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CRB METHOD

ABSTRACT:

Calculations of the half-width and line shift of ozone perturbed by N₂ based upon complex implementation of the formalism of Robert and Bonamy (CRB) have been made. The theoretical calculations were then plotted against observed values (J. Mol. Spectroscopy 1994; 164:239-59 and Applied Optics 1991; 30:2431-36). The O₃-N₂ intermolecular potential, which includes the sum of electrostatic, atom-atom, induction and dispersion, was adjusted so as to bring the calculated values into closer agreement with the experimental data. Calculations of the line shift of ro-vibrational transitions of ozone are strongly dependent on the vibrational dependence of the polarizability of ozone. Initially the pure rotation band was analyzed in order to assess the atom-atom term. Subsequently the coefficients describing the vibrational dependence of the polarizability was empirically evaluated. This evaluation involved statistical analysis of the absolute average deviation of the calculated values of both the half-width and line shift from the observed data. Additionally, graphical analysis improved the variability of the theoretical values to better resemble the range of measured values.

The calculations are based on the Robert-Bonamy (CRB) semi-classical formalism. The method is complex valued so that the half-width and line shift are obtained from a single calculation. The dynamics are developed to second order in time giving curved trajectories based on the isotropic part of the intermolecular potential. This has important consequences in the description of close intermolecular collisions (small impact parameters).

Within the CRB formalism the half width, γ , and line shift, δ , of a ro-vibrational transition $F \leftarrow i$ are given by minus the imaginary part and the real part, respectively, of the diagonal elements of the complex relaxation matrix. In computational form the a second order successive expansion of the S matrix is made. This approach yields a first order term that is purely isotropic and imaginary term, S_1 , and a complex second order term, S_2 . Both S_1 and S_2 depend on the intermolecular potential. The number of terms in the intermolecular potential depends on the collision system. The potential for the O₃-N₂ system is described below.

INTERMOLECULAR POTENTIAL

- Leading electrostatic components (well-known)

- Atom-atom potential (known to 5-15%)

The Atom-Atom potential is the sum of isotropic 12-6 potentials (expressed in terms of the Lennard-Jones parameters: ϵ, σ)

$$V^{a-a} = \sum_{ij} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

- The vibrational dependence of the isotropic potential which uses the induction and London dispersion potentials (unknown)

$$S_1 = - \frac{\alpha_2}{R_c^2} \frac{3\pi}{8} \left[\frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} (\alpha_{1,f} - \alpha_{1,i}) - (I_{1,f}^2 - I_{1,i}^2) \right]$$

where

$$\alpha = \alpha_0 + C_1 \left(v_1 + \frac{1}{2} \right) + C_2 \left(v_2 + \frac{1}{2} \right) + C_3 \left(v_3 + \frac{1}{2} \right)$$

and C_1 , C_2 , and C_3 are to be calculated.

The theoretical calculations which have been performed for this project utilize the Complex Robert-Bonamy Formalism (CRB) yielding the half-width and line shift.

ATOM-ATOM (PURE ROTATION)

Initially the Atom-Atom Lennard-Jones parameters (ϵ and σ) were adjusted on the pure rotation bands (i.e. 000-000). Thirty-four iterations from the initial values were needed to yield the best-fit to measurement (Figure 2 and Table 1).

REFERENCES

Gamache, R., Lynch, R., Neshyba, S. "New Developments in the Theory of Pressure-Broadening and Pressure Shifting of Spectral Lines of H₂O: The Complex Robert-Bonamy Formalism" *J. of Quant. Spectrosc. Radiat. Transfer*, Vol. 59, Nos. 3-5, 319-335, 1998.

Hartmann, D. *Global Physical Climatology*, Academic Press, Inc. San Diego, CA, 1994.

ACKNOWLEDGEMENTS

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Iteration POTrb34			
ϵ/k (K)	σ (Å)	Abs. Dev.	Std. Dev.
42.8 (±2.5%)	3.227 (±2.5%)	2.79	3.62

Measurement Sources	
Line No.	Reference
1-4	Connor BJ, Radford HE. Pressure broadening of the 110.8 GHz ozone line by atmospheric gases. <i>J. Mol. Spectrosc.</i> 1986;117:15-29.
5-6	Oh JJ, Cohen EA. Pressure Broadening of ozone lines near 184 and 206 GHz by nitrogen and oxygen. <i>J. Quant. Spectrosc. Radiat. Transfer</i> , 1992;48:405-08.
7	Prem, et al. <i>J. Mol. Spec.</i> no 204, p204-215; (2000)
8-15	Bologna, Lille. <i>J. Mol. Spec.</i> no 213, p171-187, (2005)

Note: the accuracy for 14 and 15 are in question.

Table 1. Atom-Atom values, statistics and sources.

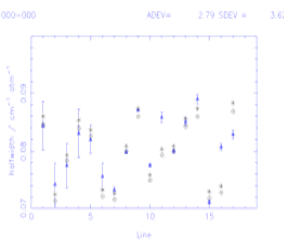


Figure 2. Comparison of O₃-N₂ calculation vs. measurement after Atom-Atom adjustment. Note: only half-width calculated.

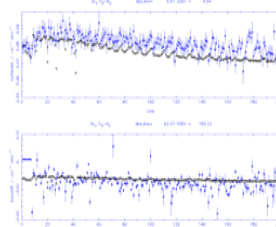


Figure 3. O₃-N₂ Calculation vs. Measurement for the 003-000 vibration band

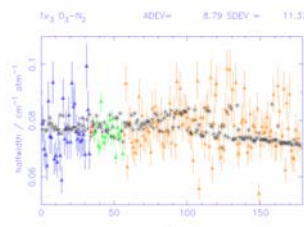


Figure 4. O₃-N₂ Calculation vs. Measurement for the 001-000 vibration band (Color-coded by reference; see Table 2b.)

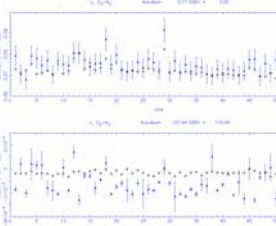


Figure 5. O₃-N₂ Calculation vs. Measurement for the 100-000 vibration band

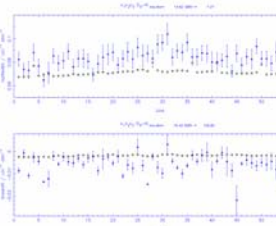


Figure 6. O₃-N₂ Calculation vs. Measurement for the 111-000 vibration band

VIBRATIONAL BANDS

After estimating the Atom-Atom parameter, vibrational dependence of the polarizability of O₃ was adjusted through a semi-empirical process with a focus upon the statistical fit of the line shift (when available) to measurement for each vibration band (i.e. [003-000], [001-000], [100-000], [111-000]). The polarizability constants C_1 , C_2 , and C_3 were calculated for each vibrational band (i.e. 3v₃ corresponding to C₃) and are tabulated below (with the corresponding figure noted in the table).

Band: 003-000 (3v ₃), figure 3			
Calculation: CRB (12th order expansion)			
C_3 0.18375			
Half width	Std. Dev.	Line shift*	Std. Dev.
Abs. Avg.		Abs. Avg.	
6.87	4.94	63.37	160.22

Sources:

Line No.	Reference
1-7	Barbe, et al.; <i>Applied Optics</i> 1991; 30:2431-36
*Note: there were no measurements for line shift for these values, hence these values were inserted to perform the run, consequently skewing the statistics.	
8-198	Smith, et al. <i>J. Mol. Spectroscopy</i> 1994, 164: 239-59

Band: 001-000 (v ₃), figure 4			
Calculation: CRB (12th order expansion)			
C_3 0.18375			
Half width	Std. Dev.	Line shift*	Std. Dev.
Abs. Dev.		Abs. Dev.	
8.79	11.37	na	na

Sources:

Line No.	Reference
1-33	Spencer, MN, et al.; <i>J. Mol. Spectroscopy</i> 1991; 146:314-25 (Blue)
34-35	Sokabe, N., et al. <i>J. Mol. Spectroscopy</i> 1992; 152:420-33 (Red)
36-56	Spencer, MN, et al. <i>Spectrochimica Acta</i> 1992; 48A:1273-81 (Green)
57-177	Margolis, JS, et al. <i>J. Quant. Rad. Transfer</i> 1983; 23:539-42 (Orange)

*Note: there were no measurements for line shift

Band: 100-000 (v ₁), figure 5			
Calculation: Ma-Tipping-Boulet (8th Order expansion)			
C_3 0.029366875			
Half width	Std. Dev.	Line shift	Std.
Avg. Abs. Dev.		Avg. Abs.	
3.77	3.50	107.44	115.46

Sources:

Line No.	Reference
1-60	Smith, MAH, et al.; <i>J. Opt. Soc. Am. B.</i> 1988; 5: 585-92.

Band: 111-000 (v ₁ , v ₂ , v ₃), figure 6			
Calculation: Ma-Tipping-Boulet (8th Order expansion)			
C_2 -0.08625			
Half width	Std. Dev.	Line shift	Std. Dev.
Avg. Abs.		Avg. Abs.	
14.62	7.27	79.42	102.82

Sources:

Line No.	Reference
1-57	Smith, MAH, et al. <i>J. Mol. Spectroscopy</i> 1994; 164:239-59.

Tables 2a-d. Polarizability constants, statistics and references for the calculated vibrational bands.

FURTHER WORK

The calculations will be rerun for all the vibrational bands using 12th-order expansion atom-atom potential to insure convergence of the potential. The fit criterion will be made using the average absolute error to determine the line shift best-fit statistics. Additionally, as an independent check, in collaboration with Prof. Vladimir Tyuterev from the University of Reims he will be performing ab initio calculations to determine the polarizability constants, C_1 , C_2 , and C_3 . Finally CRB calculations will be performed and the results compared with measurements.