Temperature dependence of N$_2$-, O$_2$-, and air-broadened half-widths of water vapor transitions: insight from theory and comparison with measurement

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Theory

Semi-classical formalism of Robert and Bonamy

- Complex formalism - halfwidths and line shifts
- Free from cut-off procedure and adjustable parameters
- Trajectories from solution of Hamilton’s eqs. or R-B parabolic approximation
- General spherical tensor expansion for the intermolecular potential
Intermolecular Potential

H$_2$O-N$_2$ and H$_2$O-O$_2$ systems

- Leading electrostatic components: d-q, q-q
- Atom-atom potential: expanded to 8$^{th}$ order
- The vibrational dependence of the isotropic potential uses the induction and London dispersion potentials
Spherical Tensor Expansion of the Potential

\[ V = \sum_{l_1, l_2} \sum_{n_1, w} \sum_{m_1, m_2} \frac{U(l_1, l_2, n_1 w)}{R^{q + l_1 + l_2 + 2w}} \]

\[ \otimes C(l_1 l_2, m_1 m_2 m) D_{m_1 n_1}^{l_1} (\Omega_1) D_{m_2 0}^{l_2} (\Omega_2) Y_{l m} (\omega) \]

- where \( C(l_1 l_2, m_1 m_2 m) \) is a Clebsch-Gordan coefficient, \( \Omega_1=(\alpha_1, \beta_1, \gamma_1) \) and \( \Omega_2=(\alpha_2, \beta_2, \gamma_2) \) are the Euler angles describing the molecular fixed axis relative to the space fixed axis. \( \omega=(\theta, \phi) \) describes the relative orientation of the centers of mass.

- Electrostatic interactions: \( q=1 \) and \( w=0 \)

- Atom-atom interactions: \( q=12 \) or \( 6 \) and \( w \) defined by the order of the expansion where \( \text{Order}=l_1 + l_2 + 2w \)
$S_1$ term


$$\alpha = 9.86 + 0.29 \left( v_1 + \frac{1}{2} \right) + 0.03 \left( v_2 + \frac{1}{2} \right) + 0.28 \left( v_3 + \frac{1}{2} \right)$$
$S_1$ term


$$\alpha = 9.86 + 0.29 \left( \nu_1 + \frac{1}{2} \right) + 0.03 \left( \nu_2 + \frac{1}{2} \right) + 0.28 \left( \nu_3 + \frac{1}{2} \right)$$

Note, stretch modes have roughly the same contribution.
Halfwidth and Line Shift in RB theory

\[(\gamma - i\delta)_{f \leftarrow i} =\]

\[
\frac{n_2}{2\pi c} \left\langle v \times \left[ 1 - e^{-R_{S_2}(f,i,J_2,v,b)} e^{-i[S_1(f,i,J_2,v,b) + S_2(f,i,J_2,v,b)]} \right] \right\rangle_{v,b,J_2}
\]

Real terms                  Imaginary terms
Connecting states

Absorbing Molecule ↔ V ↔ Perturbing Molecule

Optical transitions

Collisionally induced transitions
$N_2$ and $O_2$ as perturbers

$B(N_2) = 2.0006 \, \text{cm}^{-1}$  $B(O_2) = 1.4377 \, \text{cm}^{-1}$

Energy gaps

$\sim 24 \text{ to } 960 \, \text{cm}^{-1}$  $\sim 17 \text{ to } 690 \, \text{cm}^{-1}$

Most probable states

$\Delta E = \sim 150 \, \text{cm}^{-1}$  $\Delta E = \sim 110 \, \text{cm}^{-1}$
Energies of collisionally connected states
Low J transitions

\[ \Delta E \text{ small} \]

\[ \Delta E_{i \rightarrow 1'} \]

\[ \Delta E_{j2 \rightarrow j2'} \]

On resonance collisions, collisional contributions dominate the half-width
High J transitions

$\Delta E_{i \to 1'}$

$\Delta E_{J_2 \to J_2'}$

$\Delta E$ large

Off-resonance collisions, collisional contributions small, half-width dominated by vibrational terms.
ν₂ H₂O-N₂ P and R Doublet Transitions

(J±1₁,₁₁→₀,₀ and J±₁₀,₁₁→₁,₁)

● and ○ are calculated values associated with P and R lines such that (Kₐ’-Kₐ”)=(J’-J”) and (Kₐ’-Kₐ”)=-(J’-J”), respectively.

The horizontal dashed line indicates the pure dephasing contribution.

\( \nu_2 \) \( \text{H}_2\text{O}-\text{N}_2 \) P and R Doublet Transitions

\[(J_{\pm 1_1, J_{\pm 1}} \leftarrow J_{0, J} \text{ and } J_{\pm 1_0, J_{\pm 1}} \leftarrow J_{1, J})\]

- and \( \bigcirc \) are calculated values associated with P and R lines such that \((K_a' - K_a'') = (J' - J'')\) and \((K_a' - K_a'') = -(J' - J''),\) respectively.

The horizontal dashed line indicates the pure dephasing contribution

ν₂ H₂O-N₂ P and R Doublet Transitions

(J±1,₁₁,J±0,J and J±1,₀,J±0,J₁,J)

● and ○ are calculated values associated with P and R lines such that (Kα’-Kα”)=(J’-J”) and (Kα’-Kα”)=-(J’-J”), respectively.

The horizontal dashed line indicates the pure dephasing contribution

ν₂ H₂O-N₂ Doublet Q-branch Transitions

The J₁, J⁻¹ ← J₀, J and J₀, J ← J₁, J⁻¹) Q line doublets of the ν₂ band.

I are experimental values. ● and ○ are calculated values of the Ka’-Ka”=1 and Ka’-Ka”= -1 transitions, respectively.

The horizontal dashed line indicates the pure dephasing contribution

Calculated H$_2$O-N$_2$ $\gamma$ and $\delta$ for the $J-1_{0,J-1} \leftarrow J_{1,J}$ transitions
Calculated $\text{H}_2\text{O-}N_2 \ \gamma$ and $\delta$ for the $J-1_0, J-1 \leftarrow J_1, J$ transitions

A factor of 8
Transitions with $Kc=J$ in bands involving three quanta of stretching vibration

[Graph showing data points with error bars, labeled as three quanta of stretch and $\nu_2$ band, with measurement markers.]
Transitions with Kc=J in bands involving four quanta of stretching vibration
Calculations agree well with measurement.

What can theory tell us about the temperature dependence of the half-width?
Temperature Dependence “Rule-of-thumb”

For “on resonance” collisions the temperature dependence of the half-width is given by

\[ \gamma \propto T^{\frac{(n+4)}{2n}} \]

Interaction  n  Interaction  n

d-d  4  d-q, q-d  6
q-q  8  dispersion  10
Temperature Dependence of $\gamma$

- **Power law form**

$$\gamma(T) = \gamma(T_0) \left[ \frac{T_0}{T} \right]^N$$

- **In practice plot (fit)**

$$\ln \left\{ \frac{\gamma(T)}{\gamma(T_0)} \right\} = N \ln \left\{ \frac{T_0}{T} \right\}$$
H$_2$O-N$_2$ system

“Dipole-Quadrupole” system – “rule-of-thumb” gives temperature dependence of $5/6$
H$_2$O-N$_2$ system

“Dipole-Quadrupole” system – “rule-of-thumb” gives temperature dependence of 5/6
T-dependence for individual lines

13 temperatures studied from 150-400 K
150., 200., 212., 225., 238., 275.,
Low J’’

half-widths are dominated by rotational contributions ($S_2$, on resonance).
Results of fit: Slope = 0.66969  Correlation Coefficient = 0.99996

H₂O−N₂ (010)−(00)  4 2 3 <--  4 3 2
High J”

half-widths are dominated by vibrational contributions ($S_1$, off resonance).
Results of fit: Slope = -0.22065  Correlation Coefficient = -0.99246
Power law is not theoretically correct. Fit can be reasonable over small T range.

Results of fit: Slope = -0.22065  Correlation Coefficient = -0.99246
Intermediate J”

a mixture of rotational and vibrational contributions. \((S_1 \text{ and } S_2)\)
\[ \ln \left( \lambda/\lambda_0 \right) \] vs. \[ \ln \left( T_0/T \right) \]

Results of fit: Slope = -0.01031, Correlation Coefficient = -0.24803
Results of fit: Slope = -0.01031  Correlation Coefficient = -0.24803
Results of fit: Slope = -0.01540  Correlation Coefficient = -0.58501
Results of fit: Slope = -0.01540  Correlation Coefficient = -0.58501
Results of fit: Slope = -0.02650  Correlation Coefficient = -0.40953
Temperature Range of the fit

The derived temperature exponents are dependent on the range of the fit.
H₂O–air \( \nu_2 \) 5 0 5 \( \rightarrow \) 4 1 4

296-225 K

Results of fit: Slope = 0.59379  Correlation Coefficient = 0.99997
\( H_2O - air \)  \( \nu_2 \)  5 0 5  --  4 1 4

700-200 K

~11%

Results of fit: Slope = 0.65870  Correlation Coefficient = 0.99894
$\text{H}_2\text{O–N}_2$

$8_{26} \leftrightarrow 8_{17}$
\[14_{\text{H}_2\text{O}} \leftrightarrow 15_{\text{N}_2}\]

\(42\%\)
Comparison with measurement

Calculations are Ref 710, fit to 4 temperatures: 200, 225, 275, 296 K

Ref 70 Remedios, J. J., PhD University of Oxford, (1990)


Ref 155 M. Birk and G. Wagner, DLR, Private Communication, 2006. (5% error bar added)
H₂O−air

(010) ←→ (000) 3 3 0 ←→ 4 4 1
$200-700 \text{ K}$

$218-742 \text{ K}$

$\nu_2$
200-700 K
218-742 K

H$_2$O-air (010)-(000)  5 0 5 <--  6 1 6

CRB Results of fit: Slope= 0.55367  Correlation Coefficient=0.99705
DLR Results of fit: Slope= 0.61982  Correlation Coefficient=0.99786
Intermediate J line

$H_2O$–air (010)–(000)  9 0 9 <--  10 1 10

200-700 K
218-742 K

CRB Results of fit: Slope= -0.02931  Correlation Coefficient= -0.61465
DLR Results of fit: Slope= 0.01774  Correlation Coefficient= 0.09387
Temperature exponent and error in the measurement
Add the error

0.1% change

H₂O-air → ν₂ → 202 ←→ 313

CRB Results of fit: Slope= 0.76876  Correlation Coefficient=1.00000

DLR Results of fit: Slope= 0.75729  Correlation Coefficient=0.99949
subtract the error

0.1% change

H₂O-air

\[ \nu_2 \]

2 0 2 <-- 3 1 3
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Add the error
-83% change

CRB Results of fit: Slope= -0.02931  Correlation Coefficient= -0.61465
DLR Results of fit: Slope=  0.03245  Correlation Coefficient= 0.20687
subtract the error

88% change

\text{CRB Results of fit: Slope=-0.02931 Correlation Coefficient=-0.61465}

\text{DLR Results of fit: Slope=0.00212 Correlation Coefficient=0.00938}
HITRAN Algorithm
for temperature exponents of $\text{H}_2\text{O}$
Temperature exponents on the HITRAN database

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$H_2O-N_2$

$\nu_2$ band transitions

$0.83 > N > -1.3$
$\nu_2$ band transitions

$0.83 > N > -1.3$
Conclusions

- When $\gamma$ and $N$ are from rotational contributions. Vibrational dependence of $\gamma$ is small, $N$ is positive and follows the power law.
Conclusions

- When $\gamma$ an $N$ are from rotational contributions. Vibrational dependence of $\gamma$ is small, $N$ is positive and follows the power law.

- When $\gamma$ an $N$ are from vibrational contributions. Vibrational dependence of $\gamma$ is large, $N$ can be negative, the power law is approximate.
Conclusions

- When $\gamma$ an $N$ are from a mix of rotational and vibrational contributions. $N$ is not described by the power law expression.
Conclusions

- When $\gamma$ an $N$ are from a mix of rotational and vibrational contributions. $N$ is not described by the power law expression.
- $N$ is dependent on the temperature range of the fit.
Conclusions

- When the temperature range is large, the power law becomes less valid.
Acknowledgments

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