Forbidden transitions in the VUV spectrum of N_2

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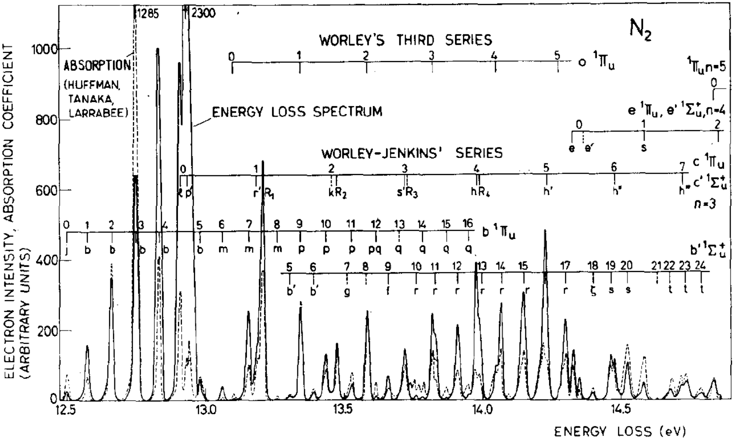
Motivation and objective

- N_2 photodissociation is interesting and astrochemically important
- This is predissociative – controlled by $S = 1$ triplet states which are not easily observable from the $S = 0$ ground state
- Objective: Quantify these states in absorption at high column density or through their perturbative effects

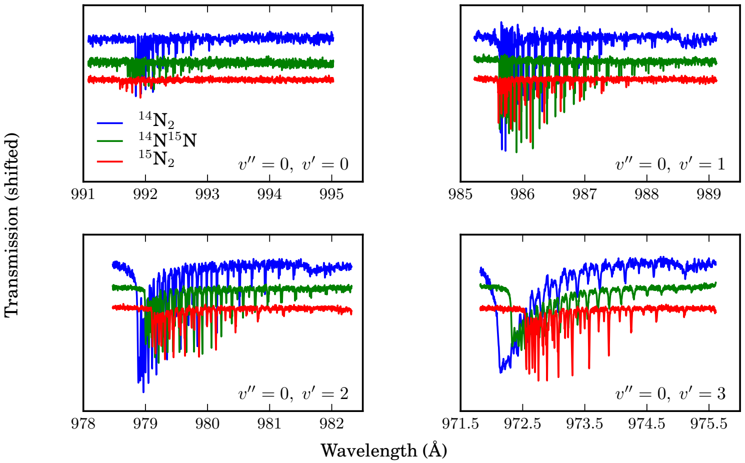
N_2 electron energy-loss spectrum



Geiger and Schröder (1969)

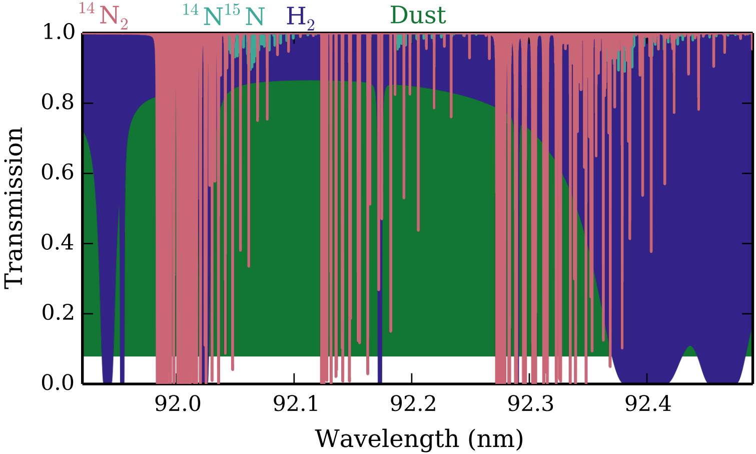
- Photoabsorption threshold: 100 nm
- Photoionisation threshold: 15.58 eV / 80 nm
- All states predissociate $\sim$ 30–100%

$N_2\ b\,^1\Pi_u(v') \leftarrow X\,^1\Sigma_g^+(v'')$ photoabsorption



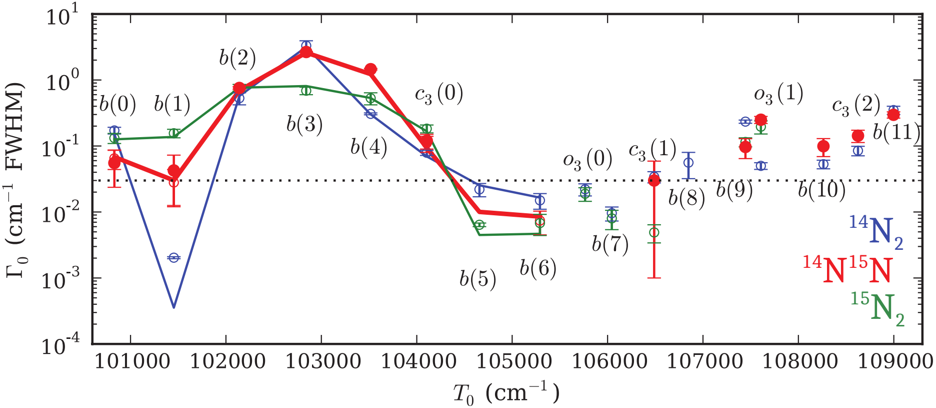
- Mostly sharp rotational structure
- In some cases predissociation broadened

N_2 astronomical self-shielding



- Sharply peaked $^{14}N_2$ lines quickly saturate
- $^{14}N^{15}N$ is unaffected by a saturated $^{14}N_2$ column
- Comparable or more important effect than shielding by H_2 and dust

N_2 experimental linewidths of $^1\Pi_u$ states

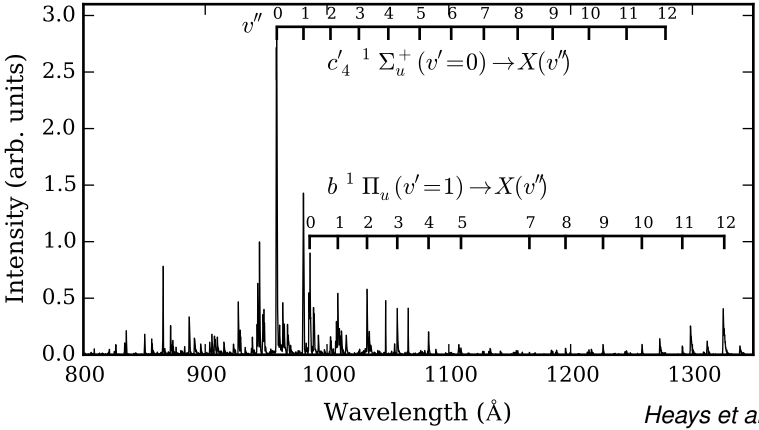


Heays et al. (2011)

Predissociation linewidth, Γ, varies with:

- Electronic state: b, c_3, o_3
- Vibrational level
- Isotopologue

Electron-excited emission spectrum

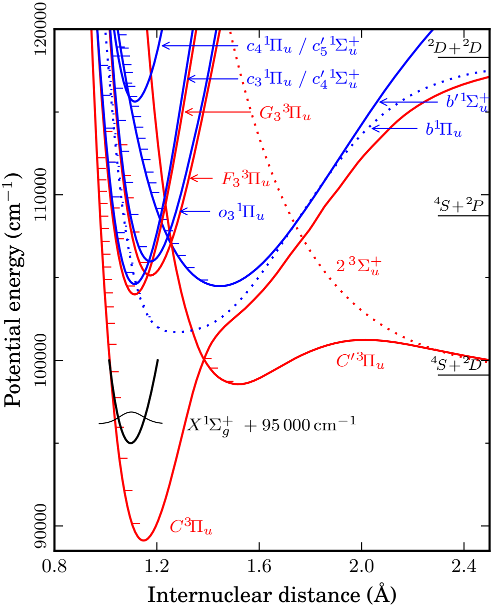


Heays et al. (2014)

Emission seen from:

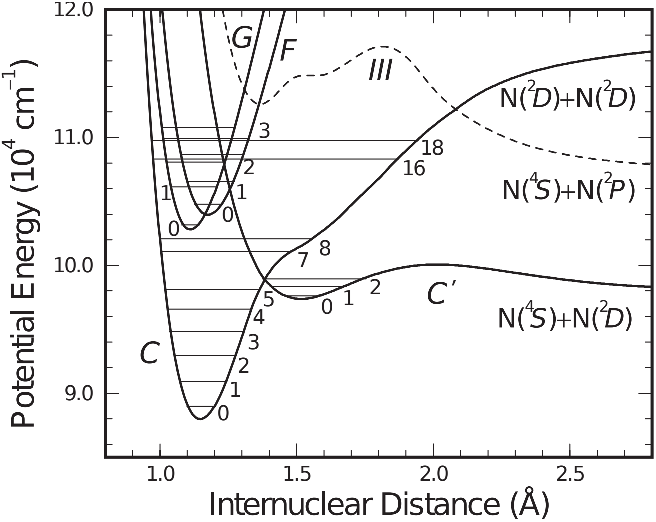
- $b\,{}^1\Pi_u(v = 1, 4, 5, 6, 7)$
- $b'\,{}^1\Sigma_u^+(v = 1, 4, 7 - 19)$
- $c_3\,{}^1\Pi_u(v = 0, 1, 2)$
- $c_4\,{}^1\Pi_u(v = 0)$
- $c'_4\,{}^1\Sigma_u^+(v = 0, 1, 2, 3, 4, 6)$
- $c'_5\,{}^1\Sigma_u^+(v = 0)$
- $o_3\,{}^1\Pi_u(v = 0, 1, 2, 3, 4)$

N_2 potential-energy curves



- ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ states absorb and emit photons
- ${}^3\Pi_u$ and ${}^3\Sigma_u^+$ states have an open dissociation channel
- Spin-orbit coupling leads to predissociation of ${}^1\Pi_u$ and ${}^1\Sigma_u^+$ states

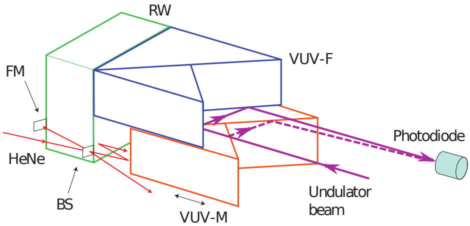
Known $^3\Pi_u$ potential-energy curves



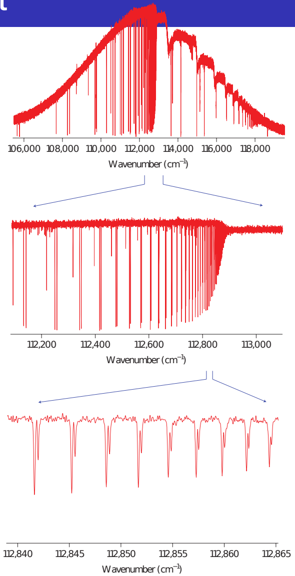
Lewis et al. (2008a)

- Levels known from optical spectroscopy, electron-energy loss, or induced perturbations

The SOLEIL/DESIRS experiment



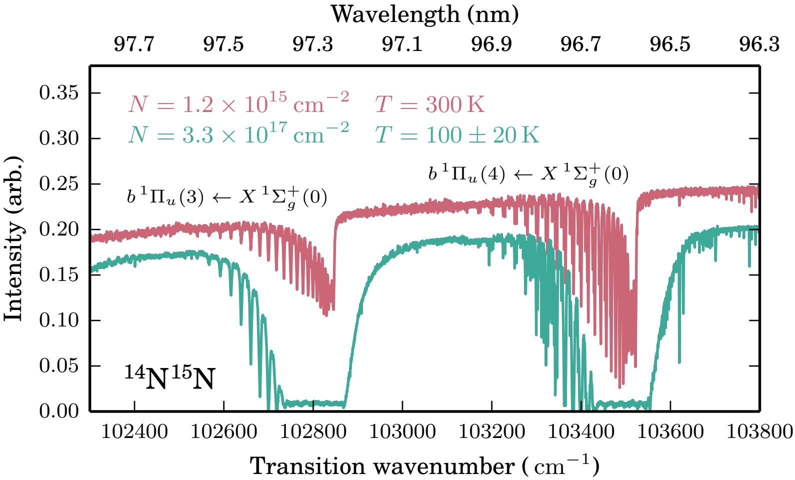
- Interferometric spectrometer
- Maximum path difference: 10 cm
- Maximum resolution: $\sim 0.07\,\mathrm{cm}^{-1}$ / 10^{-4} nm
- Beam bandwidth: 5 nm
- Sample temperature: 90 – 1000 K



Krypton absorption spectrum

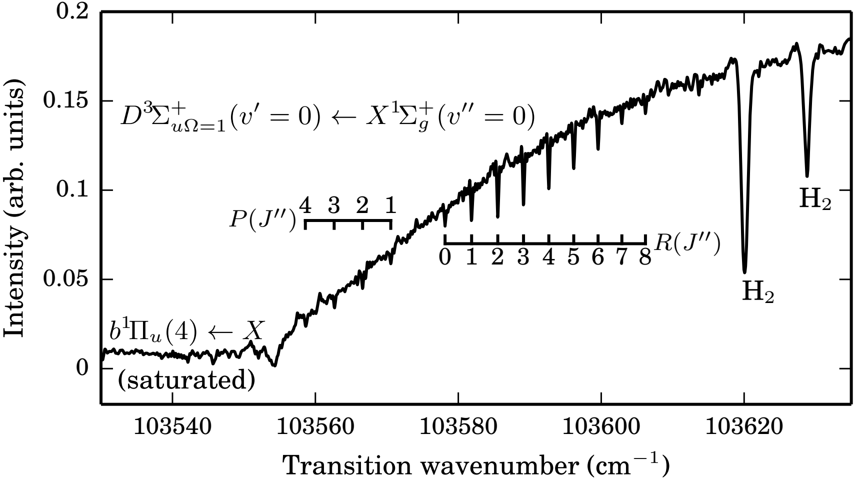
de Oliveira et al. (2011)

New photoabsorption spectra



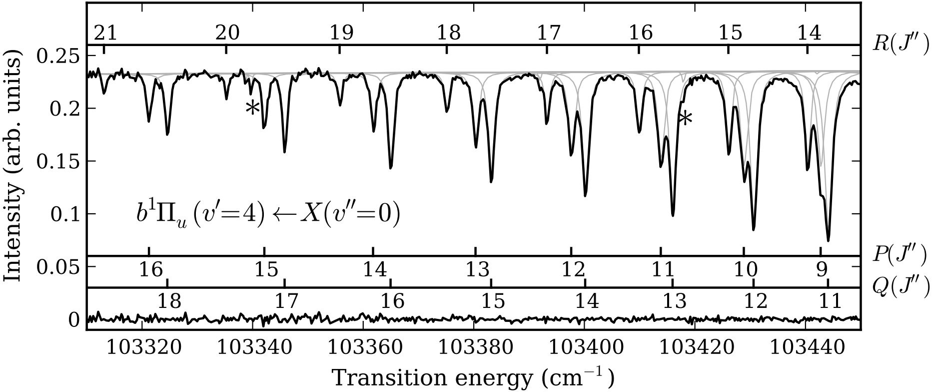
- Weak lines become visible
- Highly-excited rotational lines are suppressed

$^{14}N^{15}N\ D\,^3\Sigma_u^+(v=0)$



- Known in $^{14}N_2$ and $^{15}N_2$ (Lewis et al. 2008b)

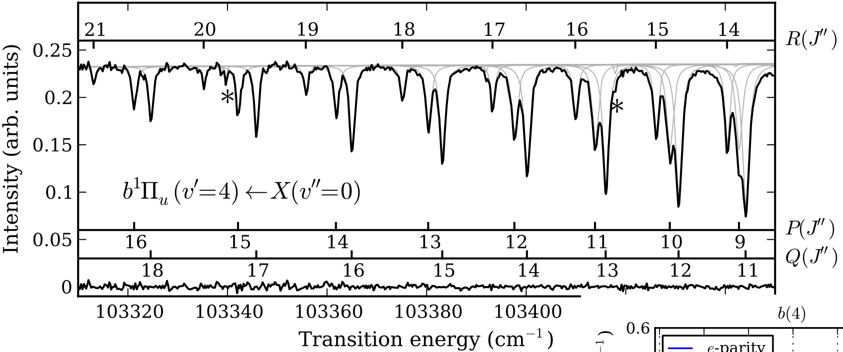
$^{14}N^{15}N\ b\,^1\Pi_u(v = 4)$ and perturber



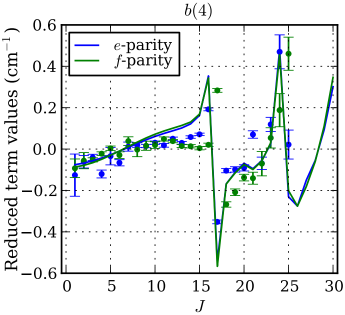
Heays et al. (2011)

- $N = 1.2 \times 10^{15}\,\mathrm{cm}^{-2}$ and $T = 300\,\mathrm{K}$
- Two extra lines

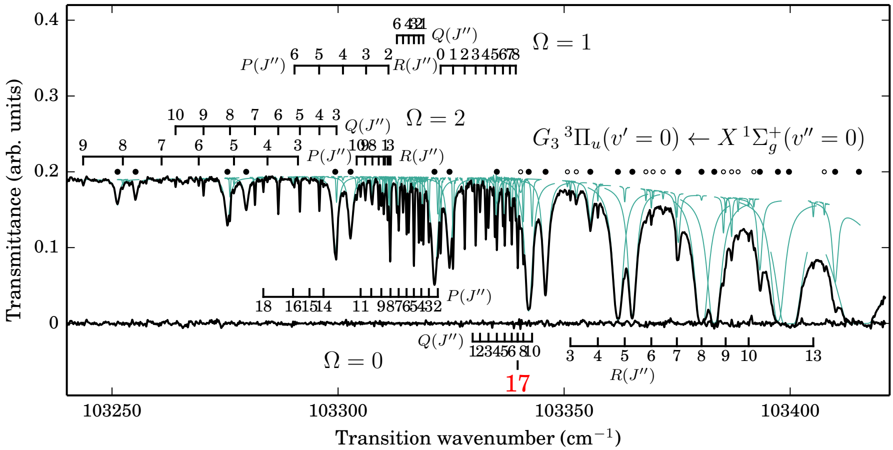
$^{14}N^{15}N$ $b\,^1\Pi_u(v=4)$ and perturber



- Extra lines are $Q(17)$ and $R(15)$ transitions
- $G\,^3\Pi_u(v=0)$ predicted by Lewis et al. (2008a)
- *Error bars*: Exp. term values.
- *Lines*: CSE model.

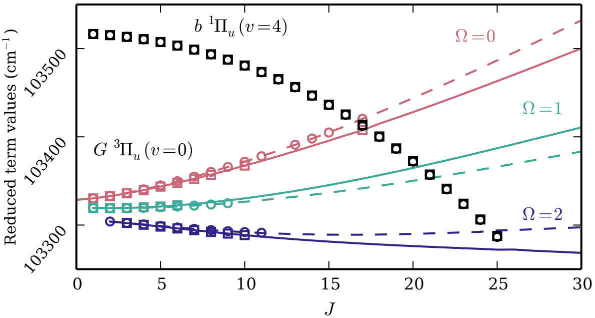


$^{14}N^{15}N$ $b\,^1\Pi_u$(v=4) and $G\,^3\Pi_u(v = 0)$



- $N = 3.3 \times 10^{17}\,\text{cm}^{-2}$ and $T = 300 \pm 20\,\text{K}$
- Previously observed extra line
- Now lines from 9 rotational branches: $\Delta J = -1, 0, 1$ and "Ω"$= 0, 1, 2$

$^{14}N^{15}N$ $b\,^1\Pi_u$(v=4) and $G\,^3\Pi_u(v=0)$

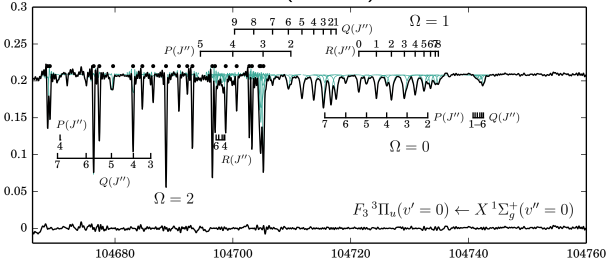


Parameters (cm^{-1})	
T_0	103316.70(2)
B	1.8057(4)
D	0.000020(2)
A	-8.12(3)
A_D	0.047(4)
λ	–
λ_D	–
γ	-0.133(8)
o	–
p	0.020(4)
q	-0.0360(3)

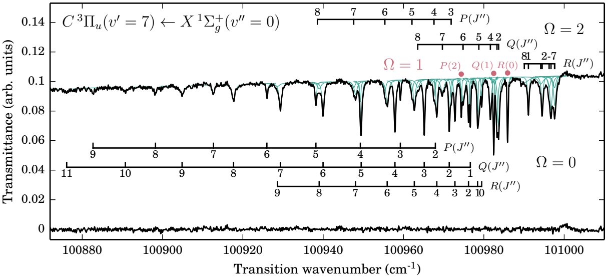
- Information from the observed $G(0)$ levels and the perturbed $b(4)$ levels

Other bands in $^{14}N^{15}N$

$F\,^3\Pi_u(v=0)$



$C\,^3\Pi_u(v=7)$



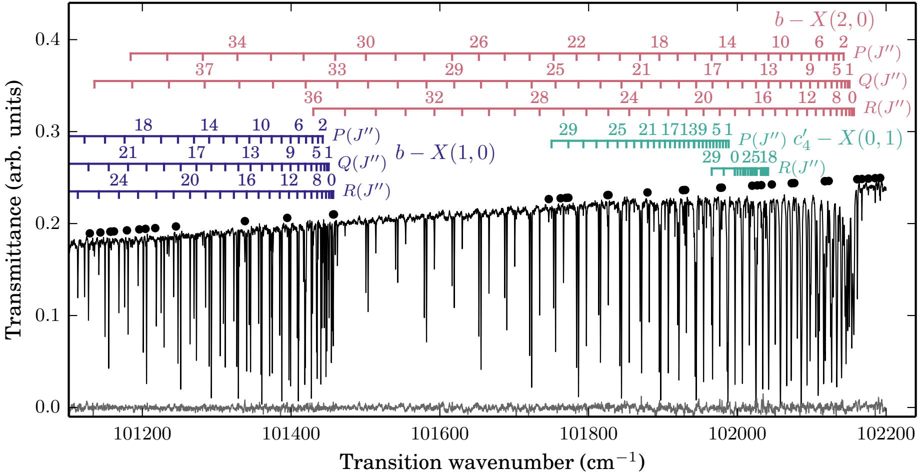
Other preliminary identifications in $^{14}N^{15}N$:

- $D\,^3\Sigma_u^+(v=0)$
- $D\,^3\Sigma_u^+(v=1)$
- $G\,^3\Pi_u(v=1)$
- $C\,^3\Pi_u(v=8)$
- $C\,^3\Pi_u(v=14)$ $\sim F\,^3\Pi_u(v=1)$
- $C\,^3\Pi_u(v=15)$
- $C\,^3\Pi_u(v=16)$

Other identifications in $^{14}N_2$ with $T = 1000\,K$ (Niu et al. 2015):

- $C\,^3\Pi_u(v=16)$ $\sim G\,^3\Pi_u(v=2)$

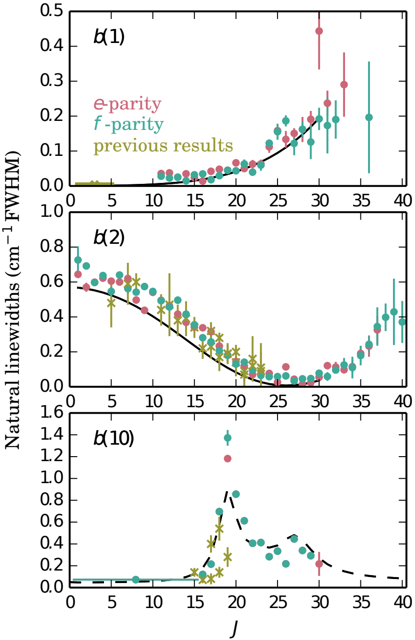
High temperature photoabsorption



(Niu et al. 2015)

- 900 K ground-state excitation
- Observed lines as high as $J = 40$, $v = 1$

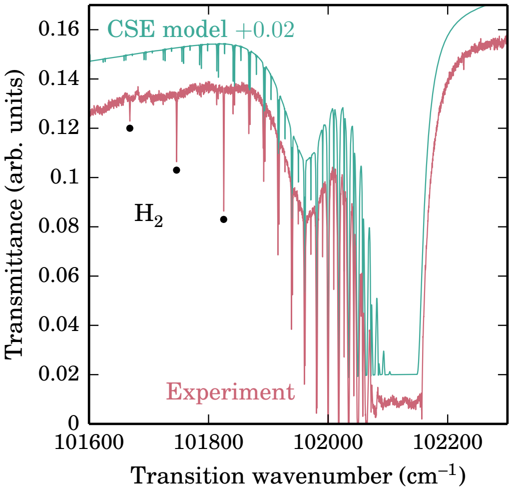
High temperature photoabsorption – Linewidths



- Rotational effects due to particular spin-orbit interacting levels
- $b\,^1\Pi_u(2) \sim C\,^3\Pi_u(8)$
- $b\,^1\Pi_u(10) \sim G\,^3\Pi_u(2) \sim C\,^3\Pi_u(16)$

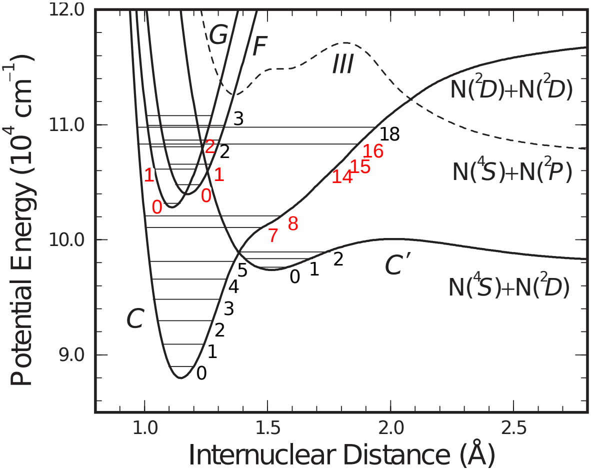
  Fitted perturber parameters intermediate to what is predicted for $G(2)$ and $C(16)$:
  - $B \simeq 1.5\,\mathrm{cm}^{-1}$
  - $A \simeq 30\,\mathrm{cm}^{-1}$
  - Predissoc. width $\simeq 20 \rightarrow 80\,\mathrm{cm}^{-1}$

$^{14}N^{15}N\ C\,^3\Pi_u(v=8)$



- Main saturated band: $b\,^1\Pi_u(v=2) \leftarrow X(0)$
- Broad feature: $C\,^3\Pi_u(v=8) \leftarrow X(0)$
- Confirms an existing CSE model (Lewis et al. 2008a; Heays et al. 2011)

Summary



- Newly observed levels in $^{14}N^{15}N$ and $^{14}N_2$
- Also levels of $D\,^3\Sigma_u^+$ – not shown

- This information will be used to refine the potential-energy curves of $S = 1$ states, and spin-orbit interaction with $S = 0$ states
- Leading to an improved CSE model of N_2 photodissociation for astrophysical / atmospheric purposes