Room temperature line parameters of the self- and air-broadened fundamental vibrational transition of carbon monoxide: experimental results and calculations

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Abstract. We have analyzed 10 room temperature spectra of the fundamental band of CO and CO-air using the Voigt, speed-dependent Voigt, speed-dependent Rautian line shape models. Line positions, intensities, air- and self-broadening coefficients, pressure induced air- and self-shift coefficients, and line-mixing parameters have been retrieved. The CO- and N₂-broadened carbon monoxide half width coefficients have been calculated using a potential energy surface based on Tipping-Herman intermolecular interaction potential and taking the electrostatic interactions into account.

1. Introduction
The correct interpretation of atmospheric spectra recorded at different altitudes, by spectroscopic remote sensing instrumentation, requires having available accurate spectral line parameters and their temperature dependences for all molecular absorbers and their isotopologues, stored in the HITRAN database [1] with a desired accuracy better than 1%.

The first study of self- and foreign-broadened carbon monoxide was published by Nakazawa and Tanaka [2], who measured the line intensities and CO-, O₂-, N₂-, CO₂-broadened line widths in the fundamental band at room temperature (300 K). The self-broadening and self-shift coefficients were measured for 61 transitions in the 1←0 band of CO by Devi et al. [3] while Predoi-Cross et al. [4] measured the N₂-broadening coefficients and temperature dependence exponents for many P- and R-branch transitions. The spectra recorded with a difference frequency laser system at 300 K and 348 K were analyzed using the Voigt, Lorentzian and speed-dependent hard collision models with asymmetric components accounting for line mixing [4]. A follow-up room temperature study for CO- and N₂-broadened transitions in the 2←0 band has been published by Predoi-Cross et al. [5] and the results were compared with those of semi-classical calculations and other previously published results.

The line parameters of self- and air-broadened CO transitions in the fundamental and the first overtone bands were studied by Zou and Varanasi [6] at temperatures between 174 and 296 K. A set of high quality FTS spectra of CO in the overtone band was studied by Brault et al. [7], who tested several line shape...
models. The authors report accurate line positions, intensities, self-broadening, self-pressure shift and line mixing coefficients retrieved using the speed-dependent Voigt profile.

The temperature dependences of broadening and shift coefficients in the 3←0 band of CO- and N₂-broadened CO were studied over a range of temperatures by Predoi-Cross et al. [8]. The line profiles of 48 self- and H2-broadened transitions of the 1←0 band were studied by Devi et al. [9]. The air- and H₂-line broadening and pressure-induced line shift coefficients for transitions in the 1←0 and 2←0 bands were reported by Regalia-Jarlot et al. [10].

The temperature dependences of line parameters for self- and air-broadened transitions in the 2←0 band were studied by Devi et al. [11] using a multispectrum constrained analysis, the first study of CO spectra carried out using this technique. Devi et al. [12] then extended this study to cover the air-broadened line parameters of ¹³C¹⁶O and ¹²C¹⁸O.

The most recent measurements of self-broadening and self-shift coefficients for transitions in the 1←0 band of CO have been published by Ngo et al. [13]. The authors used a specially designed absorption cell with variable pathlength between a few microns and a few mm, allowing them to retrieve accurate line parameters for the strongest transitions in this band. Air-broadened line shape studies of the isotopologues ¹³C¹⁶O, and ¹²C¹⁸O in the 1←0 band were recently published in Ref. [14].

The present study reports accurate room temperature line parameters of air-broadened CO in the 1←0 band using the Voigt, speed-dependent Voigt, and speed-dependent Rautian line shape models. Line mixing and line narrowing effects were also accounted for as needed.

2. Experimental Details

All 10 spectra used in this study were recorded at 0.0052 cm⁻¹ resolution using the former McMath-Pierce Fourier transform spectrometer located on Kitt Peak, AZ. The spectrometer was set up with an Oriel globar source, two LN₂ cooled InSb detectors, a KCl beamsplitter, InAs and Si Nas filters. Two coolable gas absorption cells made of copper attached to a CTI-Cryogenics Model 22C Cryodyne cryocooler were used. The gas sample temperatures were measured within ±0.01 K with a platinum resistor temperature sensor and Lakeshore temperature controllers. Further details of the gas cells are given in Ref. [15], where the same setup was used to record He-broadened spectra of the CO 1←0 band. The gas pressures were measured using calibrated pressure sensors for the 0-10 and 0-1000 Torr MKS Baratron pressure gauges. The absolute calibrations of the wavenumber scale were performed using carbon dioxide lines in the ν₃ fundamental band [1], present in the spectra due to residual gas in the evacuated FTIR tank.

3. Spectroscopic Analysis

All 10 spectra in our study were analyzed using a constrained multispectrum analysis technique. As in Refs. [11,12,14], rather than fit the line positions and intensities, we fitted the entire band at once using the multispectrum fit software developed by Dr. DC Benner [16]. We used the speed-dependent Voigt (SDV), Voigt, and speed-dependent Rautian (SDR) line shape models. In the absence of measured published narrowing parameters for CO and not being able to retrieve them during our analysis, we proceeded to calculate them approximating that the narrowing coefficient is equal to the dynamic friction coefficient, as previously done in our study of the CO-He system [17]. The dynamic friction coefficients (cm⁻³atm⁻¹) were calculated using the expression:

$$\beta_{\text{eff}}^0 = 0.1664 - \frac{\sigma_{\text{eff}}}{\sqrt{\frac{\sigma_{\text{eff}}^2}{2} + \frac{\alpha_{\text{eff}}^2}{\tau_{\text{eff}}}}},$$

(1)

The reduced dimensionless collision integrals $\Omega_{12}^{11}(T_{12})$, where $T_{12} = \frac{k_B T_{12}}{\epsilon_{12}}$, were taken from Ref. [18]. The well depth of the isotropic potential is $\epsilon_{12}$, $\sigma_{12}$, given in Å, is chosen such that $V_{\text{iso}}(\sigma_{12}) = 0$. The masses of the absorber and perturber molecules are given in g/mol. In Eq. (1) the mass ratio of perturber to absorber (active) molecules is labelled $\lambda$. The values for the parameters $\epsilon_{12}$ and $\sigma_{12}$ were taken from the literature for each of the three systems of interacting molecules: CO-CO [19], CO-O₂ [20], CO-N₂ [21]. The potential energy surface was provided by Dr. A van der Avoird [22].

We retrieved the ro-vibrational constants in the upper state according to Eq. (2), that are needed to calculate the line positions:

$$v_i = G' - G'' + \frac{[B'J'(J' + 1) - D'J'(J' + 1)]^2 + H'[J'(J' + 1)]^3}{2J''(J'' + 1)}$$
\[ -\left \{ B'J'(J' + 1) - D'[J'(J' + 1)]^2 + H'[J'(J' + 1)]^3 \right \} \]  
(2)

The spectroscopic information from line intensities was used to determine the vibrational band strength, \( S_V \), and Herman-Wallis expansion coefficients \( a_1 \) to \( a_5 \), according to Eqs. (3-5).

\[ S_V(T_o) = \frac{\nu_v \omega_v}{\nu_v \nu_o} q_i \exp\left(-\frac{C_v E''}{T_o}\right) \left[ 1 - \exp\left(-\frac{C_v \nu_i}{T_o}\right) \right] \]  
(3)

\[ F = [1 + \alpha_1 m + \alpha_2 m^2 + \alpha_3 m^3 + \alpha_4 J(J + 1)]^2 \]  
(4)

\[ S_V = \frac{\nu_v \omega_v q_i}{\exp\left(-\frac{C_v \nu}{T}\right)} \]  
(5)

Here \( \nu_i \) are the line positions, \( L_i \) the Hön-London factors, \( C_v \), the second radiation constant, \( J \), the rotational quantum numbers, \( F \), the Herman-Wallis terms with coefficients \( a_1 \) to \( a_5 \), \( Q \), the rotational partition number, \( \nu_o \), the band center, and \( E'' \) the lower state energies and \( T_o = 296 \) K. \( S_V \) is the band strength at 296 K.

Table 1 shows the results for the ro-vibrational parameters in the upper state, band intensity obtained using the speed-dependent Voigt model and the lower state ro-vibrational parameters that were kept fixed during the fit. Three Herman-Wallis coefficients were needed to reproduce the intensities.

| Table 1. Ro-vibrational parameters, band intensity and Herman-Wallis expansion parameters. |
|---------------------------------|-----------------|-----------------|-----------------|
| Ro-vibrational Parameter       | Ro-vibrational constants (cm\(^{-1}\)) | Intensity parameter | Intensity constants |
|--------------------------------|------------------------------------------|-----------------|-----------------|
| \( G'\cdot G'' \)              | 2143.2709667(3)                           | \( S_V \) (cm/molec.) | 1.02689 \times 10^{-17} |
| \( B' \)                       | 1.9050254282(4)                           | \( a_1 \)         | 0.28424 \times 10^{-3} |
| \( D' \)                       | 0.6116316(17) \times 10^{-5}              | \( a_2 \)         | -0.12868 \times 10^{-4} |
| \( H' \)                       | 0.2361796(17) \times 10^{-11}             | \( a_3 \)         | 0.40588 \times 10^{-6} |
| \( B'' \) (fixed)             | 1.92252895(4)                             |                  |                  |
| \( D'' \) (fixed)             | 0.61211137 \times 10^{-5}                 |                  |                  |
| \( H'' \) (fixed)             | 0.58097981 \times 10^{-11}                |                  |                  |

\(^{a}\)Ref: http://doi:10.1088/0067-0049/216/1/15

Regardless of the line shape model used, Eqs. (6-8) are used to retrieve the self- and air-broadening coefficients and corresponding pressure induced shift coefficients.

\[ b_L(p, T) = p \left[ b_L^0 \exp \left( \frac{\nu_i T}{T_o} \right) + b_L^1 \exp \left( \frac{\nu_i T}{T_o} \right)^2 \left( \frac{T_o}{T} \right)^n \right] \]  
(6)

\[ \nu = \nu_o + p \left[ \delta^0(\text{air})(1 - \chi) + \delta^0(\text{self})\chi \right] \]  
(7)

\[ \delta^0(T) = \delta^0(T_o) + \delta(T - T_o) \]  
(8)

Above, \( b_L^0 \) are the broadening coefficients at 1 atm and 296 K. The volume mixing ratio is given by \( \chi \). The temperature dependences of line broadening parameters \( n_1, n_2, \delta^0 \) were not needed.

The speed dependence coefficients were determined for a reduced number of transitions using the SDV and SDR line shape models (one set for both CO-CO and CO-air collisions). Where we were unable to retrieve the speed dependence parameters from the spectra, we used the average of calculated speed-dependence [23] for CO-CO and CO-air collisions.

Line mixing was quantified through the relaxation matrix formalism (see for example Refs. [11,12,14]). The diagonal elements of the relaxation matrix, \( W_{j,j} \), have the broadening parameters, \( b_L^0 \), as real part and the pressure shift coefficients, \( \delta^0_{j,j} \), as the imaginary part.

\[ W_{j,j} = b_L^0 + i \delta^0_{j,j} \]  
(9)

The off-diagonal elements are related through the detailed balance relation given by Eq. (10)

\[ W_{j,k} = W_{k,j} \rho_{j,k} \rho_{k,j} \]  
(10)

The weak line mixing coefficients can be calculated using the effective dipole moments, \( d_j \).

\[ Y_k^0(T) = 2 \sum_{j \neq k} \frac{d_j}{d_k} W_{j,k} \]  
(11)

4. Theoretical Calculations

Classical impact theory is applied to calculate the half-widths of CO absorption lines in CO-CO and CO-N\(_2\).
collisions. The calculations use simple vibrationally independent intermolecular interaction potential (Tipping-Herman+ electrostatic). Both molecules are treated as rigid rotors. The dependences of CO half-widths on $J$ for $J \leq 26$ are computed and compared in figure 1 with measured half-widths.

Figure 1. The self- and air-broadening coefficients plotted against the index $m$ in panels (a) and (b). Overlaid with our results obtained with the SDV and Voigt models for transitions in the $0\rightarrow1$ band, are previously published results. (c) Measurement results obtained using the SDV model and the corresponding calculated values. ($m$ is $J''$ for $P$ branch transitions and $J'+1$ for $R$-branch transitions.)

Figure 2. Self- (panel (a)) and air- (panel (b)) pressure shift coefficients plotted against the index $m$. Overlaid are published measurements for different vibrational bands. Panel (c) presents our measured air-shift coefficients obtained with the Voigt, SDV and SDR line shape models.

Figure 3. Measured speed dependence parameters obtained with the Speed-Dependent Voigt and Speed-Dependent Rautian line shape models. Plotted overlaid are measurements of speed dependence parameters in the $2\rightarrow0$ band and in the $01\rightarrow0$ band for the isotopologues $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$. Also overlaid are calculated values for pure CO and CO-air mixtures.

Figure 4. Self and air off-diagonal relaxation matrix elements (a) and weak line mixing coefficients (b) plotted against $m$. Overlaid are published results obtained for other bands.

5. Conclusions
This paper reports the line parameters of the self- and air-broadened fundamental transitions of CO as retrieved of CO in the $1\rightarrow0$ band retrieved using a constrained multispectrum analysis carried out using
three line shape models: Voigt, SDV, and SDR. The line narrowing parameters used by the SDR model were calculated. Line mixing was implemented using the off-diagonal relaxation matrix formalism. The figures presented above show good agreement between the present results and previously published values for transitions in either $1\rightarrow0$, $2\rightarrow0$ and the $3\rightarrow0$ bands. The agreement between measured self- and air-broadened half widths and the corresponding values calculated through a fully classical approach is better in some ranges of J than in others, due to imperfections in the knowledge of potential energy surfaces used.

**Acknowledgements**

Dr. D. Chris Benner of the College of William and Mary is thanked for allowing us to use the suite of programs he had developed over the years. We also thank Dr. Arlan Mantz of Connecticut College for his assistance in recording the spectra. The research carried out at the College of William and Mary and Langley Research Center was funded through NASA contracts. Mr. Nazrul Islam and Dr. A. Predoi-Cross received financial support from the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS and Russian Science Foundation (Project No.18-55-16006) in part of classical trajectory calculations.

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