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Galatry versus speed-dependent Voigt profiles for millimeter lines of O_3 in collision with N_2 and O_2

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ABSTRACT

Experimental and theoretical investigations of ozone lines broadened by nitrogen as well as oxygen have been carried out in the 300–320 GHz frequency range. Lineshape analysis has demonstrated clear departures from the usual Voigt profile, actual lineshapes being narrower and higher than expected. More refined models, such as the Galatry and speed-dependent Voigt profiles, have been used. Both of them have been found to reproduce the experimental lineshapes well. However, while for the latter, the narrowing parameter shows a linear behavior with pressure, for the Galatry profile a strong nonlinear behavior is observed. Such observations demonstrate that the Dicke narrowing effect, related to molecular diffusion, cannot be the leading process involved. Experimental results have also been compared to the theoretical ones. The relaxation rate dependence on molecular speed has been computed employing the Robert–Bonamy semiclassical theory. These calculations confirm the leading role of molecular speed dependence effects. Finally, it is inferred that optical diffusion rates are much lower than the kinetic diffusion rate, a conclusion well supported from the comparison of optical and Lennard–Jones radii.

1. Introduction

A previous paper [1] was devoted to an extensive intercomparison, in the millimeter-wave region, of ozone-broadening parameters retrieved by laboratories in Lille (Laboratoire de Physique des Lasers, Atomes et Molécules, PhLAM) and Bologna (Laboratory of Millimeter-wave Spectroscopy of Bologna, LMSB). The main goal was to get information on the reproducibility of pressure broadening parameters and, above all, on the systematic effects affecting them. In this study, we will essentially reconsider the ozone transitions of Ref. [1] focusing on a detailed analysis of observed lineshapes, namely the departures from the Voigt profiles that clearly show up as soon as a good signal to noise ratio can be obtained. Indeed, nowadays, the spectral resolution and sensitivity achieved by spectrometers allow one to point out deviations from the usual Voigt profile, so that actual lineshapes appear narrower and higher than expected. These discrepancies result from the fact that the Voigt profile does not take into account correlations existing between molecular velocities and collisional processes. Such correlations may be ascribed to different physical effects, either to velocity/speed changing collisions (the so-called Dicke-narrowing effect that reduces the Doppler broadening) [2–4] or to the dependence of relaxation rates on molecular speeds [5,6], or in some cases to both effects as well [7]. In the literature different models have been introduced for describing the observed line profiles (for a review, see for instance Ref. [8]).

In the present work we mainly focus on two models: the Galatry profile [3] and the speed-dependent Voigt (SD-Voigt) profile [5,6]. The former accounts for the Dicke-narrowing effect in a soft collisional model, whereas the second one accounts for the molecular speed dependence of relaxation rates. Relaxation coefficients related to either velocity changing effect (Galatry profile) or to speed dependence effect (SD-Voigt profile) are expected to show a linear behavior versus the gas pressure in the binary collisions regime, which should be well fulfilled in our experimental conditions. Actually, it will be exactly this expected linear behavior that will help us in sorting out the best model to be used.

In fact, in this study it will be shown that, as already seen in the literature for various molecules [8–18], both the Galatry and SD-Voigt profiles are able to well recover the observed lineshapes as well as provide reliable and accurate retrieved broadening parameters. Therefore, lineshape analysis itself and pressure-broadening parameters do not allow us to discriminate between the two models, although they are based on completely different processes. On the other hand, it will be shown that the diffusion rate B^G, defined

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in the Galatry model, does not have the proper linear behavior in all the pressure range considered and it is even not determinable for the higher pressure values considered. On the contrary, it will be shown that the speed-dependence rate Γ_2^{SDV} behaves well in the pressure range considered and it is always determinable. Therefore, it is a deeper investigation of these narrowing parameters that can help us to get the right clue.

In this view, we have compared the experimental results obtained for some rotational lines of ozone in collision with nitrogen and oxygen: the 301.8 GHz ($J = 14_{0,14} \leftarrow 13_{1,13}$) transition observed in Lille in the 235–300 K temperature range; the 301.8 GHz, 317.2 GHz ($J = 5_{3,3} \leftarrow 6_{2,4}$) and 320.0 GHz ($J = 20_{1,19} \leftarrow 20_{0,20}$) transitions observed in Bologna in the 195–300 K temperature range. After a short description of the main features of the spectrometers employed (Section 2) and of line profile models considered (Section 3), Section 4 is devoted to a detailed analysis of the lineshapes observed in both laboratories. For all studied transitions, whichever the temperature and collisional partner are, it is shown that the Galatry model leads to non physical behaviors of relaxation rates in the high pressure regime, in full contrast with the SD-Voigt model. A detailed comparison of Galatry and SD-Voigt models (Section 5) allows us to explain these features and to claim that the Galatry profile must be disregarded. In Section 6, the retrieved relaxation parameters have been compared to those obtained from semiclassical theoretical calculations. It is concluded that observed departures from the Voigt profile result mainly from the dependence of relaxation rates on molecular speeds and that the optical diffusion parameter must be much smaller than the kinetic diffusion one. Finally, Section 7 is devoted to a short conclusion.

2. Experimental details

The spectrometers used have been described in details in previous papers [1,19]; therefore, here, we only report the main details related to the present study.

At PhLAM (Lille) a video type spectrometer has been employed. Electromagnetic sources are backward wave oscillators (BWO) that are phase-locked to an emission harmonic of a 1–20 GHz synthesizer, locked onto a GPS reference signal. The intermediate frequency beat near 320 MHz is compared to the 32nd harmonic of a 10 MHz signal issued from a second frequency synthesizer that also provides the linear frequency scan at a 20 Hz rate. The resulting electromagnetic power is detected by a liquid-He cooled bolometer, amplified and average about 500× to give the true absorption lineshape. The whole spectrometer is managed by a computer that controls the frequency sweep and stores the corresponding absorption signal that consists of about 500–600 data points. The gas sample has been set in a 110 cm long cell that can be thermo-regulated between 230–350 K with a stability better than 1 K. Gas pressures have been measured with a MKS Baratron capacitance transducer having a 0.1 mTorr resolution and a stated accuracy of 0.12% of the reading scale.

At LMSB (Bologna) the spectrometer employed is a frequency modulated spectrometer whose radiation source is a Gunn-driven frequency multiplier. The source is phase-locked to a Rubidium frequency standard. The frequency modulation is performed by sine-wave modulating (1.666 kHz) the 90 MHz reference signal of the source-synchronizer. The lock-in amplifier is tuned at twice the modulation frequency so that the recorded signal looks like the second derivative of the natural lineshape. The cell is a Pyrex tube either 148 or 55 cm long and 5 cm in diameter. In both cases, the cell is thermally insulated. The measurements have been performed at 195, 240 and 296 K. For measurements at 240 and 296 K, the temperature has been kept controlled by a cryostat, while in the case of measurements at 195 K, the temperature has been maintained by employing an ethyl alcohol—dry ice bath. In both cases, the temperature accuracy is ±1 K. The sample pressure has been measured by a Baratron gauge (MKS type 220 B) with a measurable pressure range of $10^{-4} - 1$ Torr ($\sim 1.33 \times 10^{-2}$–133 Pa), and with a 0.1 mTorr resolution. The spectrometer is equipped with a liquid-Helium cooled InSb detector.

In both laboratories, ozone was prepared using the silent electrical method in a sample of pure dry oxygen (see Ref. [6] of Ref. [1]). After cryogenic pumping, ozone purity was estimated better than 95%, a sufficient value for foreign gas broadening experiments since measurements consisted of about 5–20 lineshape recordings obtained with the same ozone pressure (about 5–20 mTorr) and various buffer gas partial pressures in the 0–500 mTorr pressure range. Buffer gases were commercial grades of N_2 and O_2 having stated purities better than 99.5%.

At PhLAM the true lineshape has been observed and the exponential form of the Lambert–Beer law has been used for the line profile analysis:

$$I = I_0 \cdot \exp[-\alpha(\nu - \nu_0) \cdot L], \tag{1}$$

where $\alpha(\nu - \nu_0)$ is the absorption coefficient at the detuning frequency $(\nu - \nu_0)$ and L the effective cell length.

As accurately explained in Ref. [20], the approximate linear expression of the absorbed intensity

$$I = I_0 \cdot [1 - \alpha(\nu - \nu_0) \cdot L] \tag{2}$$

should be used for the modulated line profile analysis performed at LMSB. This expression is valid only if the maximum absorption is lower than 6% ($\alpha_{max} L \leqslant 0.06$), therefore, this requirement has been checked to be fulfilled during all the measurements employing amplitude modulation of the signal [1].

3. Lineshape models

For the fitting of experimental lineshapes, each laboratory used its own nonlinear least-squares code. They are both based on a Fourier transform technique since true lineshapes $\alpha(\nu - \nu_0)$ can be expressed as proportional to the real part of the Fourier transform of the molecular correlation function $\Phi(t)$. This function describes the time domain evolution of the sample polarization after a pulse excitation occurring at time $t = 0$ [21]. In the case of frequency modulation technique with the lock-in amplifier tuned at twice the modulation frequency, the Fourier transform technique can be applied by replacing the correlation function $\Phi(t)$ with [22]

$$\mathrm{J}_2\left[m\, t \cdot \mathrm{sinc}\left(\frac{\omega_m t}{2}\right)\right] \cdot \cos(\omega_m t) \cdot \Phi(t), \tag{3}$$

where $\mathrm{J}_2[x]$ is the second order Bessel function, with m and ω_m representing the modulation depth and frequency, respectively, and $\mathrm{sinc}(x) = \sin(x)/x$. Numerical tests on artificial lineshapes showed that both codes agree within 0.1% on retrieved broadening parameters.

Lineshapes considered in this work are:

(i) the usual Voigt model which considers that molecular displacements and collisions are statistically independent. Its correlation function is

$$\Phi_V(t) = \exp\left[\mathrm{i}\omega_0 t - \Gamma t - \left(\frac{k v_{a0} t}{2}\right)^2\right], \tag{4}$$

where ω_0 is the line center frequency, Γ the collisional relaxation rate (in s^{-1}), $k = \omega_0/c$ the wave number and $v_{a0} = \sqrt{2k_B T/m_a}$ the most probable value of the absorber speed defined by the Boltzmann constant k_B, the temperature T and the molecular mass m_a of the absorber.