



## PRESSURE BROADENING PARAMETERS FOR NITRIC ACID IN THE $\nu_5$ BAND



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**Abstract:** A number of satellite instruments are measuring nitric acid,  $\text{HNO}_3$ , in the Earth's atmosphere. In order to do retrievals of temperature and concentration profiles, the spectral parameters for many thousands of  $\text{HNO}_3$  transitions must be known. Currently the pressure-broadened half-width is estimated on the HITRAN database. To help ameliorate this situation, complex Robert-Bonamy calculations were made to determine  $\text{N}_2$ -broadened half-widths and line shifts for some 5000 transitions of  $\text{HNO}_3$  in the  $\nu_5$  band. The intermolecular potential is a sum of electrostatic terms (dipole-quadrupole and quadrupole-quadrupole), isotropic induction and London dispersion terms, and the atom-atom potential expanded to eighth order. The trajectory parameters were adjusted to yield better agreement with measurement. Velocity integrated calculations were made at seven temperatures in order to determine the temperature dependence of the half-widths. The data are compared with measurements of Goyette *et al.* (*J. Quant. Spectrosc. Radiat. Transfer* 60, 77, 1998). The average percent difference between the measured and calculated half-widths is -0.31. The temperature, vibrational, and rotational state dependence of the half-width are investigated.

### Complex Robert-Bonamy Theory

The model chosen is the semiclassical complex formalism of Robert and Bonamy (CRB) for several reasons.

- 1) The formalism is complex valued, yielding halfwidths and line shifts from a single calculation.
- 2) The cumulant expansion incorporated in the RB formalism allows for the inclusion of higher order terms in the S matrix, eliminating an awkward cutoff procedure that characterized earlier theories.
- 3) The intermolecular dynamics are treated more realistically than in earlier theories, i.e. using curved rather than straight line trajectories.
- 4) Connected to item (3) is the incorporation in the CRB theory of a short range (Lennard-Jones 6-12) atom-atom component to the intermolecular potential. This component has been shown to be essential for a proper description of pressure broadening.

### Half-width and Line Shift in CRB theory

In computational form the half-width and line shift are usually expressed in terms of the Liouville scattering matrix

$$(\gamma - i\delta) = \frac{n_2}{2\pi c} \left\langle v \left[ 1 - e^{-R S_2(f, i, J_2, v, b)} e^{-i S_2(f, i, J_2, v, b)} \right] \right\rangle_{v, b, J}$$

where  $n_2$  is the number density of perturbers and  $\langle \rangle_{v, b, J}$  represents an average over all trajectories (impact parameter  $b$  and initial relative velocity  $v$ ) and initial rotational state  $J_2$  of the collision partner.

### Spherical Tensor Expansion of the Potential

$$V = \sum_{\ell_1 \ell_2} \sum_{m_1 m_2} \sum_{w, q} \frac{U(\ell_1 \ell_2 \ell, m_1 w)}{R^{q + \ell_1 + \ell_2 + 2w}}$$

$$\otimes C(\ell_1 \ell_2 \ell, m_1 m_2 m) D_{m_1}^{(\ell_1)}(\Omega_1) D_{m_2}^{(\ell_2)}(\Omega_2) Y_m(\omega)$$

where  $C(\ell_1 \ell_2 \ell; m_1 m_2 m)$  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  $Order = \ell_1 + \ell_2 + 2w$

### Wavefunctions

The wavefunctions used to evaluate the reduced matrix elements are obtained by diagonalizing the Watson Hamiltonian in a symmetric top basis. The wavefunctions for the ground vibrational state are determined using the Watson-Hamiltonian constants of Goldman *et al.* (*J. Mol. Spectrosc.* **131** (1988) 195-200) and those for the  $\nu_5$  vibrational state use the Watson constants of Maki and Wells (*J. Mol. Spectrosc.* **152** (1992) 69-79). The molecular constants for  $\text{N}_2$  are from Huber and Herzberg (Molecular Spectra and Molecular Structure: Constants of Diatomic Molecules. Van Nostrand, New York 1979)

### Molecular Parameters

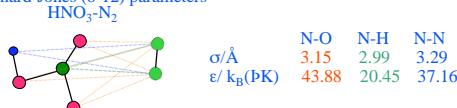
The dipole moment of  $\text{HNO}_3$  takes the lower limit from the work of Cox and Riveros (*J. Chem. Phys.* **42** (1965) 3106-3112),  $\mu=2.15$  D.

The quadrupole moments of  $\text{HNO}_3$  are from Albinus *et al.* (*J. Mol. Spectrosc.* **133** (1989) 128-147) taken with  $\text{HNO}_3$  in the IR representation:

$$Q_{xx} = -3.34 \pm 0.23 \cdot 10^{-26} \text{ esu}, \quad Q_{yy} = +1.06 \pm 0.33 \cdot 10^{-26} \text{ esu}, \quad Q_{zz} = +2.28 \pm 0.23 \cdot 10^{-26} \text{ esu}.$$

The quadrupole moment of nitrogen from Mulder *et al.* (*Mol. Phys.* **39** (1980) 407-425):  $Q_{zz} = -1.4 \pm 0.1 \cdot 10^{-26}$  esu.

Lennard-Jones (6-12) parameters



### Preliminary Calculations

In the parabolic trajectory approximation the isotropic part of the interaction potential is taken into account in determining the distance, effective velocity, and force at closest approach. To simplify the trajectory calculations the isotropic part of the atom-atom expansion is fit to an isotropic Lennard-Jones 6-12 potential. In order to improve agreement with measurement the isotropic Lennard-Jones parameters were adjusted to yield better agreement with measurement. Velocity integrated calculations were made at seven temperatures in order to determine the temperature dependence of the half-widths. The data are compared with measurements of Goyette *et al.* (*J. Quant. Spectrosc. Radiat. Transfer* 60, 77, 1998). The average percent difference between the measured and calculated half-widths is -0.31. The temperature, vibrational, and rotational state dependence of the half-width are investigated.

### Results for adjusting the trajectory parameters.

Initial parameters:  $\epsilon=369.99$   $\sigma=3.178$   
Final parameters:  $\epsilon=165.0$   $\sigma=3.117$

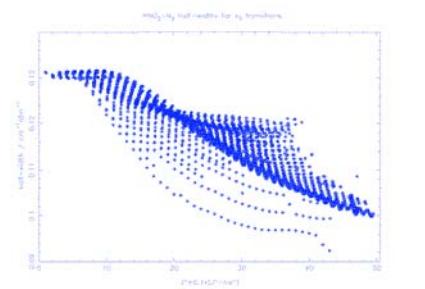
| Transition                                  | Exp     | cal <sub>initial</sub> | cal <sub>final</sub> |
|---|---------|------------------------|----------------------|
| 16 <sub>0.16</sub> ← 15 <sub>0.15</sub>     | 0.11966 | 0.13299                | 0.12641              |
| 14 <sub>2.12</sub> ← 13 <sub>2.11</sub>     | 0.12676 | 0.13493                | 0.12832              |
| 13 <sub>3.10</sub> ← 12 <sub>3.0</sub> *    | 0.13385 | 0.13346                | 0.12697              |
| 12 <sub>4.0</sub> ← 11 <sub>4.7</sub>       | 0.12650 | 0.13564                | 0.12899              |
| 11 <sub>5.6</sub> ← 10 <sub>5.5</sub>       | 0.13335 | 0.13556                | 0.12885              |
| 24 <sub>8.16</sub> ← 24 <sub>8.17</sub> *   | 0.11053 | 0.12590                | 0.11702              |
| 25 <sub>9.16</sub> ← 25 <sub>9.17</sub> *   | 0.11915 | 0.12394                | 0.11479              |
| 26 <sub>10.16</sub> ← 26 <sub>10.17</sub> * | 0.11433 | 0.12368                | 0.11427              |

300 K

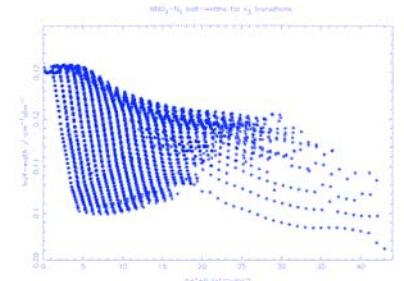
### Calculations

A list of 15 609  $\nu_5$  transitions in the 841.5-930.9  $\text{cm}^{-1}$  region was provided by the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) in Paris. From this list we extracted transitions with line intensities greater than  $5 \times 10^{-22} \text{ cm}^{-1} / (\text{molecule} \cdot \text{cm}^2)$  and  $J \leq 45$ . This yields a list of 5011 transitions.

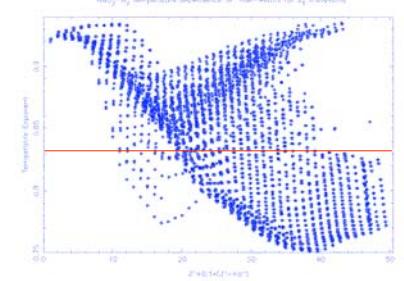
Due to limitations in the wavefunction codes calculations could only be made for 4979 of these transitions.



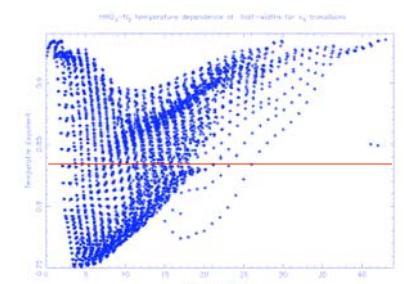
$\text{HNO}_3\text{-N}_2$  half-widths in units of  $\text{cm}^{-1} \text{ atm}^{-1}$  versus  $J''+0.1(J''\text{-}K_a'')$



$\text{HNO}_3\text{-N}_2$  half-widths in units of  $\text{cm}^{-1} \text{ atm}^{-1}$  versus  $K_a''+0.1(J''\text{-}K_a'')$



Temperature exponents of  $\text{HNO}_3\text{-N}_2$  half-widths versus  $J''+0.1(J''\text{-}K_a'')$



Temperature exponents of  $\text{HNO}_3\text{-N}_2$  half-widths versus  $K_a''+0.1(J''\text{-}K_a'')$

### Conclusion

The eight-order CRB calculations were made for 4979  $\nu_5$  band transitions of  $\text{HNO}_3$  broadened by  $\text{N}_2$  at seven temperatures (200., 225., 275., 296., 300., 375., 500. K) by explicitly performing the averaging over the Maxwell-Boltzmann distribution of velocities. These data are now being used at LISA to simulate retrievals of nitric acid concentrations in the terrestrial atmosphere

### Future Plans

Do  $\text{O}_2$ -broadening of  $\text{HNO}_3$  so that with  $\text{N}_2$ -broadening air-broadening can be determined. Extend the calculations to transitions with weaker intensities

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