A SEMI-EMPIRICAL ADJUSTMENT OF THE VIBRATIONAL DEPENDENCE OF THE POLARIZABILITY OF OZONE FOR USE IN LINE SHIFT CALCULATIONS

Carlos Szembeck, Bobby Antony, and Robert Gamache, Department of Environmental, Earth, and Atmospheric Sciences and The Intercampus Graduate School of Marine Sciences and Technology, University of Massachusetts Lowell, Lowell, MA

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 been 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 no-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.

CRB METHOD

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, \( \gamma \), and line shift, \( \delta \), of a ro-vibrational transition \( f \leftrightarrow i \) are given by.

\[
\gamma = \frac{\pi}{2} \sum_{\nu} \left( \alpha_{\nu} + C_1 \nu + C_2 \nu^2 \right) \frac{1}{\nu^2} \frac{1}{\nu^2} \left( \beta_{1 \nu} \chi_{1 \nu} + \beta_{2 \nu} \chi_{2 \nu} \right)
\]

where

\[
\alpha_{\nu} = \alpha_0 + C_1 \nu + C_2 \nu^2 + C_3 \nu^3 + C_4 \nu^4 + C_5 \nu^5 + C_6 \nu^6
\]

and \( C_1, C_2, C_3 \) 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.

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 \( \varepsilon \) and \( \sigma \)).

\[
\begin{align*}
\varepsilon &\approx \sum_{ij} \frac{\varepsilon_{ij}}{\rho_{ij}} \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \\
\end{align*}
\]

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

\[
S_i = -\varepsilon_i \lambda_i \left( \frac{1}{2} \nu_i^2 + \frac{1}{2} \nu_i^2 \right) \left( \beta_{1 i} \chi_{1 i} + \beta_{2 i} \chi_{2 i} \right)
\]

where

\[
\alpha_i = \alpha_0 + C_1 \nu_i + C_2 \nu_i^2 + C_3 \nu_i^3 + C_4 \nu_i^4 + C_5 \nu_i^5 + C_6 \nu_i^6
\]

and \( C_1, C_2, C_3 \) 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 \( \varepsilon \) and \( \sigma \) 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).

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], [010-000], [110-000]). The polarizability constants \( C_1, C_2, C_3 \) were calculated for each vibrational band (i.e. \( C_3 \)), corresponding to \( C_3 \) and are tabulated below (with the corresponding figure noted in the table).

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 \( \varepsilon \) and \( \sigma \)).

\[
\begin{align*}
\varepsilon &\approx \sum_{ij} \frac{\varepsilon_{ij}}{\rho_{ij}} \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \\
\end{align*}
\]

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

\[
S_i = -\varepsilon_i \lambda_i \left( \frac{1}{2} \nu_i^2 + \frac{1}{2} \nu_i^2 \right) \left( \beta_{1 i} \chi_{1 i} + \beta_{2 i} \chi_{2 i} \right)
\]

where

\[
\alpha_i = \alpha_0 + C_1 \nu_i + C_2 \nu_i^2 + C_3 \nu_i^3 + C_4 \nu_i^4 + C_5 \nu_i^5 + C_6 \nu_i^6
\]

and \( C_1, C_2, C_3 \) 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 \( \varepsilon \) and \( \sigma \) 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).

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], [010-000], [110-000]). The polarizability constants \( C_1, C_2, C_3 \) were calculated for each vibrational band (i.e. \( C_3 \)), corresponding to \( C_3 \) and are tabulated below (with the corresponding figure noted in the table).

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, \( C_1, C_2, C_3 \). Finally CRB calculations will be performed and the results compared with measurements.