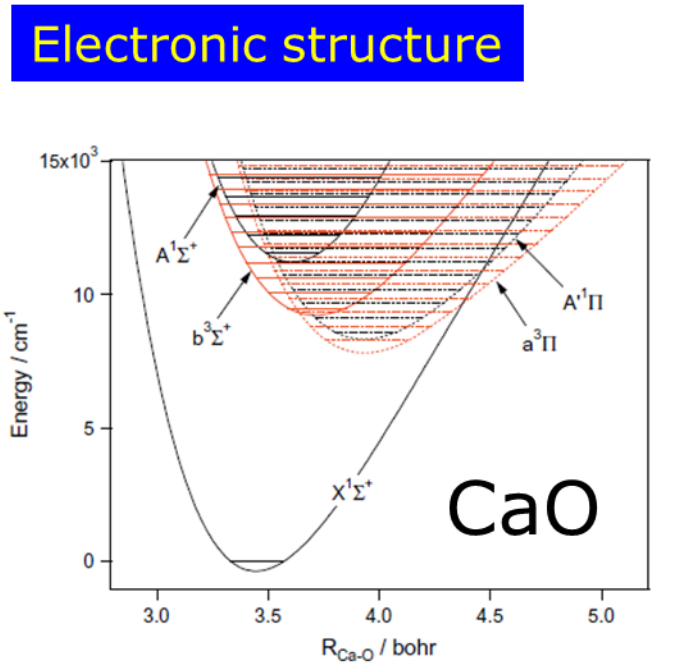
Assumes transitions are instantaneous/vertical
ie nuclei don't move.



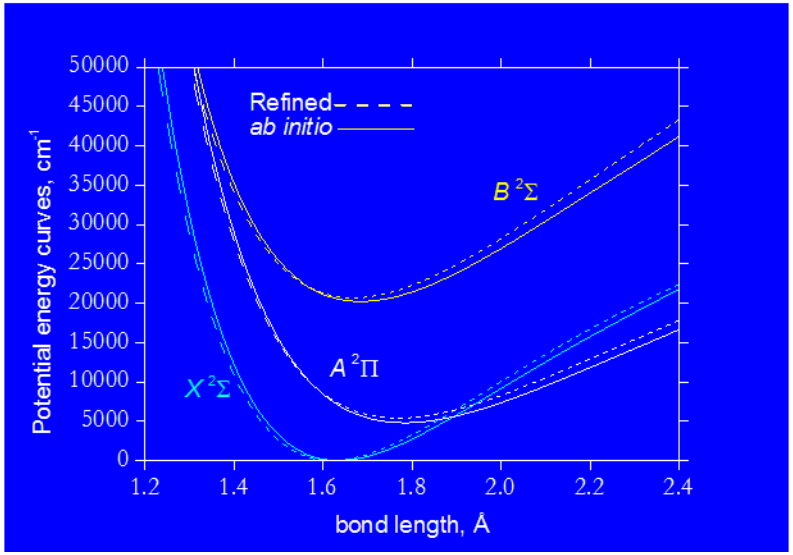
Electronic spectra depends on potential energy curves

State labels like atoms

Eg X $^2\Pi$

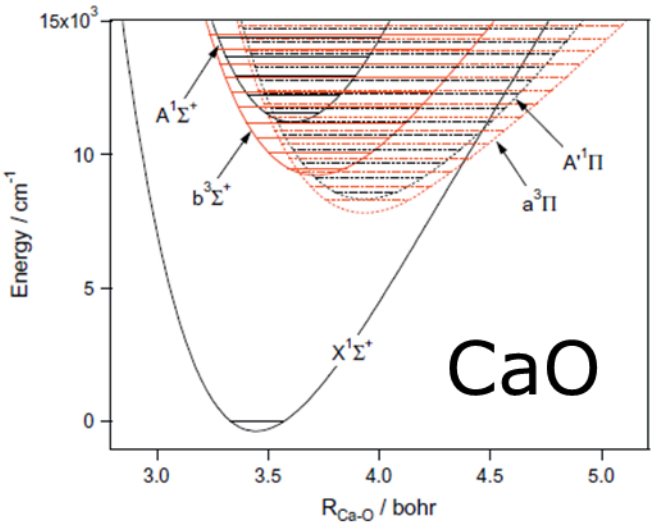


AlO



Electronic spectra depends on potential energy curves

Electronic structure



State labels like atoms

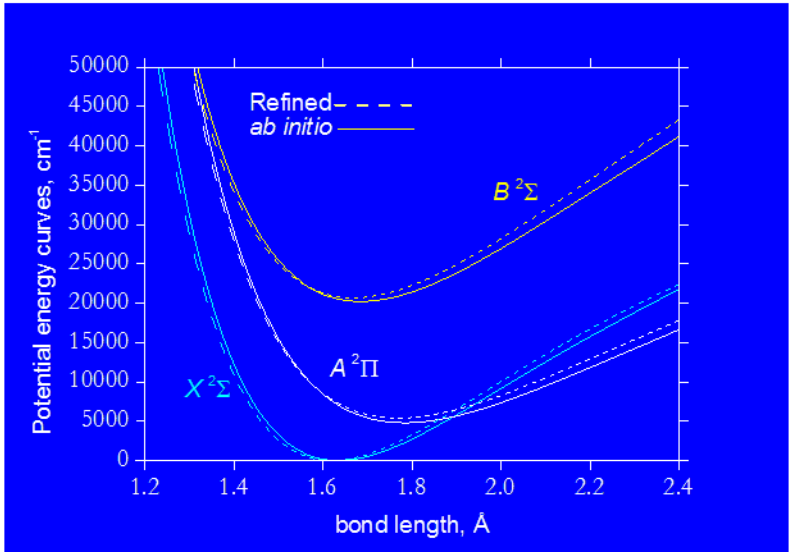
spin 2S+1

Eg X $^2\Pi$

Angular momentum projection, Λ

State label
X ground state
A, B, C excited states same spin
a,b,c excited states different spin
Rules are made to be broken!

AlO



Electronic spectra: selection rules

- Involves changes in electronic state

  $\Delta S = 0$, $\Delta\Lambda = 0,+/-1$, (g $\leftrightarrow$u for symmetric species)
- And vibrational state (Any, Franck-Condon approx.)
- And rotational state ($\Delta J = -1, (0), 1$)

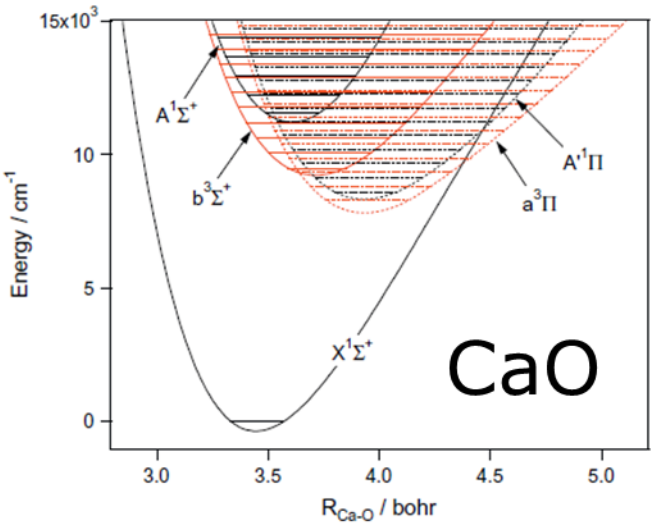
Depends on potential energy curves

Allowed transitions?

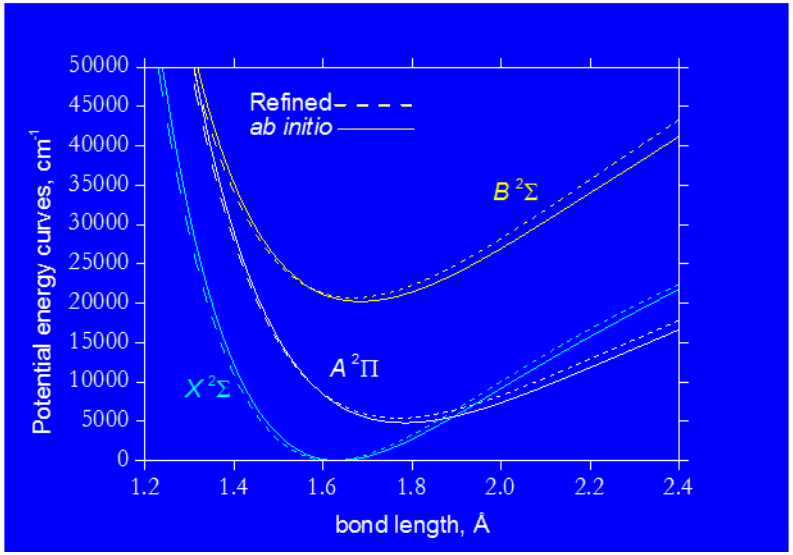
CaO X $^1\Sigma \rightarrow$

AlO X $^2\Sigma \rightarrow$

Electronic structure



AlO



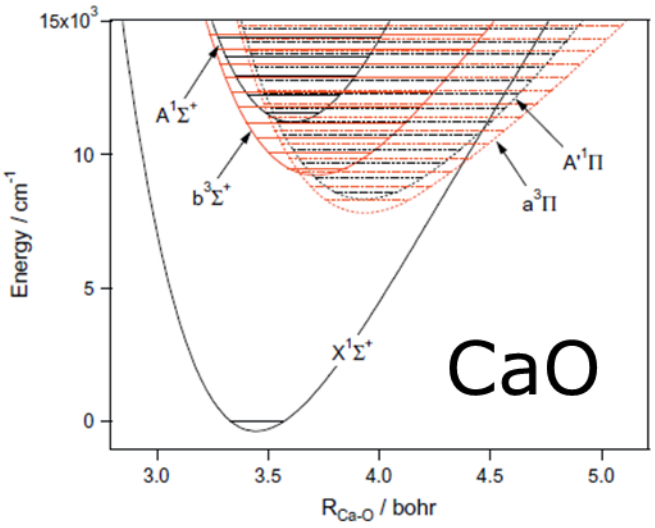
Depends on potential energy curves

Allowed transitions?

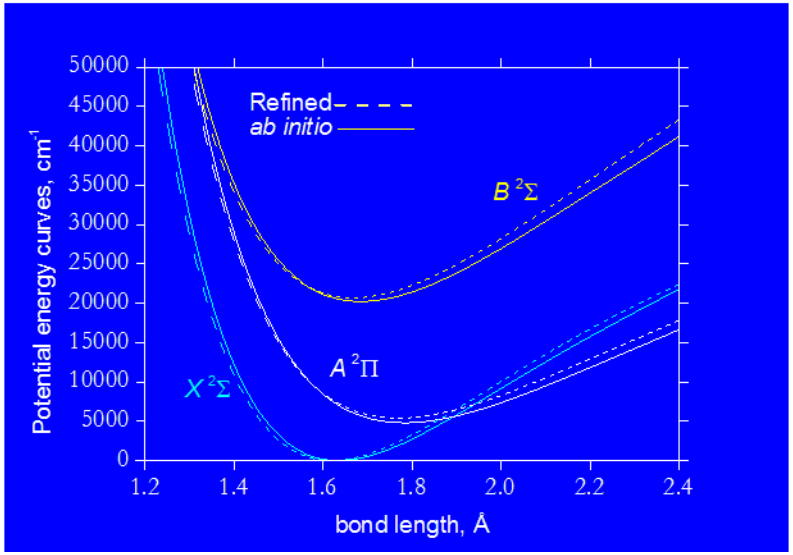
CaO X $^1\Sigma^+ \rightarrow A\ ^1\Sigma^+, A'\ ^1\Pi$

AlO X $^2\Sigma \rightarrow$

Electronic structure



AlO



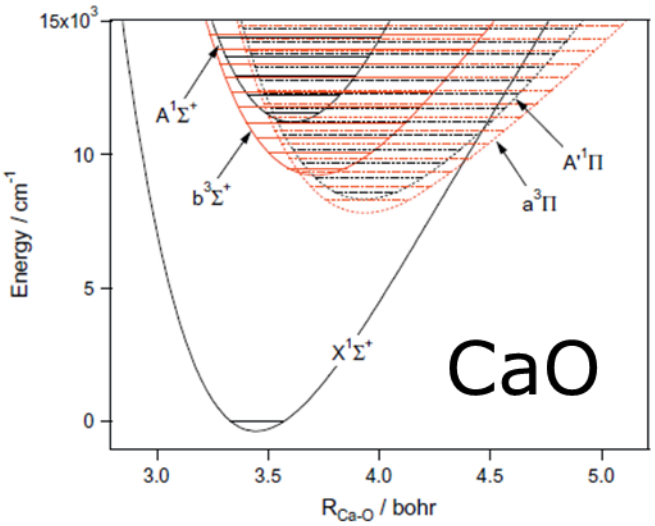
Depends on potential energy curves

Allowed transitions?

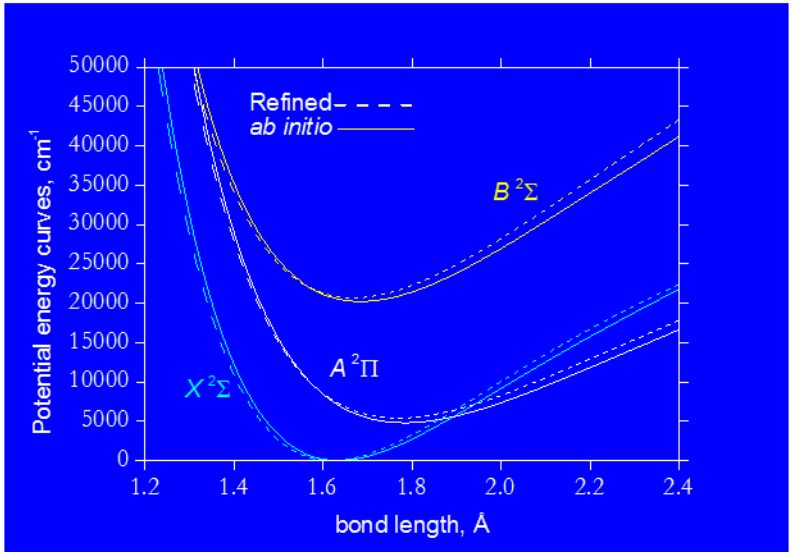
CaO X $^1\Sigma^+ \rightarrow A\ ^1\Sigma^+, A'\ ^1\Pi$

AlO X $^2\Sigma \rightarrow A\ ^2\Pi, B\ ^2\Sigma$

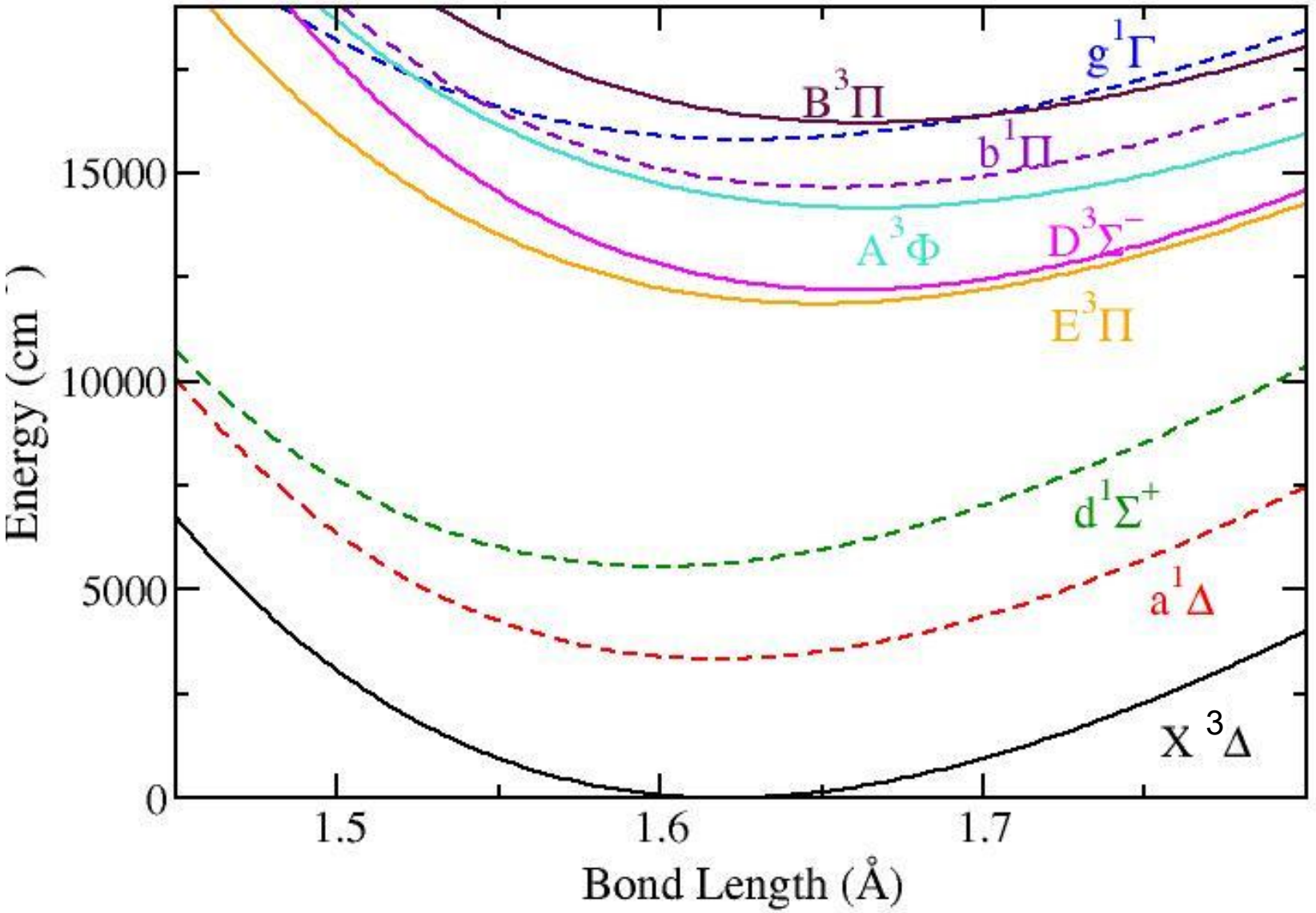
Electronic structure



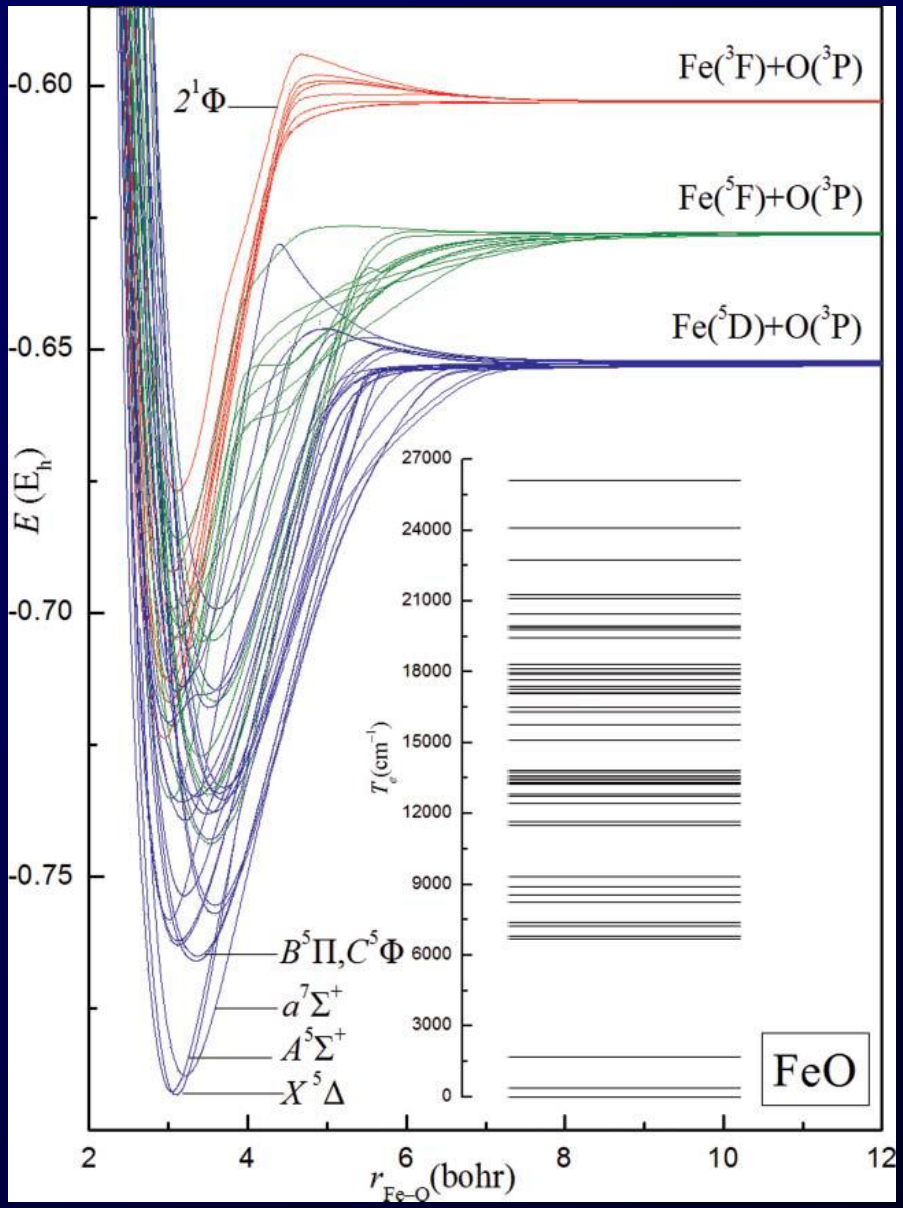
AlO



TiO: low-lying electronic states



FeO



Sakellaris, et al. J. Chem. Phys. **134**, 234308 (2011)

General (variational) diatomic code

Duo

Freely available *from* https://github.com/ExoMol/Duo

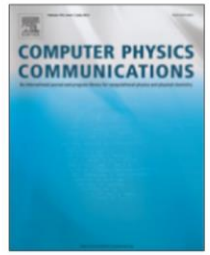
Manual and extensive examples also online

Computer Physics Communications 202 (2016) 262–275

Contents lists available at ScienceDirect

Computer Physics Communications

journal homepage: www.elsevier.com/locate/cpc



Duo: A general program for calculating spectra of diatomic molecules☆

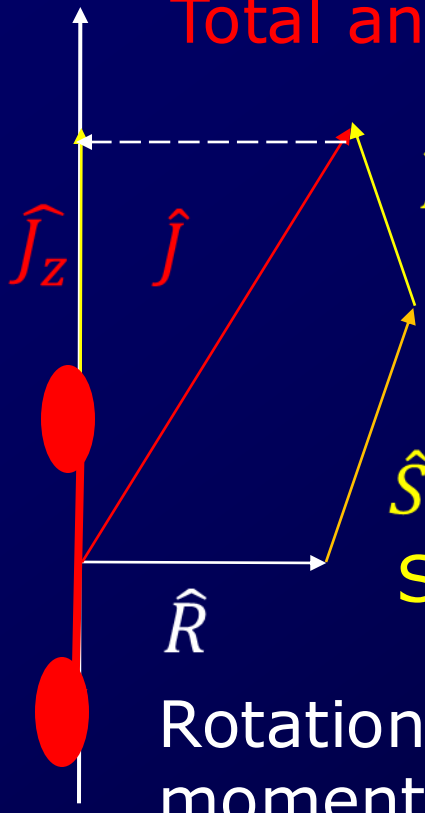
Sergei N. Yurchenko[a,*], Lorenzo Lodi[a], Jonathan Tennyson[a], Andrey V. Stolyarov[b]

[a] Department of Physics & Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

[b] Department of Chemistry, Lomonosov Moscow State University, Leninskiye gory 1/3, 119992 Moscow, Russia

Duo: a general diatomic nuclear motion code

S.N. Yurchenko, L. Lodi, J. Tennyson & A.V. Stolyarov, Computer Phys. Comm. **202**, 262 (2016).



$$\hat{R}^2 = (\hat{J} - \hat{L} - \hat{S})^2$$

$$\hat{H}_{ii} = \frac{\hbar^2}{2\mu r^2}\hat{R}^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_i(r)$$

Variational basis set
Hund's case (a)

Vibrational Spin

$$\phi_n = |v\rangle|J\Omega\rangle|S\Sigma\rangle|LS\Sigma\rangle$$

Rotational Electronic

Sergey Yurchenko

Hyperfine Structure

- Nuclear spin: final source of angular momentum in an atom or molecule
- Denoted I: for a diatomic $\underline{I}=\underline{I}_1+\underline{I}_2$
- Can couple to total angular moment J
  $\underline{F} = \underline{J} + \underline{I}$
- Leads to small (hyperfine) splittings in energy levels and transitions (often not resolved)
- Selection rule

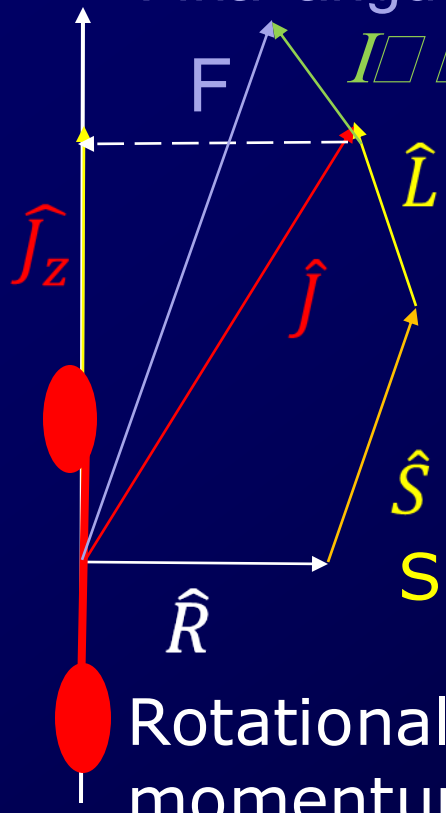
□ □ □$\Delta F = -1, (0), 1$

Can mean $\Delta J > 1$

- NMR, H 21 cm line, etc, etc

Duo: a general diatomic nuclear motion code

S.N. Yurchenko, L. Lodi, J. Tennyson & A.V. Stolyarov, Computer Phys. Comm. **202**, 262 (2016).



$F = J + I$

Qianwei Qu

$$\hat{H}_{ii} = \frac{\hbar^2}{2\mu r^2}\hat{R}^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_i(r)$$

Variational basis set, Hund's case (a_β)

Rotational Electronic

$$\phi_n = |v\rangle|J\Omega\rangle|S\Sigma\rangle|LS\Sigma\rangle$$

Dipole + quadrupole transitions

Hyperfine effects

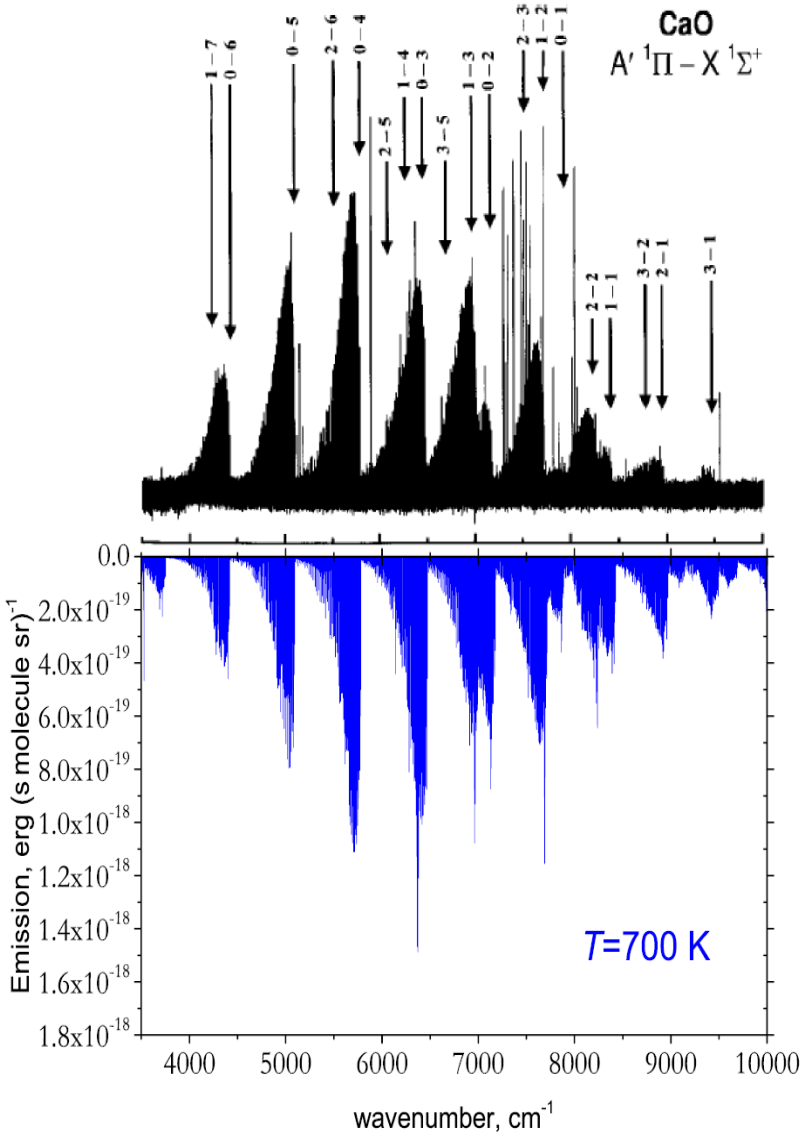
Vibrational Spin

$$\phi_n = |v\rangle|J\Omega\rangle|S\Sigma\rangle|LS\Sigma\rangle|IFM_F\rangle$$

Nuclear Spin

Qianwei Qu, S. N. Yurchenko & J. Tennyson, J. Comp. Theor. Chem., 18, 1808 (2022)

Experiment (Bernath)



Theory

Electronic spectra

- $\Delta S = 0$ is weak selection rule

  Observe $\Delta S > 0$ “intercombination bands” but weak

Eg "Cameron Band" of CO a $^3\Pi$ – X $^1\Sigma^+$

- Band heads: features observed at low resolution

Band heads

Electronic spectra $R_e'' \neq R_e'$

so $B_e'' \neq B_e'$

Typically $B_e'' > B_e'$

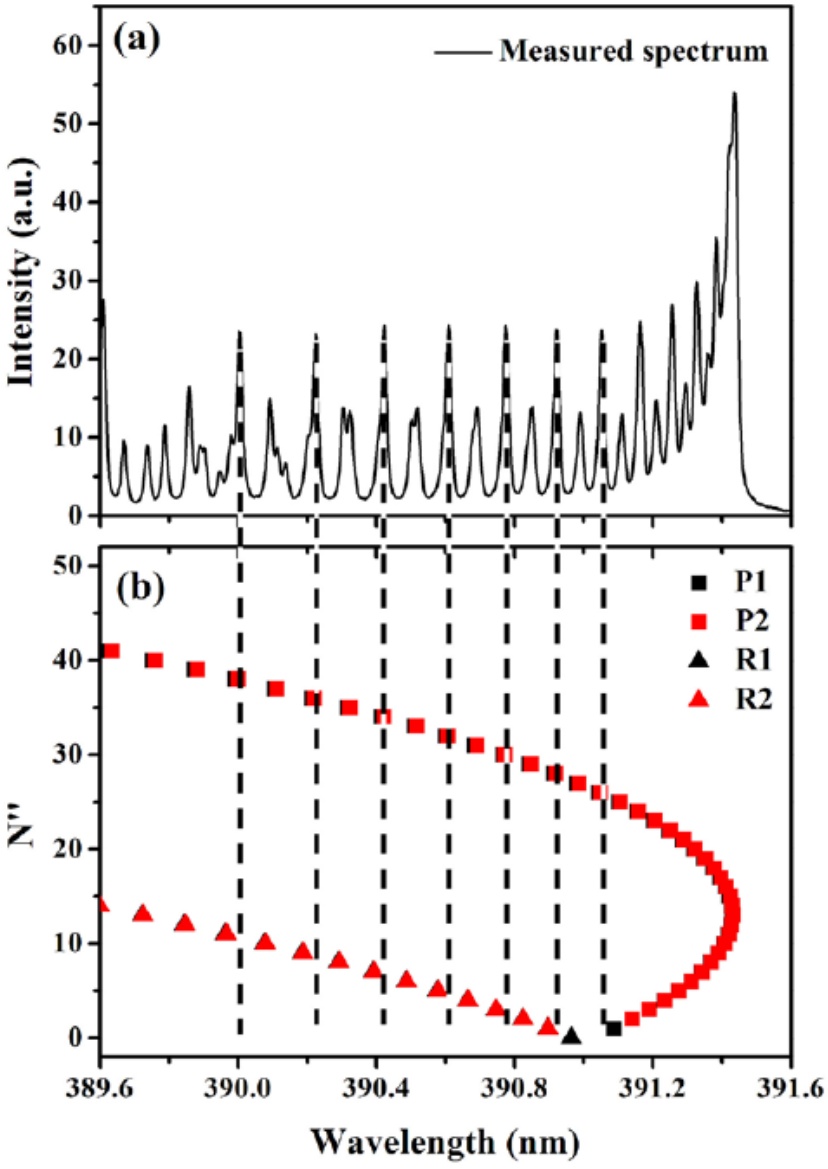
For the P-branch $J' = J'' - 1$, so that

$$\bar{\nu}_P = \bar{\nu}_{v'-v''} + B'(J''-1)J'' - B''J''(J''+1)$$
$$= \bar{\nu}_{v'-v''} - (B'+B'')J'' + (B'-B'')J''^2$$

Similarly for the R-branch $J'' = J' - 1$,

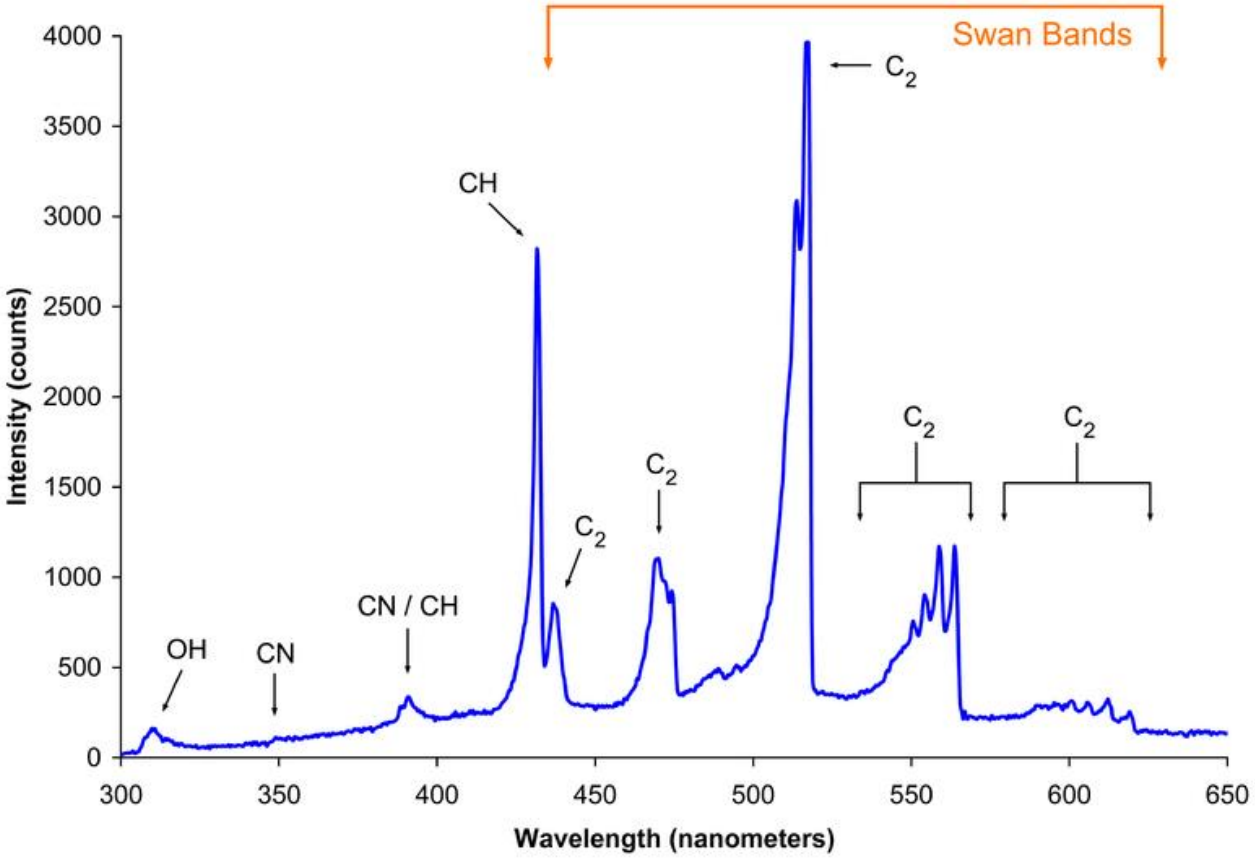
$$\bar{\nu}_R = \bar{\nu}_{v'-v''} + B'J'(J'+1) - B''J'(J'-1)$$
$$= \bar{\nu}_{v'-v''} + (B'+B'')J' + (B'-B'')J'^2$$

Leads to transitions becoming closer together and then turning over

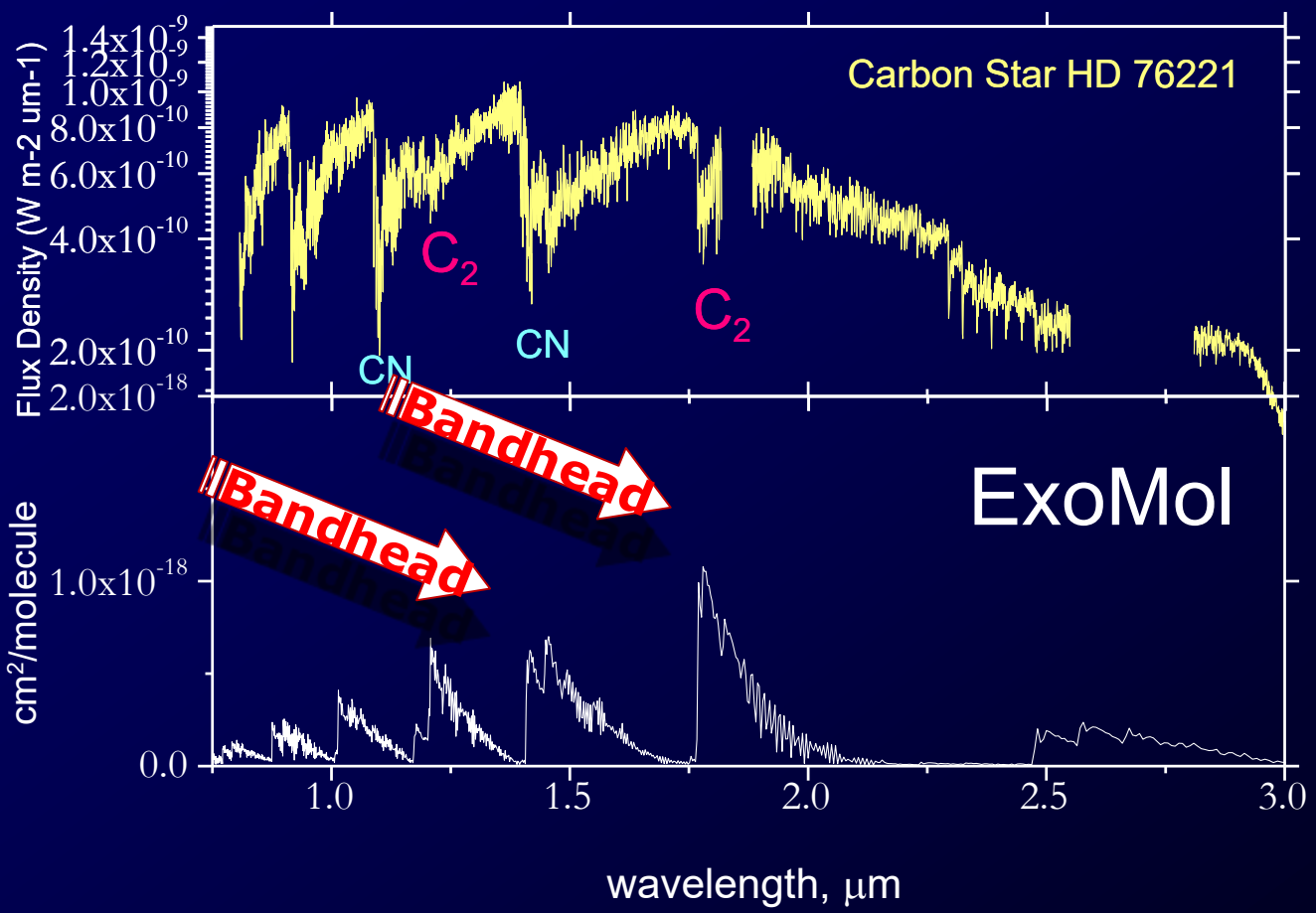


N_2 B – X (v'=0,v"=0) band

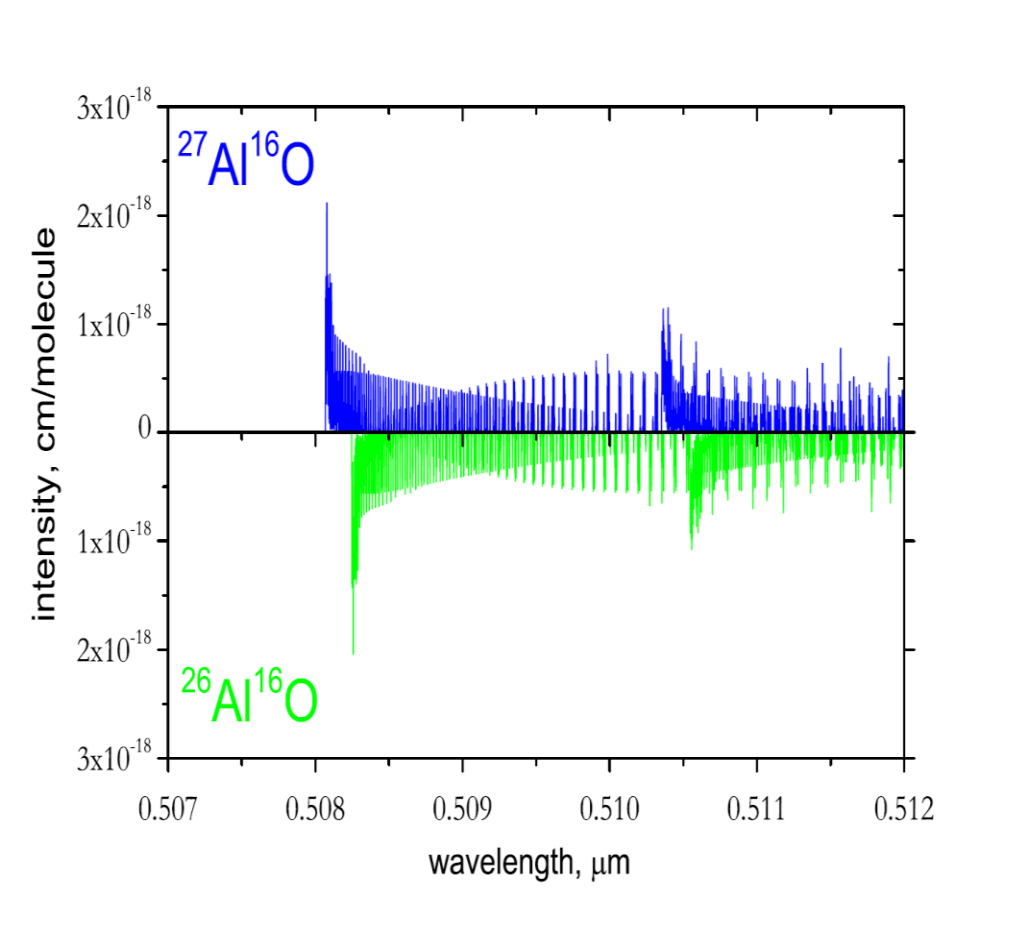
Low resolution torch spectrum



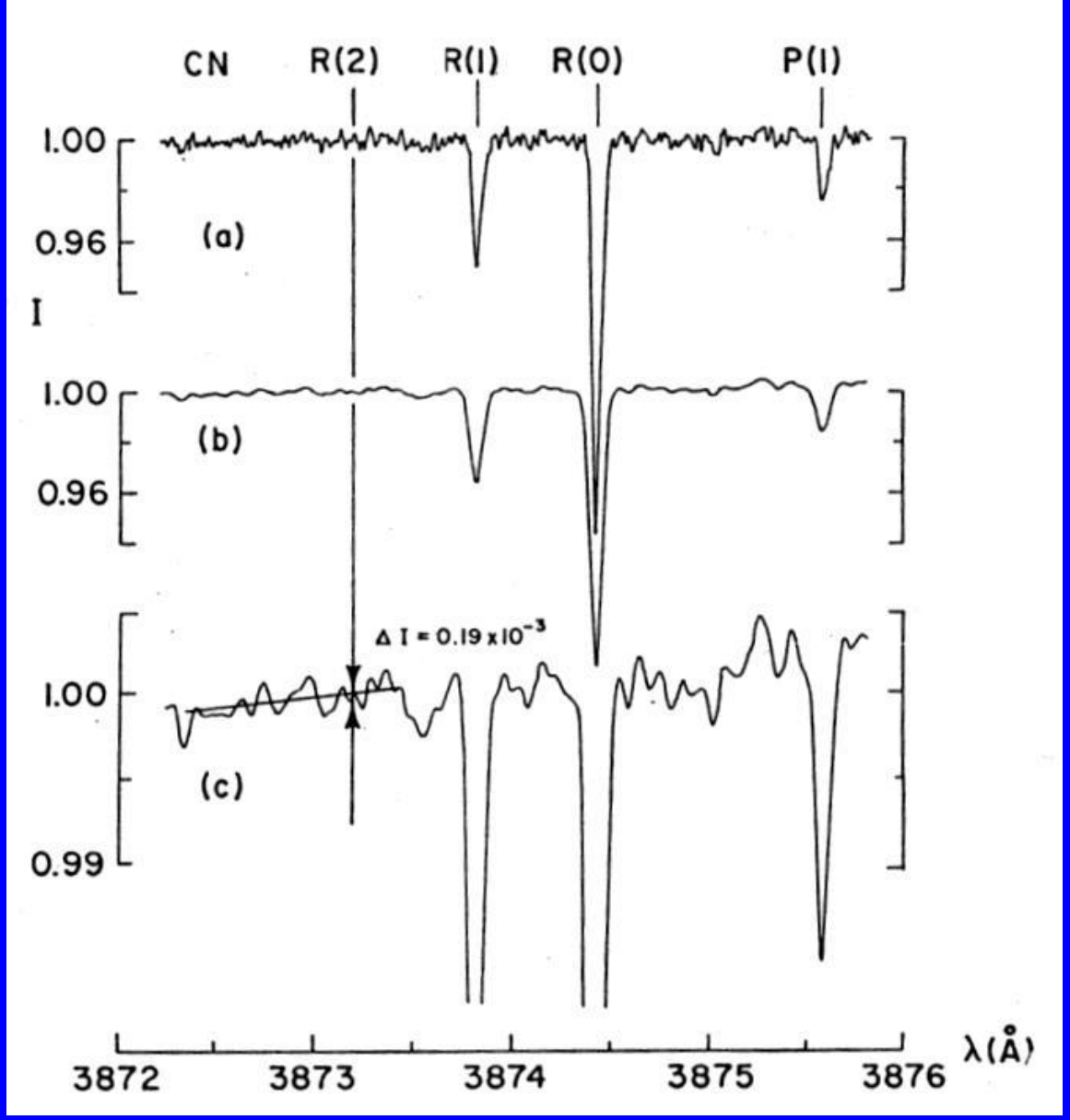
Rayner et al ApJ SS, 185, 289 (2009)



Isotope substitution: 27 to 28



ExoMol: Patrascu et al MNRAS 449, 3613 (2015)



Notation
P(J") or R(J")

J" is lower level
(J' is upper level)

So
P(1) means
J"=1 → J'=0
R(0) means
J"=0 → J'=1

etc.

Note R(2) is
Missing

Vibrations:
(v',v")

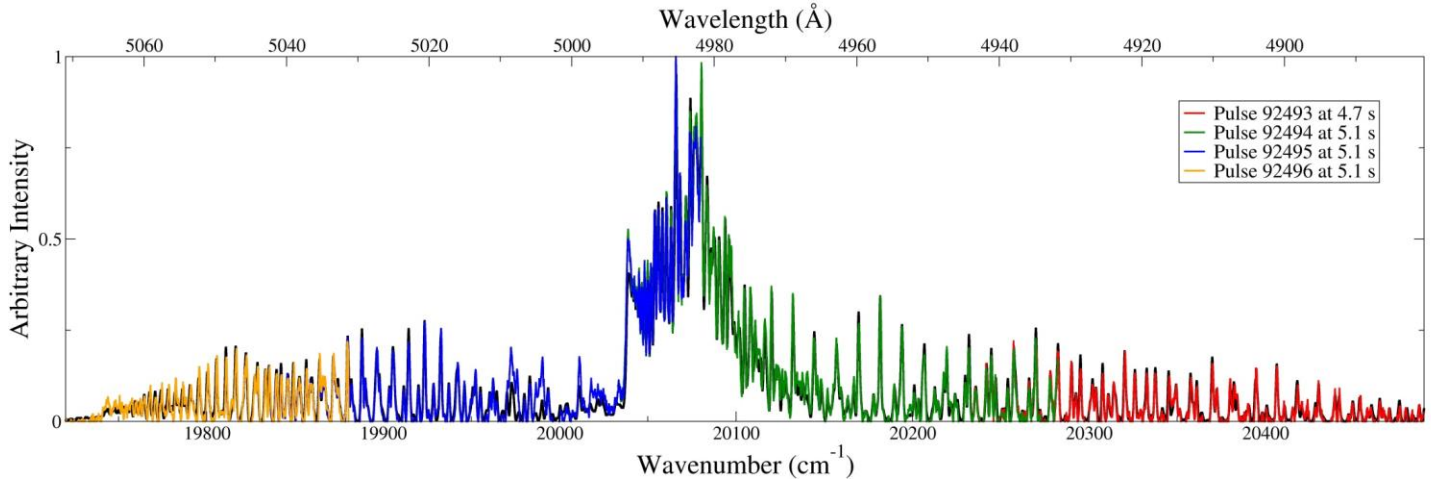
The interstellar (0,0) band of CN violet system in the spectrum of ζ Oph. T ~ 2.6 K

Fusion appications: BeH / BeD / BeT

- Be coating of walls at JET (ITER)
- BeD observed product
- Monitor Be erosion

Daniel Darby-Lewis

BeD spectra measured in JET



Red, green, blue and orange regions are different pulses.

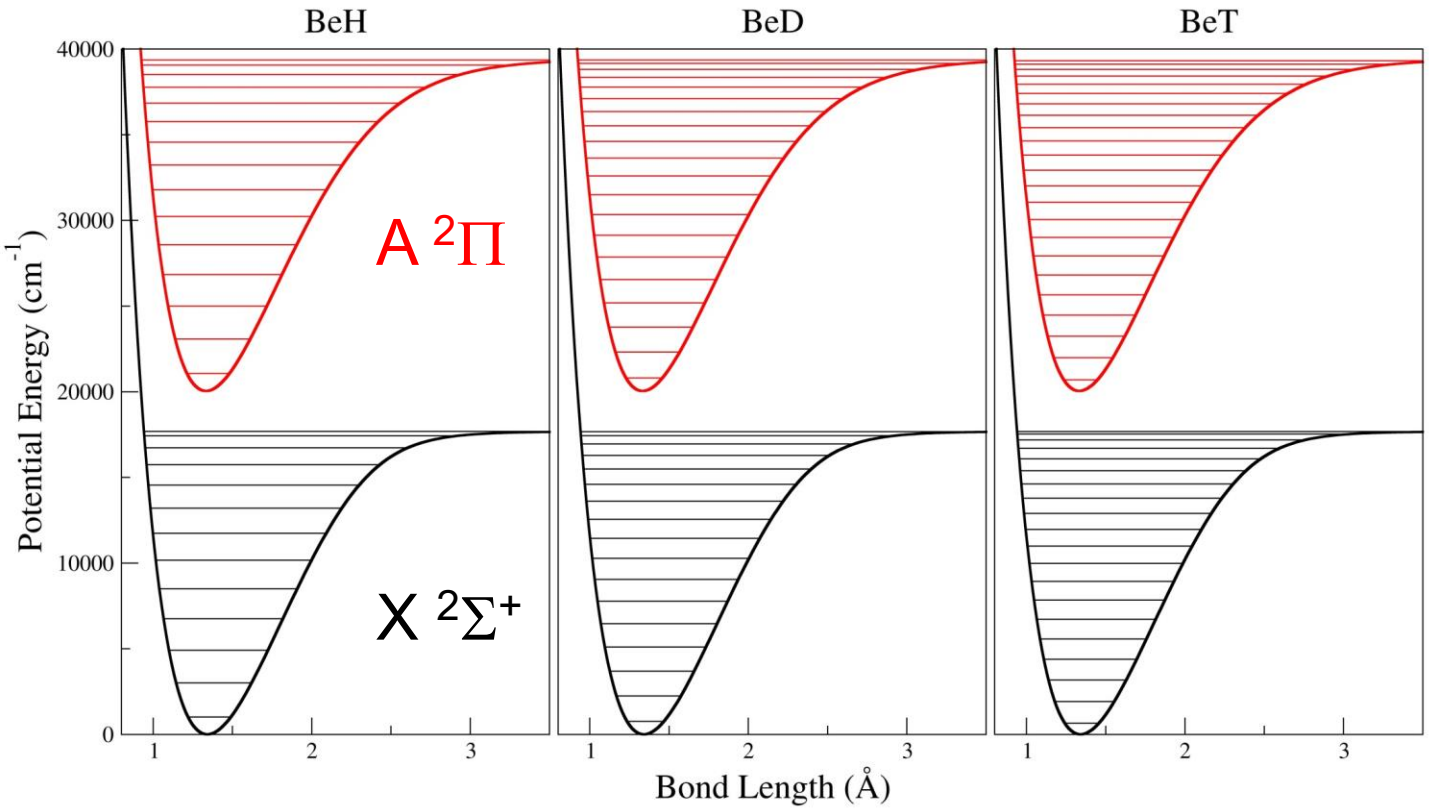
D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, (in press)

Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$) → e + BeH (A $^2\Pi$)

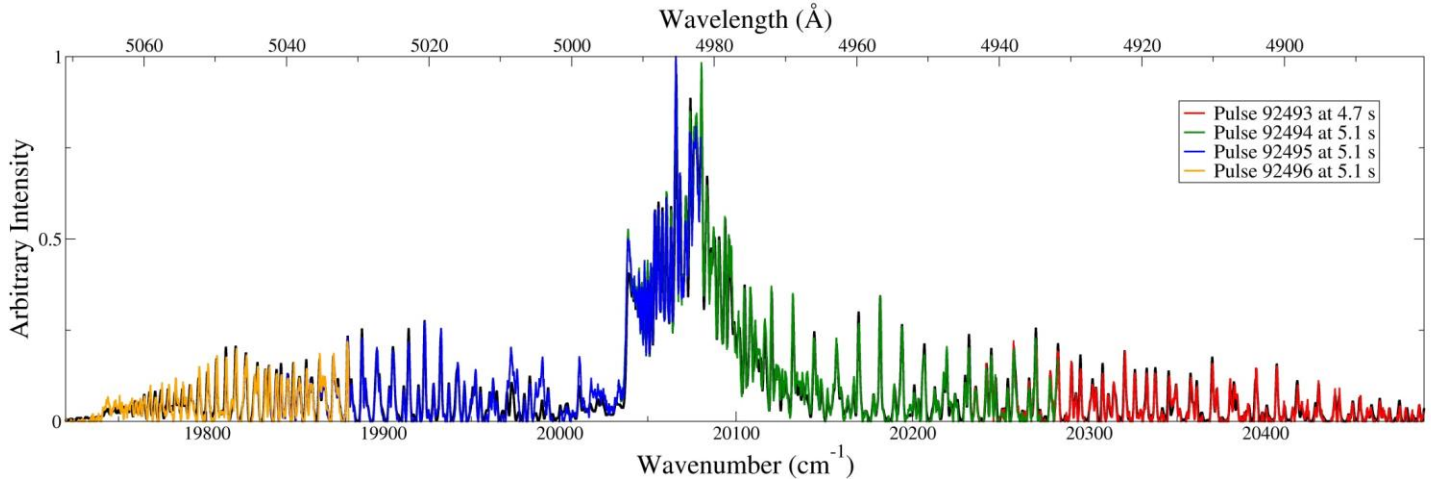
Step 2 BeH (A $^2\Pi$, *v'*,*J'*) → BeH (X $^2\Sigma^+$,*v"*,*J"*) + hν

Spectroscopic model for BeH/BeD/BeT



D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, **51**, 185701 (2018)

BeD spectra measured in JET

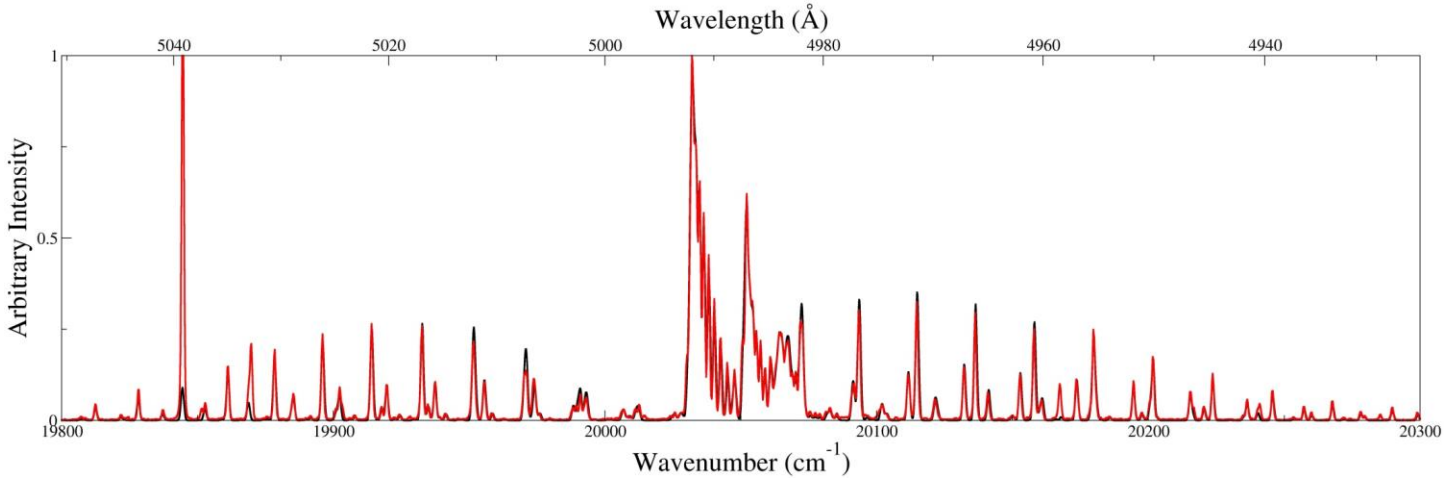


Red, green, blue and orange regions are different pulses.

Spectral fit: black lines. Gives: T_{rot} = 3800 K, T_{vib} = 4700 K

D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, **51**, 185701 (2018)

BeH spectra measured in Julich



Spectrum from a H doped lamp with a Be target: Measured red. Black synthetic generated at T_{rot} = 540 K and T_{vib} = 3440 K

Interpretation requires collisional-radiative model

Step 1 e + BeH ($X\ ^2\Sigma^+$) → e + BeH ($A\ ^2\Pi$)

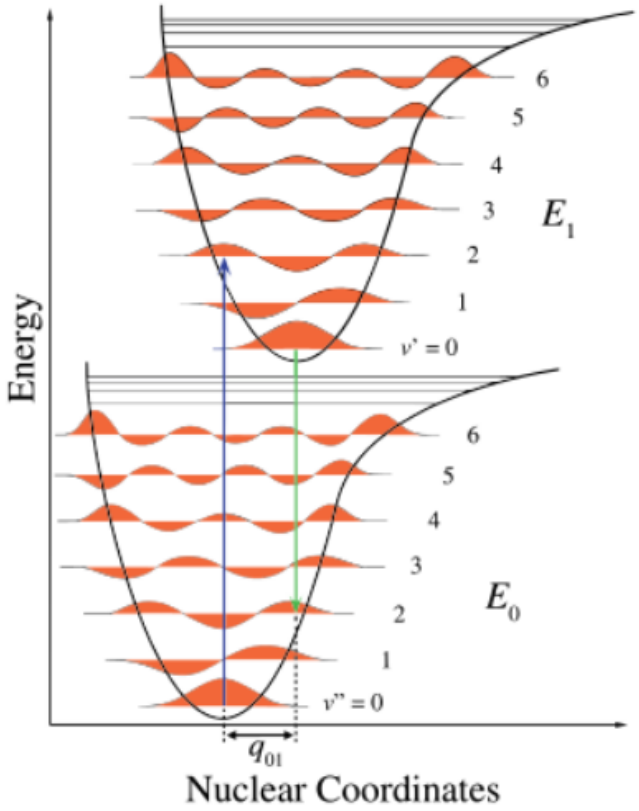
Step 2 BeH ($A\ ^2\Pi$, *v',J')* → BeH ($X\ ^2\Sigma^+$,*v",J"*) + hν

Franck-Condon approximation

For an electronic transitions:
Intensity of a vibrational band v' – v" given by a Franck-Condon factor:

$$| \langle v'' | v' \rangle |^2$$

Assumes transitions are instantaneous/vertical ie nuclei don't move.



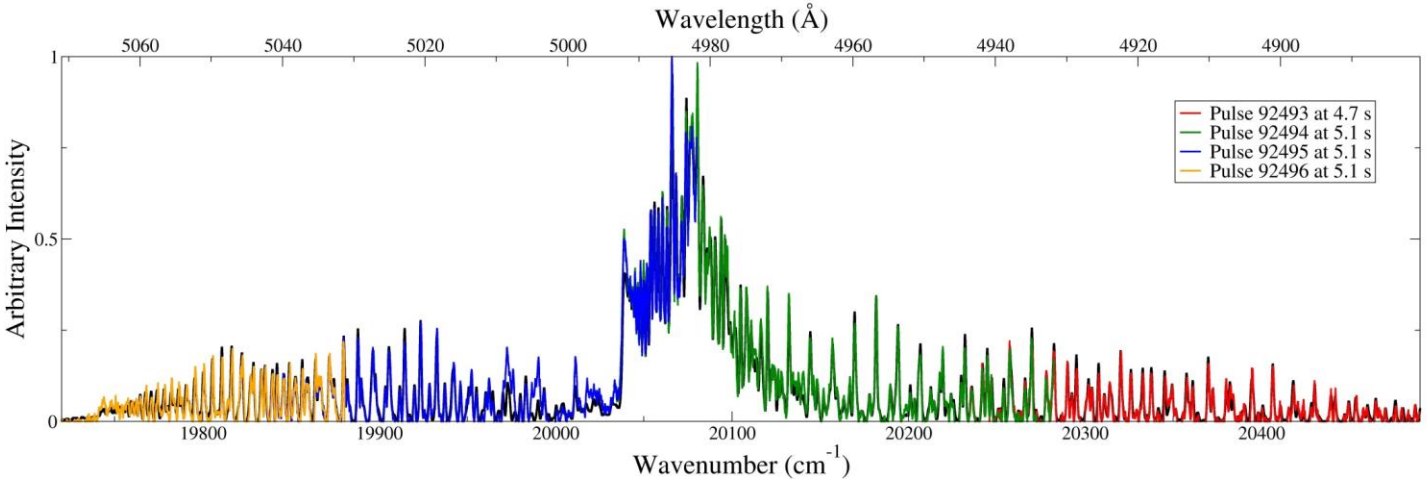
Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$,*v'*) → e + BeH (A $^2\Pi$,*v"*)

Step 2 BeH (A $^2\Pi$, *v',J'*) → BeH (X $^2\Sigma^+$,*v",J"*) + hν

D. Darby-Lewis D. Darby-Lewis, J. Tennyson, S.N. Yurchenko & K.D. Lawson,
Vibrational resolved electron impact electronic excitation of BeH,
J. Phys. B: At. Mol. Opt. Phys., **53**, 135202 (2020)

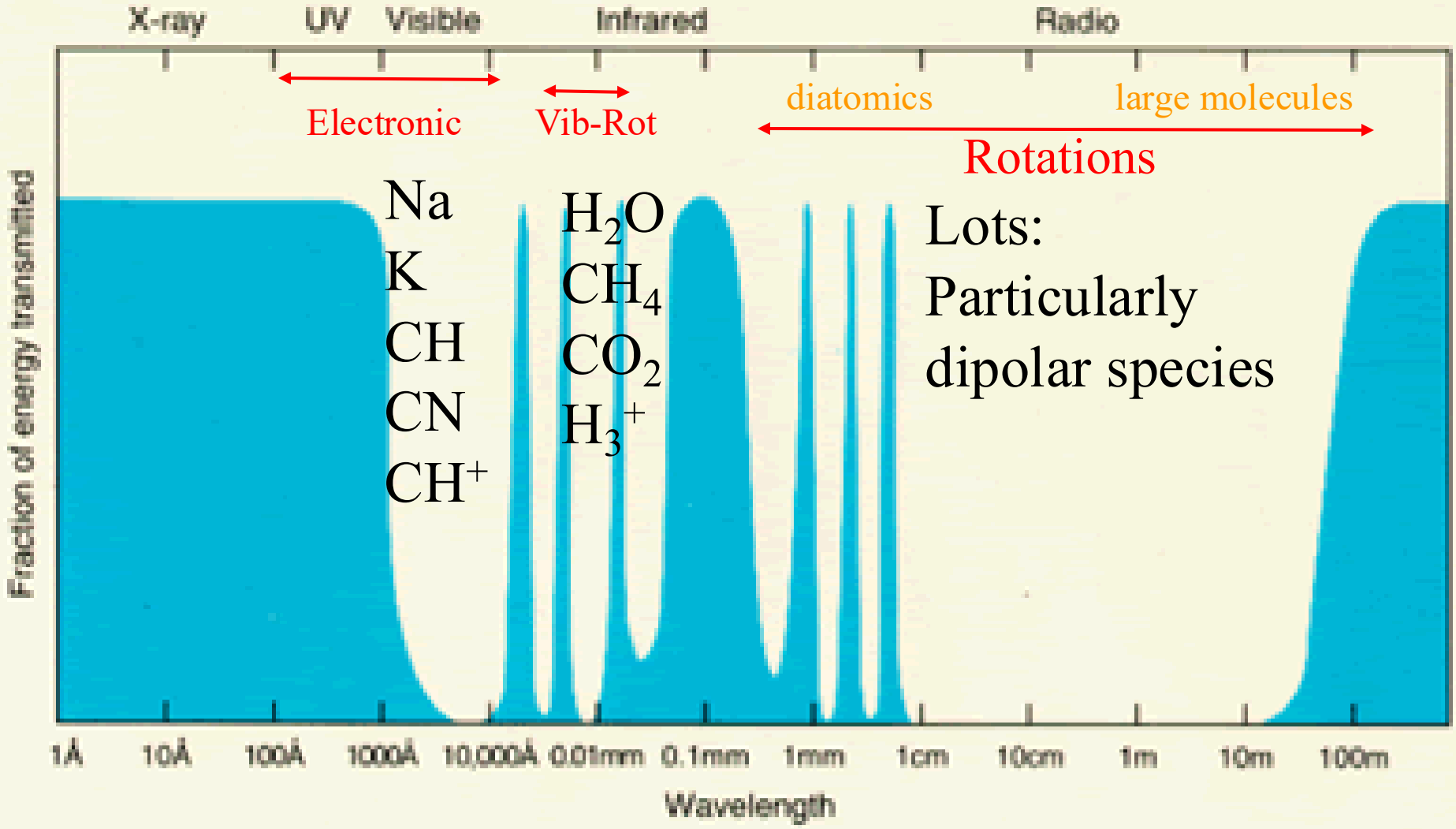
BeD spectra measured in JET



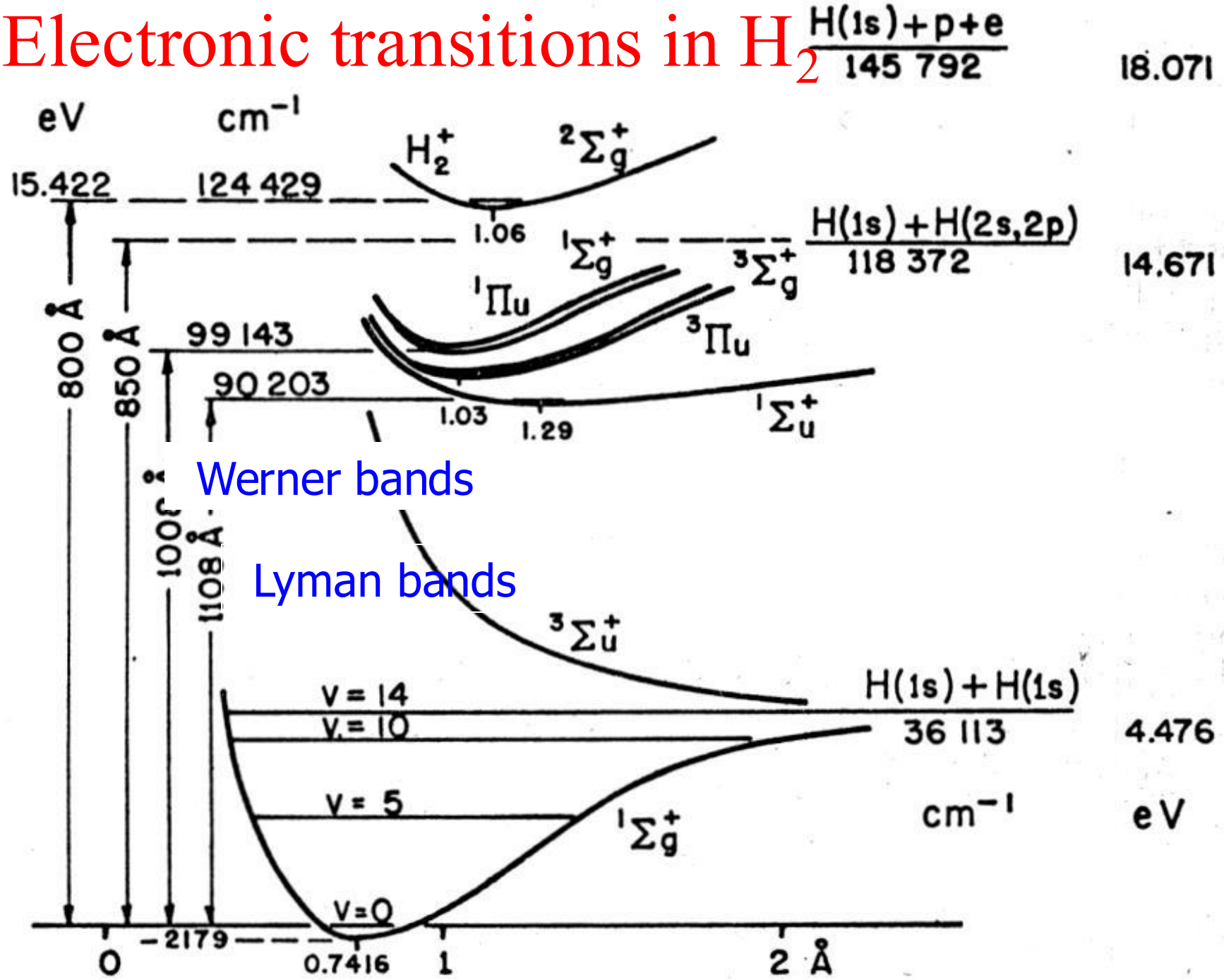
D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, **51**, 185701 (2018)

E Pawelec, D Borodin, S Brezinsek, T Dittmar, D Douai, D Mazur, A Meigs, A Shaw, B Thomas, JET Contributors and EUROfusion Tokamak Exploitation,
Internal energy distributions of BeH, BeD, and BeT molecules created during chemically assisted physical sputtering in JET tokamak plasma,
Phys. Plasmas, 31, 042516 (2024),

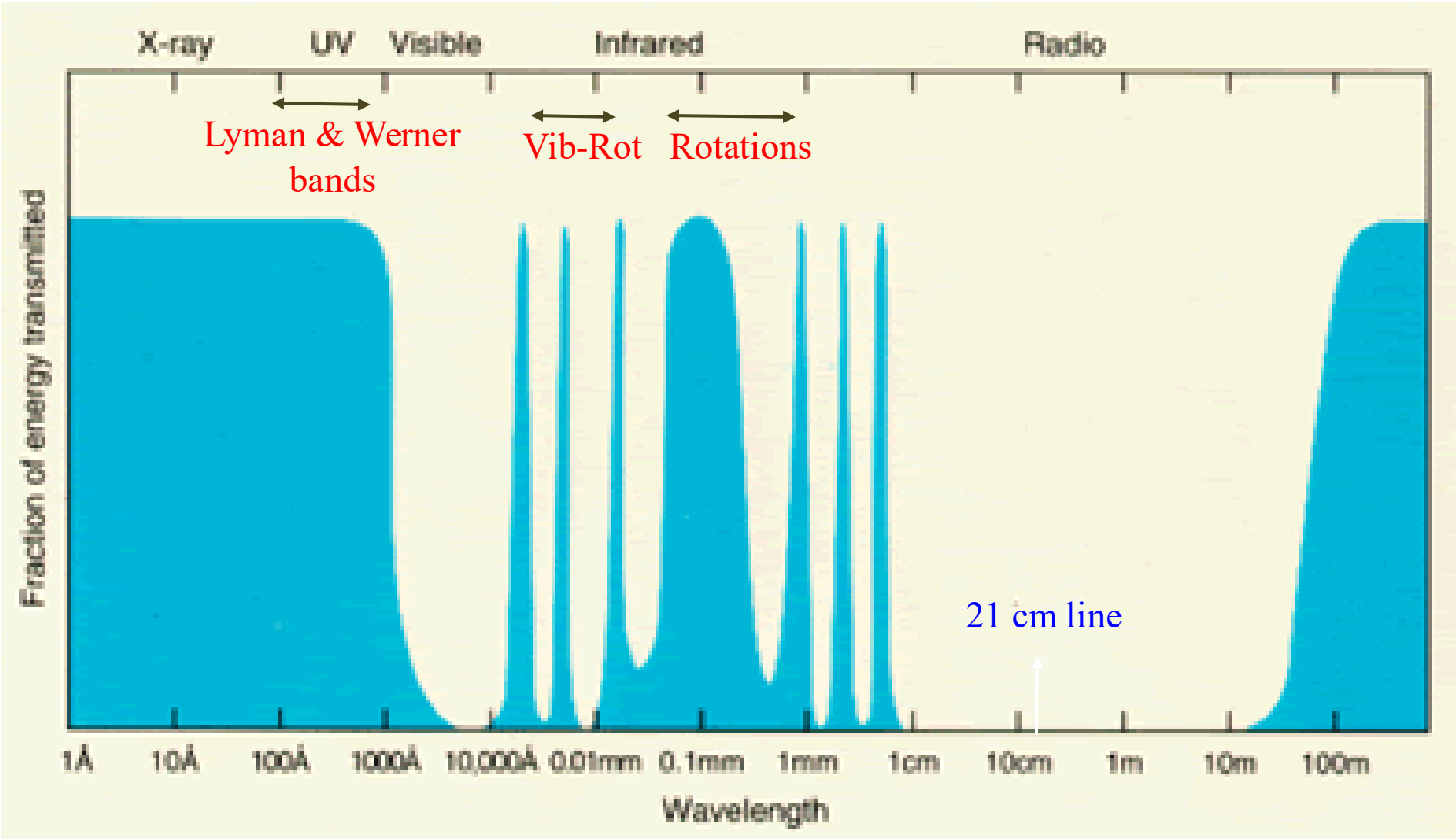
Spectral coverage from the ground



Electronic transitions in H_2

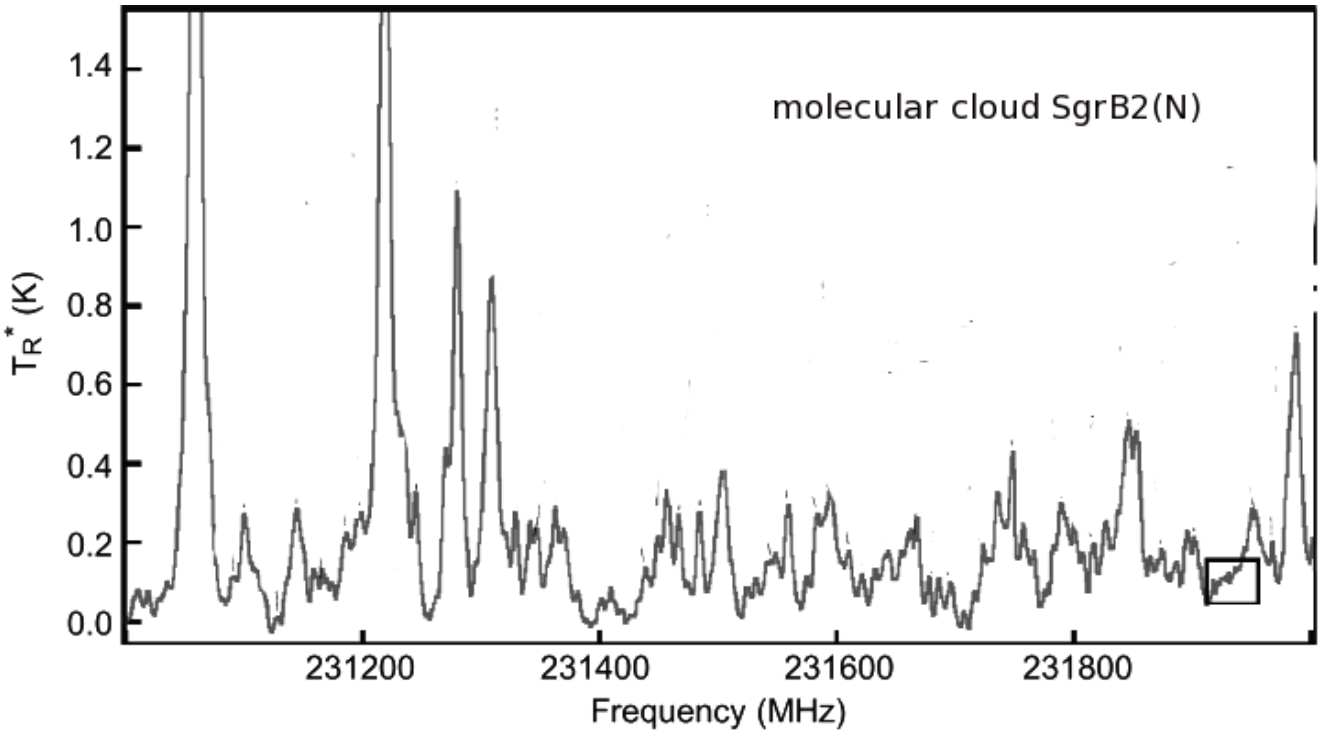


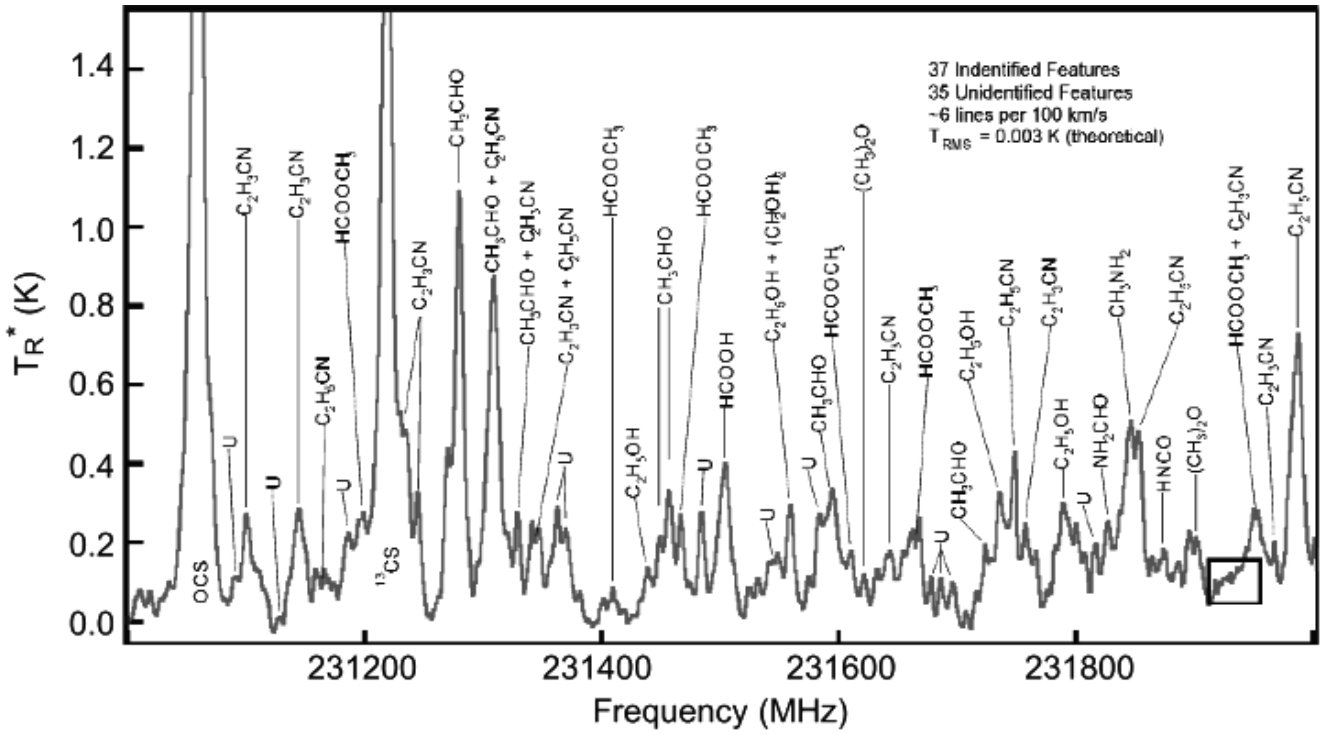
Spectra of molecular of hydrogen



Quiz question:

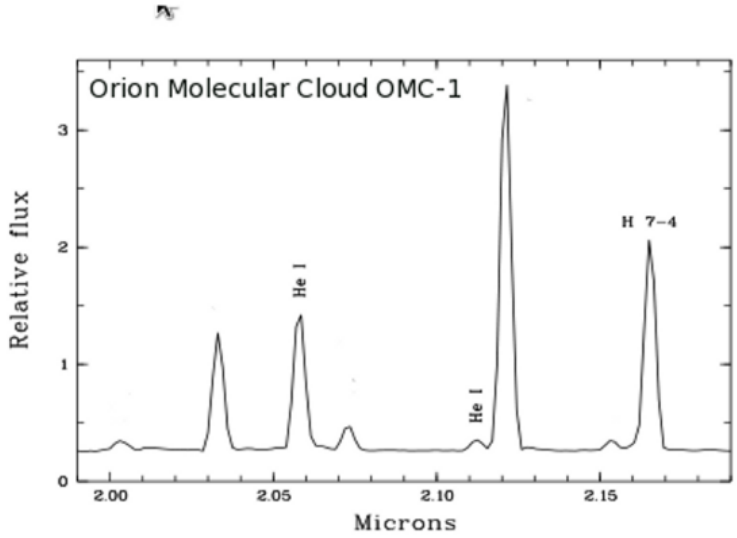
What are these emission features?
Where would one begin to look?





Source of lines: CDMS/JPL databases

Assign the lines and molecule



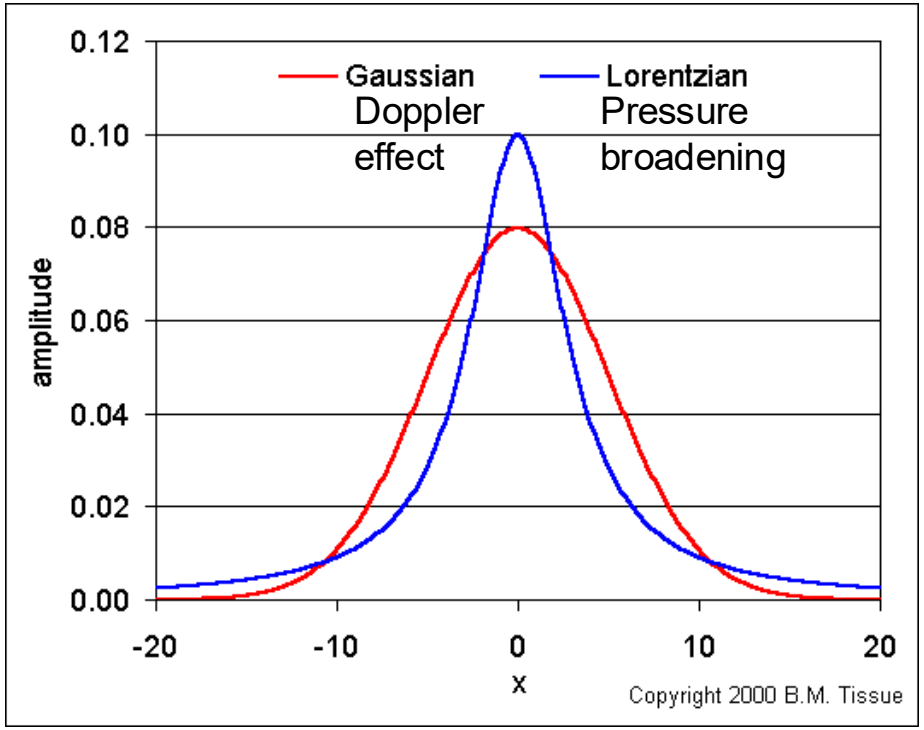
Contribution to line profiles:

1. Natural broadening: lifetime effect
   Lorentzian
2. Doppler broadening: thermal motion
   Gaussian, T-dependent
3. Pressure broadening: collisional effect
   Lorentzian (approx.), P-dependent
   Also: line mixing
4. T and P: Voigt profile

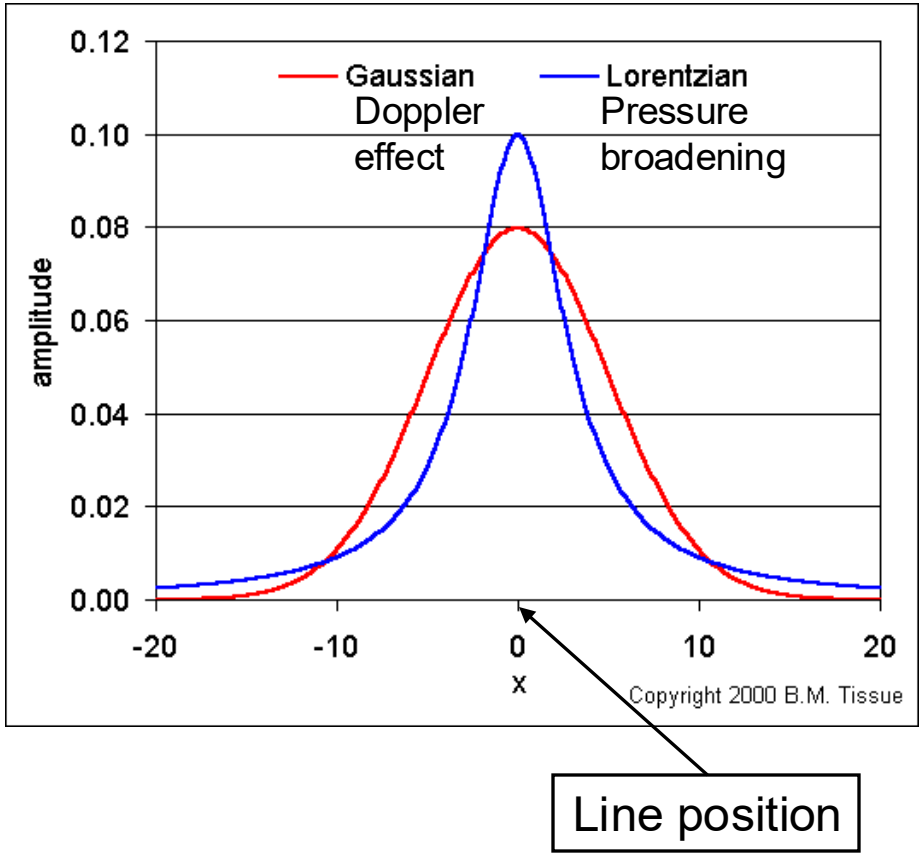
Beyond Voigt:
speed-dependence, hard/soft collisions, correlation etc

J. Tennyson et al, Pure Appl. Chem., 86 1931-1943 (2014)

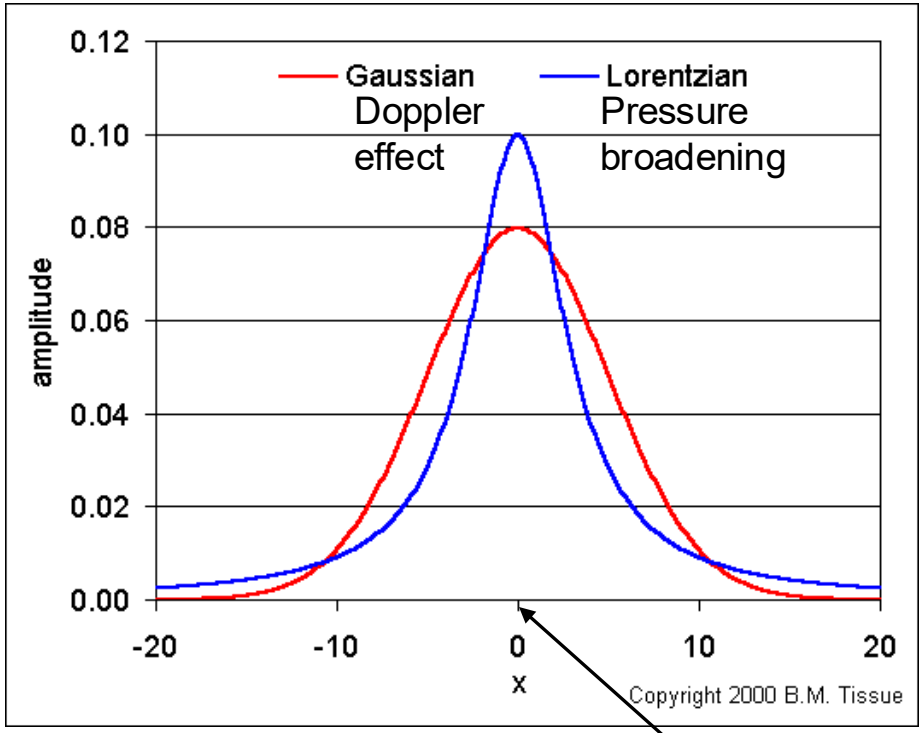
A spectral line



A spectral line



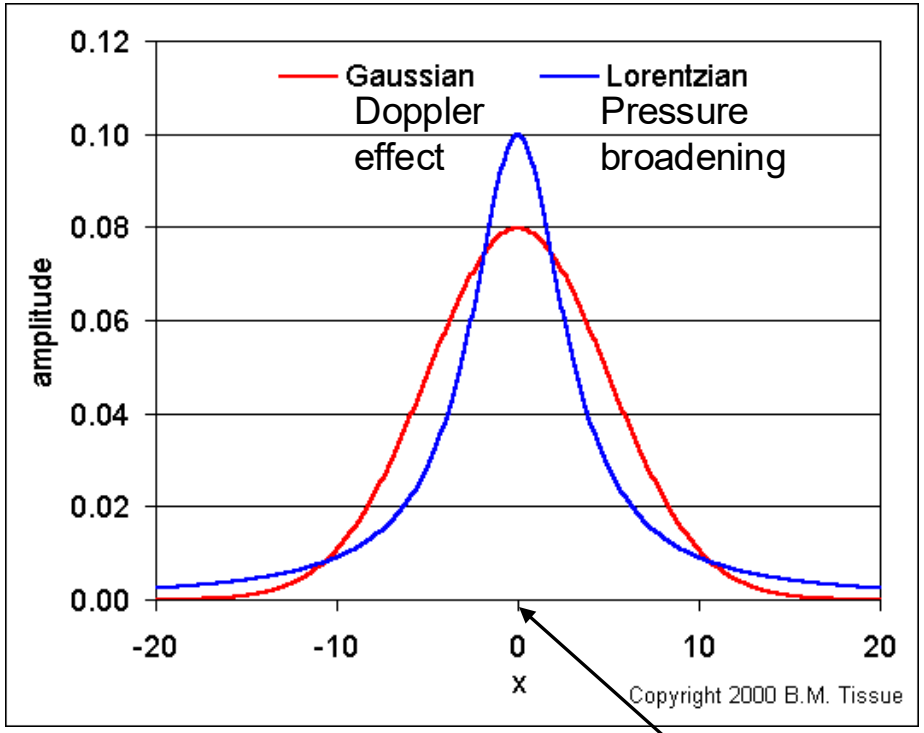
A spectral line



Line intensity:
Probability of absorbing a photon
Given by area under the curve

Line position

A spectral line

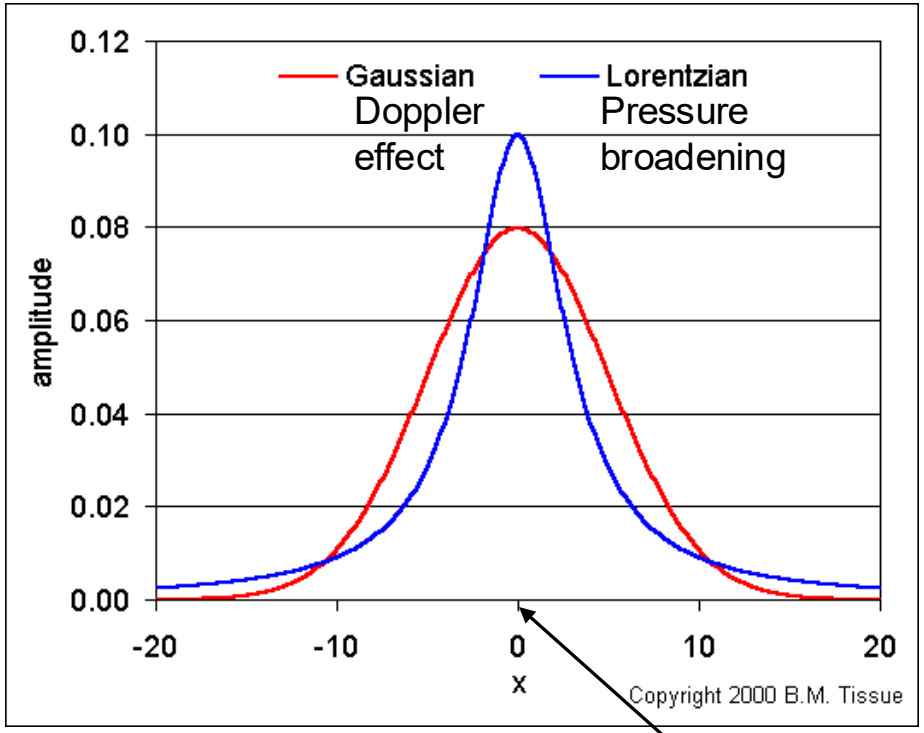


Line shape

Line intensity:
Probability of absorbing a photon
Given by area under the curve

Line position

A spectral line



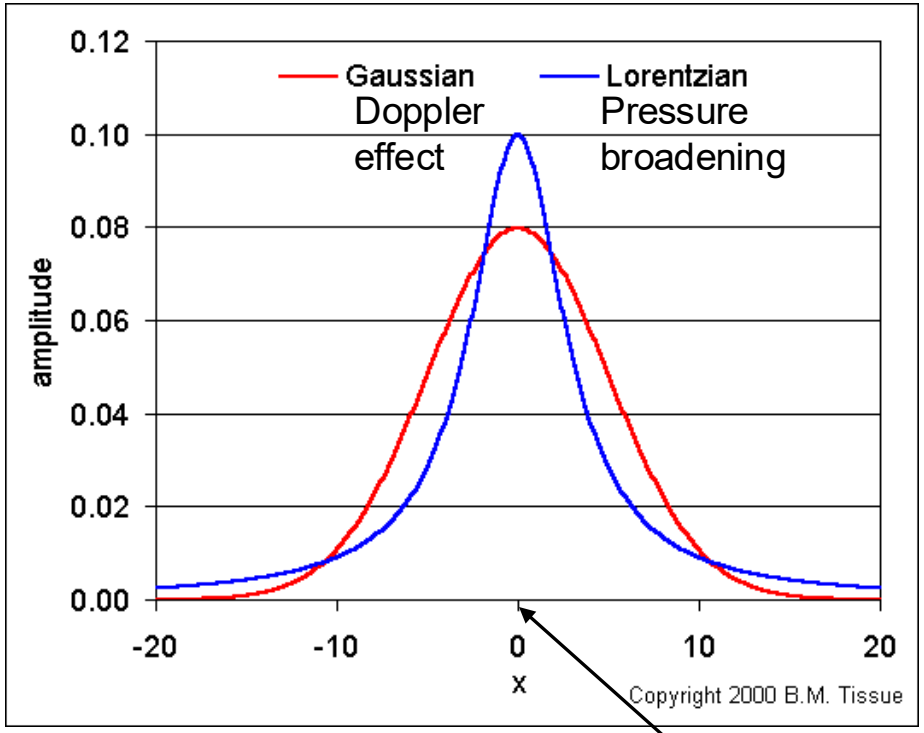
Line shape

Voigt profile:
Convolution of
Gaussian and
Lorentzian

Line intensity:
Probability of absorbing a photon
Given by area under the curve

Line position

A spectral line



Line shape

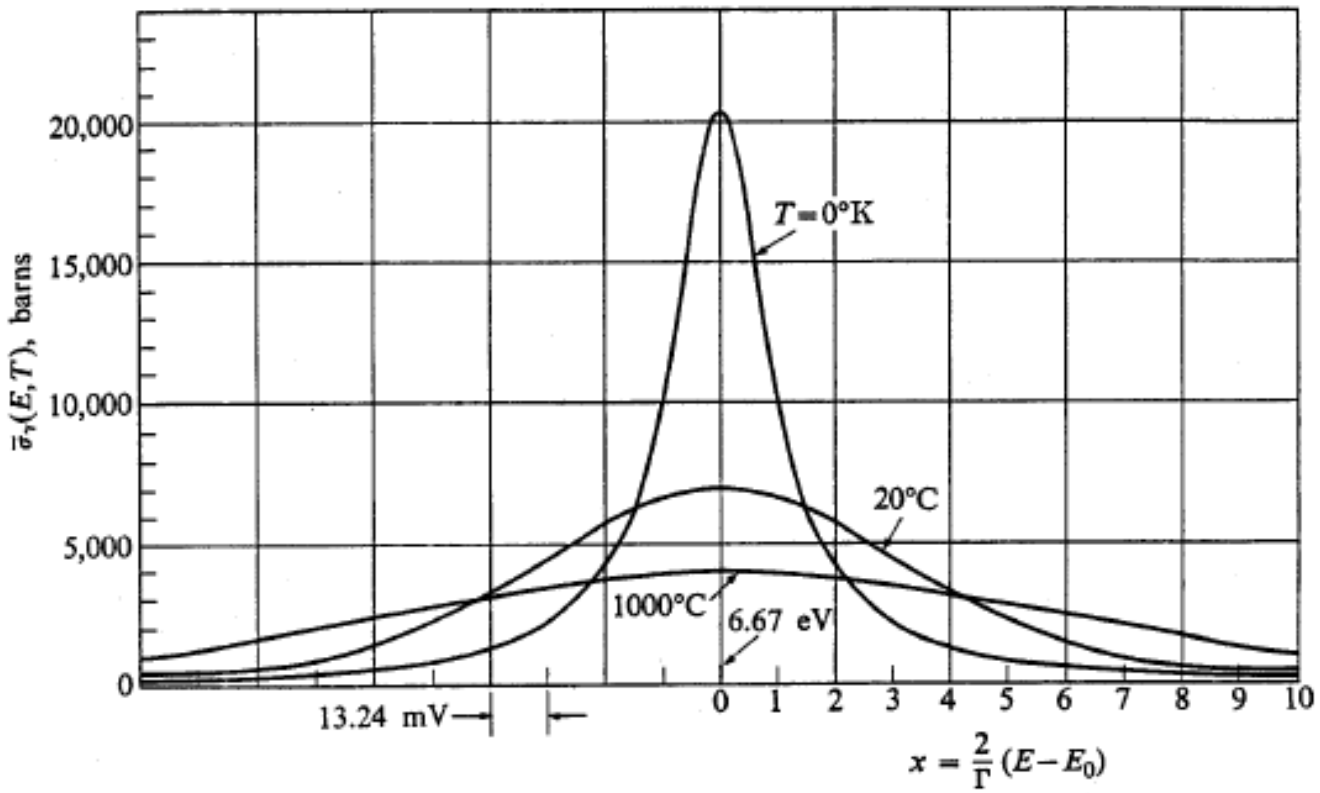
Voigt profile:
Convolution of
Gaussian and
Lorentzian

Line intensity:
Probability of absorbing a photon
Given by area under the curve

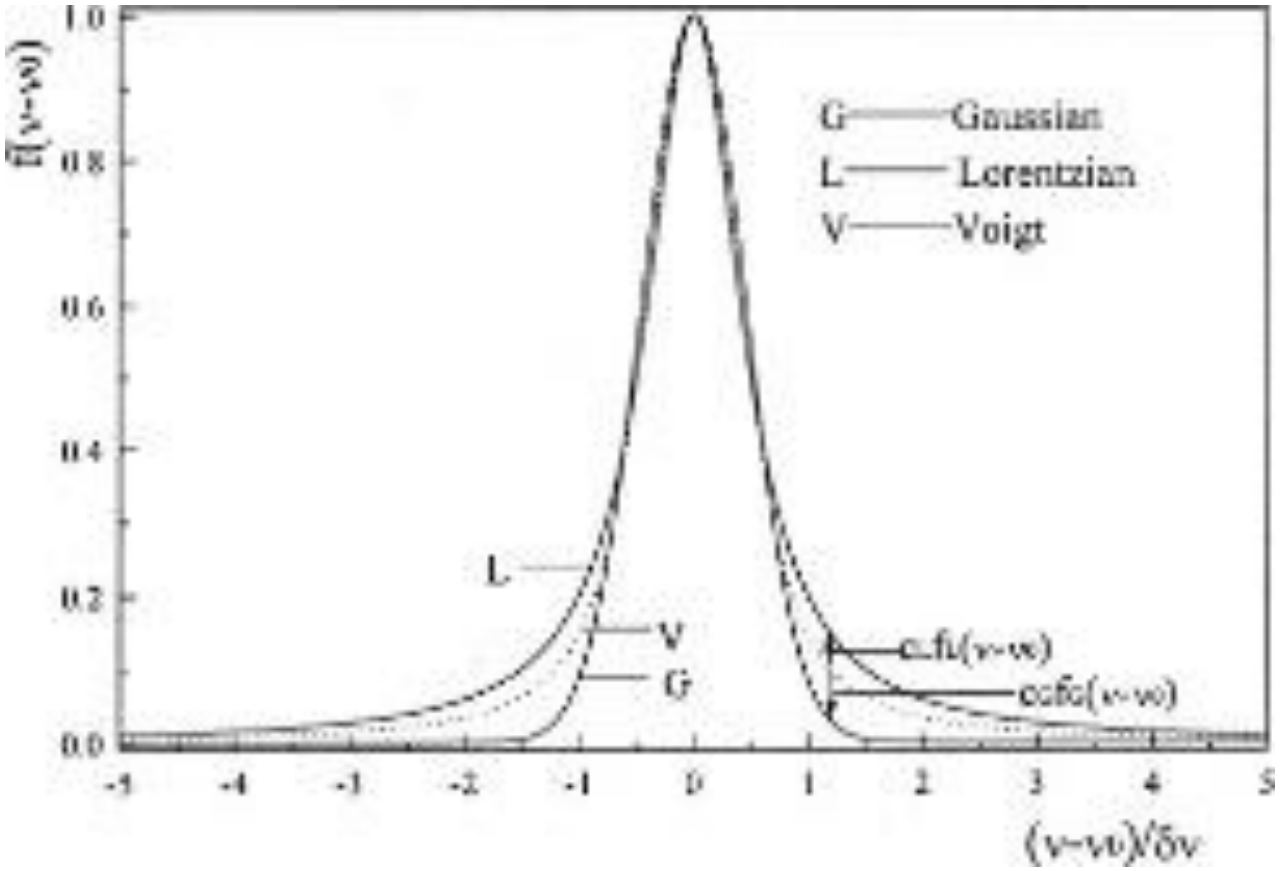
Line position

Line shape vital for optical thickness

Line profile effects: Doppler broadening



Voigt profile



Line intensity:
Probability of absorbing a photon
Given by area under the curve
Conserved with P,T if optically thin

Line profile
Import when saturated
ie optically thick

Contributions to line profiles:

1. Natural broadening: lifetime effect
   Lorentzian
2. Doppler broadening: thermal motion
   Gaussian, T-dependent
3. Pressure broadening: collisional effect
   Lorentzian (approx.), P-dependent
   Also: line mixing
4. T and P: Voigt profile

Beyond Voigt:
speed-dependence, hard/soft collisions, correlation etc

J. Tennyson et al, Pure Appl. Chem., 86 1931-1943 (2014)

Pressure broadening, general principles:

Depends on long-range interaction:

so dipoles important eg $\gamma(\text{water-water}) > 5\ \gamma(\text{water-air})$

Decreases with T

Decreases with J up to some limiting value

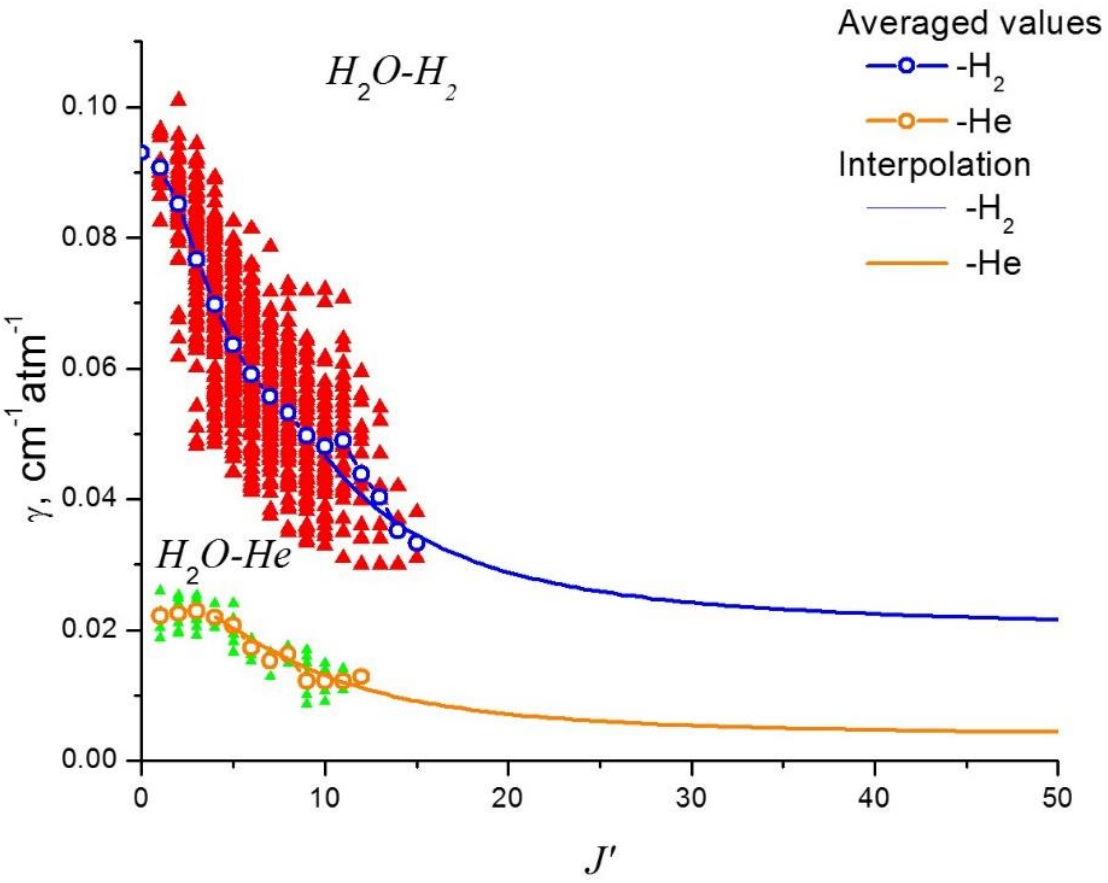
Depends on J more strongly than v

H_2 (and He) are inefficient broadeners

Pressure effects also moves line position

"pressure shift"

Dependence of water line broadening on J



Barton et al , J. Quant. Spectrosc. Rad. Transf., **189**, 60-65 (2017)

Line broadening: essential

Fortney+ 2019 The need for laboratory measurements and ab initio studies to aid understanding of exoplanetary atmospheres, Astro2020: Decadal Survey on Astronomy and Astrophysics, arXiv:1905.07064

For ExoMol:

- Need to consider ~ 10^{13} lines
- About 12 key broadeners
- High temperatures

Solution:

- Detailed semi-classical calculations with

A. Sokolov, S.N. Yurchenko, J. Tennyson, R.R. Gamache and B. Vispoel, J. Quant. Spectrosc. Rad. Transf., 330, 109225 (2024).

J. Buldyreva, S.N. Yurchenko and J. Tennyson, *RAS Tech. Instr.*, *1*, 43 (2022)
J. Buldyreva+ JQSRT, 313 108843 (2024), and ApJS 276, 23 (2025)

E.R. Guest, J. Tennyson and S.N. Yurchenko, J. Mol. Spectrosc., **401**, 111901 (2024).
and in preparation.

Data source and other issues

HITRAN: good for air- and self-broadening

designed for T=296K but approx. T dependence

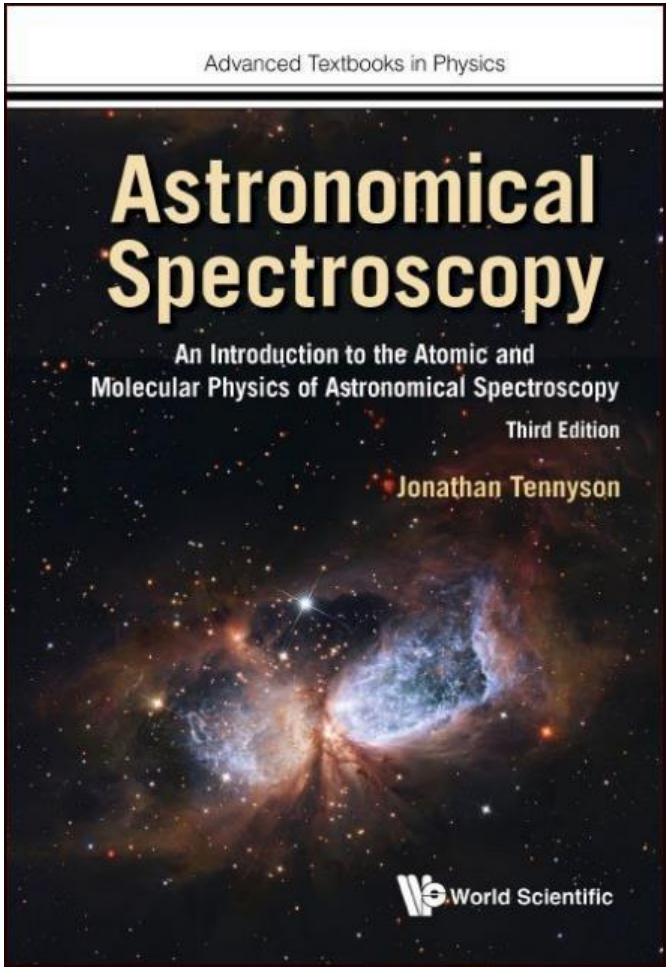
Data for H_2 and He broadening not widely available

T-dependence poorly understood at high T

ExoMol Diet: Barton et al. JQSRT 203, 490-495 (2017).

Being updated

Problems for P > 3 Atm (eg Brown dwarfs)



About the first edition
"The best book for anyone who is embarking on research in astronomical spectroscopy"
Contemporary Physics (2006)

About the third edition:
"*Makes an ideal companion … for observational aspects of spectroscopy*"
The Observatory Magazine (2019)

3rd edition published 2019

www.worldscientific.com/worldscibooks/10.1142/q0207