Buffer-gas Pressure Broadening for the Third Overtone Band of NO Measured with Continuous-wave Cavity Ring-down Spectroscopy

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The buffer-gas pressure broadening coefficients and the temperature dependent parameter of the third overtone band of NO at 1.35–1.38 μm by N_2 and rare gases for two ground electronic states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, were investigated for rotational levels of $P(7.5)$–$R(14.5)$ using continuous-wave cavity ring-down spectroscopy. Obtained pressure-broadening coefficients are consistent with literature values.

Line profile data in the near infrared (NIR) region have been accumulated with use of Fourier transform spectroscopy (FTS) and tunable diode laser spectroscopy. NIR tunable laser spectroscopy is a high precision method for a set of weak lines. Cavity ring-down spectroscopy (CRDS) is one of sensitive spectroscopic absorption techniques for use with continuous-wave (CW) lasers. A combination of the high spectral resolution of diode laser and the sensitive CW-CRDS technique makes precise measurements of pressure broadening for weak lines possible. A compact cooling cell may be used for temperature dependence measurements.

Buffer-gas pressure broadening of NO has been reported by Ballard et al.,[1] Spencer et al.,[2] and Pope et al.[3] for the fundamental band with use of FTS, Pine et al.[4] for the first overtone band with use of a tunable difference-frequency laser, and Snels et al.[5] for the second overtone band with use of a distributed feedback laser. In this paper, we have measured pressure broadening coefficients and its temperature dependence of the third overtone band of NO at 1.35–1.38 μm by N_2 and rare gases for two ground electronic states, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ using CW-CRDS.

The principle of CW-CRDS is described in the previous study.[6] The laser beam (Santec, TSL-210V, <1 pm scanning resolution, 200-MHz line width) was deflected by an acousto-optical modulator (Isomet) and directed into an optical cavity that consisted of two high reflectivity mirrors (II–VI Optics) with a separation of 55 cm. One of two mirrors was incorporated in a tube-type piezoactuator (Piezomechanik) for cavity length modulation with a rate of about 300 Hz. The transmitted light from the cavity was detected with an InGaAs photodiode (Hamamatsu Photonics) attached by a fast preamplifier (NF). The cavity ring-down time without the absorber present was typically 1.6 μs. Forty-nine ring-down events were averaged for each spectral data point, and typically 800 data points were measured in one scan with resolutions equal to $3 \times 10^{-4}\,\mathrm{cm}^{-1}$. Thus, a complete scan took about 3 min. Pressure broadening by various buffer gases (N_2, He, Ne, Ar, Kr, and Xe; 70–170 Torr) was measured at a fixed partial pressure of NO (5–12 Torr). All experiments were performed at 233–298 K.

The rovibrational spectra of NO ($^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, $v' = 4$, $v'' = 0$) are split into two lines, the *e* and *f* levels of opposite parity by the effect of Λ-doubling. These blended spectral features were fitted with a sum of two equal weight Voigt profiles by adjusting the width and line position using ORIGIN software. The following index, *m*, is used to treat simultaneously *P*- and *R*-branch transitions:

$$2m = J'(J'+1) - J''(J''+1) \tag{1}$$

$$P\ \text{branch}\ (J''-1 \leftarrow J'');\ m = -J'' \tag{2}$$

$$R\ \text{branch}\ (J''+1 \leftarrow J'');\ m = J''+1 \tag{3}$$

The spectral separation between line center positions of the *e* and *f* components was estimated to be $\Delta\nu_\mathrm{m} = (-2.36|m| + 127) \times 10^{-4}\,\mathrm{cm}^{-1}$ from literature values for the fundamental and second overtone bands because the spectral separation for these two bands are almost the same.[2,5] Obtained γ values for N_2 and rare gases are listed in the Supporting Information (SI).[7] Sensitivity of the γ value to the spectral separation, $\Delta\nu_\mathrm{m}$, was evaluated. 10% change of $\Delta\nu_\mathrm{m}$ causes about 5% change in the γ value. Obtained γ values for N_2 are plotted as a function of the rotational quantum number index, *m*, in Figure 1. Available literature data are also plotted, which were reported by Spencer et al.,[2] Pine et al.,[4] and Snels et al.[5] Our values are in agreement with those literature data.

According to Thorne et al.,[8] based on the impact approximation, γ is expressed from cross sections in terms of the Weisskopf radius. Then, γ can be modified to eq 4.[6,9]

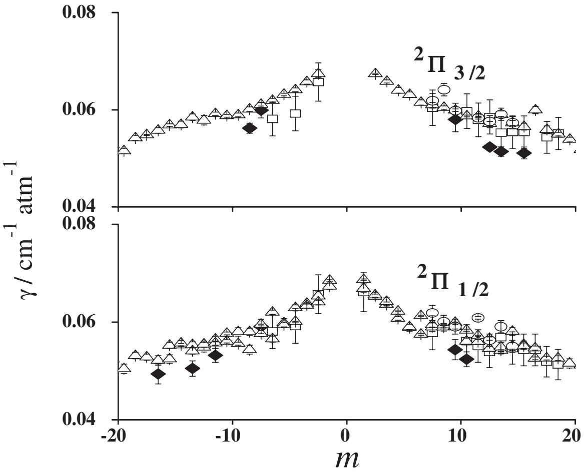

Figure 1. Pressure broadening coefficients of NO for N_2 as a function of rotational quantum number index, *m*, for the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ transitions. △: fundamental band,[2] □: first overtone band,[4] ○: second overtone band,[5] and ◆: third overtone band (this work).

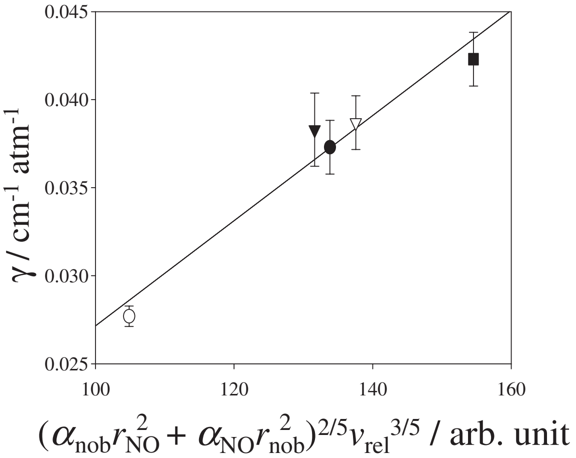

Figure 2. Averaged values of pressure broadening coefficients, γ, for $R(12.5)$, $P(7.5)$, and $P(11.5)$ as a function of product of radius, relative velocity and polarizability. ●: He, ○: Ne, ▼: Ar, ▽: Kr, and ■: Xe.

$$\gamma \approx (\alpha_{nob}r_{NO}{}^2 + \alpha_{NO}r_{nob}{}^2)^{2/5}v_{rel}{}^{3/5} \tag{4}$$

where α is the polarizability, r the atomic or molecular radius, and v_{rel} the relative velocity. "nob" stands for noble gas. Figure 2 shows results for averaged γ(noble gas) values of the $R(12.5)$, $P(7.5)$, and $P(11.5)$ transitions at room temperature. Parameters for eq 4 are listed in SI.[7] It is interesting to note that when γ values are plotted as a function of $\pi r^2 v_{rel}$ based on the simple hard collision theory, γ(He) does not fit to the straight line for γ(Ne)–γ(Xe).

Figure 3 shows the temperature plots for the $P(11.5)$ transition of ${}^2\Pi_{1/2}$. Results for changes in temperature can be expressed by the following simple equation:[10]

$$\frac{\gamma(T)}{\gamma(T_0)} = \left(\frac{T}{T_0}\right)^{-n} \tag{5}$$

where n is the power-law exponent of eq 5. T_0 is 298 K in the present study. With use of eq 5, the value of n for N_2 is obtained to be 0.77 ± 0.13.

With the collision diameter fixed, the temperature dependent parameter is given by:[11]

$$n = (q + 1)/2(q - 1) \tag{6}$$

where q is the power-law term for an intermolecular potential proportional to r^{-q}: $q = 5$ for quadrupole–quadrupole interaction, $q = 6$ for London dispersion force, and $q = 7$ for quadrupole–induced dipole interaction. Thus, in the case of $q = 5$, 6, and 7, n is expected to be 0.75, 0.70, and 0.67, respectively, for van der Waals broadening in the impact model due to temperature dependence of the Weisskopf radius. The present value, $n = 0.77 \pm 0.13$, would be well reproduced with an effective force law term $q = 5$. However, eq 5 is mostly chosen for its simplicity, and valid only for a restricted temperature range. Due to the small temperature range in the present experiment, it is difficult to determine the plausible interaction force between NO and N_2.

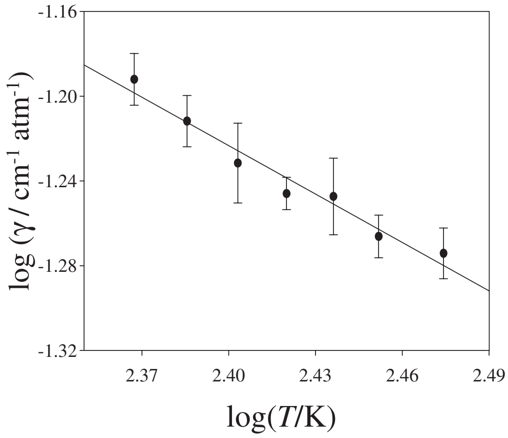

Figure 3. Temperature dependence of pressure broadening coefficients for the $P(11.5)$ transition of ${}^2\Pi_{1/2}$. Error bars indicate one standard deviation determined by the profile-fit procedure.

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