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Narrowing broadening and shifting parameters for $R(2)$ and $P(14)$ lines in the HCl fundamental band perturbed by N_2 and rare gases from tunable diode laser spectroscopy

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ABSTRACT

High resolution measurements of room temperature absorption with a controlled tunable diode laser (TDL) spectrometer have been made for $R(2)$ and $P(14)$ lines in the HCl fundamental band perturbed by N_2, Xe, Ar and He at pressures lower than one atmosphere. Pressure broadening, shift and collisional narrowing parameters have been extracted by least-squares fitting of several collisional profiles to the spectra. Asymmetries are observed for $P(14)$ broadened by Xe at the lowest pressures and attributed to correlations between velocity- and phase-changing collisions.

1. Introduction

The first measurements of broadening and shifting parameters for the HCl infrared lines were achieved at low resolution a very long time ago [1,2] Many years later high resolution measurements with a difference frequency spectrometer allowed analyzing the deviations of the line shapes from the Voigt profile for HCl fundamental band self-perturbed [3], perturbed by N_2 and air [4] and perturbed by Ar [5], at low pressure. Pine and co-authors [3,4] used the soft [6] and hard [7,8] collision models to take into account the confinement narrowing first described by Dicke [9] and Whittke and Dicke [10] and they pointed out that the narrowing parameter β^0 was larger for the lowest values of the rotational quantum number J. Recently the impact of the line narrowing onto the retrieval of atmospheric HCl and HF vertical profiles from ground-based Fourier Transform infrared measurements was examined [11]. Soft and hard collision models [12–15] taking into account both confinement narrowing [6–8] and absorber speed dependent effect [16–18] were developed to keep a constant value of the narrowing parameter when the pressure increases from a few kPa to one atmosphere. Finally several mechanisms, including correlations between velocity changing and dephasing collisions [8], and speed dependent effects on shift [16–18] have to be taken into account to reproduce the line shape asymmetries as observed by Pine in Ar-broadened HF[19,20]. The speed-dependent models were generalized for soft and hard collisions by Ciurylo [21] and Lance and Robert [22]. A partially correlated strong collision model for velocity and state changing collisions was developed by Joubert et al. [23] and a generalized speed-dependent line profile combining soft and hard partially correlated collisions by Ciurylo et al. [24]. More recently Wehr et al. [25,26] compared high-resolution absorption measurements of CO lines perturbed by Ar with theoretical calculations based on solving a transport/relaxation equation for the appropriate off-diagonal element of the density matrix. They use a realistic intermolecular potential to determine the speed-dependent collisional broadening, and a rigid sphere potential to determine the Dicke narrowing. They conclude [25] that the magnitude of the Dicke narrowing occurring in CO–Ar is 70% or 90% less than predicted from the mass diffusion constant.

We present here high resolution measurements with a controlled tunable diode laser (TDL) spectrometer for $R(2)$ and $P(14)$ lines in the HCl fundamental band perturbed by N_2, Xe, Ar and He at pressures lower than one atmosphere. Different collision models are used in a multifit program to describe the

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observed profiles and compared in order to determine the best parameters for each collision partner. Significant asymmetries are observed for $P(14)$ broadened by Xe at pressures around 0.1 atm and attributed to correlations between velocity- and phase-changing collisions. This effect appears much weaker with Ar or N_2 as a buffer gas and disappears with He. The broadening and shifting parameters for HCl perturbed by Ar may be also compared to the very recent values determined by Boulet et al. [27] from absorption measurements for pressures between 10 and 50 atm.

2. Experimental details

We used the Michelson interferometer controlled TDL system developed at LPMA and described in detail elsewhere [28–30]. Active control of the diode laser emission reduces the residual frequency fluctuations (phase noise) of the diode to less than 4×10^{-5} cm^{-1}. We recall briefly the principle on which frequency control works. The emitted wavelength λ_d is controlled through a Michelson interferometer with a path difference D fixed, holding the interference order k_d constant ($D = k_d\lambda_d$) using a feedback on the polarization current of the TDL. The control of D value and its variation is done by a stabilized He–Ne laser. An absorption line is scanned step-by-step, the step $\Delta\lambda_d$ is obtained keeping k_d constant and varying D by elementary steps ΔD; these steps are connected through the following numerical relation: $(D + \Delta D = (\lambda_d + \Delta\lambda_d)k_d)$. The spectral sampling step is equal to 0.2606×10^{-3} cm^{-1} at 2945 cm^{-1}. The part of the TDL beam used for absorption experiments is divided into two components; one beam is used as a reference signal, I_0, and the other goes through the sample cell to provide a transmitted signal, I_t. At each step the beam intensities I_0 and I_t are measured simultaneously and the ratio I_t/I_0 is determined with a relative precision of about 5×10^{-4}.

We used TDL single mode laser from Laser Photonics Inc., one TDL operating at 57 K in a cold head for the $P(14)$ line at 2544.2800 cm^{-1} and another one operating in a liquid N_2 dewar at 78 K for the $R(2)$ lines at 2944.9138 and 2942.7222 cm^{-1}. For precise line shape studies, it is necessary to describe the TDL emission shape under the same operating conditions. The analysis of several spectra at low pressure (Doppler regime) showed that the TDL emission was well described by a Voigt function defined by the half widths at half maximum (HWHM) A_G and A_L of the Gaussian component and Lorentzian component, respectively. This analysis is performed before each set of measurements. Some details on the apparatus function determination and the consequences of erroneous functions used in spectra analysis can be found in Ref. [31]. At 2544 cm^{-1} with A_L equal to 0.055×10^{-3} cm^{-1} A_G was varying from 0.83×10^{-3} to 0.85×10^{-3} cm^{-1}. The Lorentzian part of the TDL emission in the 2942–2945 cm^{-1} wavenumber range is more important, A_L was varying from 0.23×10^{-3} to 0.24×10^{-3} cm^{-1} with A_G varying from 0.42×10^{-3} to 0.45×10^{-3} cm^{-1} at 2942.7 cm^{-1} and from 0.46×10^{-3} to 0.52×10^{-3} cm^{-1} at 2944.9 cm^{-1}. Moreover it is necessary to check the residual transmitted intensity at the centre of a saturated line, due to both multimode operation and spontaneous emission. At 2544 cm^{-1} this offset was around 2.5% and for the second TDL, it was also around 2.5% at 2942.7 cm^{-1} but increased until 3.5% for the measurements at 2944.9 cm^{-1}. Generally the offset and the width of the TDL emission increase with operating time, warming and pumping the cryostat allow to recover a better single mode emission but the spectral range of emission may be affected explaining our incomplete measurements for $H^{35}Cl$ R(2) line.

The $R(2)$ and $P(14)$ line shapes of HCl were studied for different pressures between 10 and 600 Torr and different collisional partners. For each pressure three spectra were recorded. The gas mixtures for $R(2)$ were made directly in the 30 cm path length cell at the chosen highest pressure with a mixing ratio of about 0.03% and the gas mixture is pumped to achieve the different measurements. Previously pure HCl at low pressure in the cell allowed us to verify the TDL apparatus function. For pressure shift measurements of the $R(2)$ line the reference beam I_0 passes through a second 30 cm path length filled with a low pressure of pure HCl and the spectra given by each of the two beam intensities I_0 and I_t are simultaneously analyzed. The $P(14)$ line intensity is about one thousand times smaller than for the $R(2)$ line while broadening is 10 times smaller, so a mixing ratio of several percents is sufficient in a 180 cm path length cell to observe the pressure broadened line. The gas mixtures were made in balloon glasses before filling the cell at the highest pressure. A 10 cm path length cell and a 30 cm path length cell containing N_2O at low pressure can be added on the same beam to obtain a reference line ($P(21)$ at 2544.3194 cm^{-1} from the $2\nu_1$ band) for pressure shift measurements and apparatus function determination. Self-broadening and -shifting for $P(14)$ were measured using a 30 cm path length cell filled with pure HCl at three pressures. All cells were in Pyrex glass and fitted with KCl windows with faces tilted of about 0.5° to minimize channeling due to interference fringes from window reflections. The gas fill station was in Pyrex glass with Teflon gaskets for the joints and valves. The total gas pressure was measured using an Edwards Barocel with 1000 Torr full scale or a MKS Baratron manometer with 100 Torr full scale. A 10 Torr full scale capacitance manometer was also used for measuring the lowest pressures of pure gases. All these manometers have a four digit display with a stated accuracy of 0.15% of the reading. Natural isotopic HCl with a stated purity better than 99.9% was supplied by Air Liquide Company and stored in a bottle glass after purification by distillation and cryopumping at 77 K. All measurements were achieved at room temperature between 295.6 and 296.2 K for $R(2)$ and between 296.6 and 297.7 K for $P(14)$.

3. Data analysis

In analyzing the experimental spectra, calculated spectra, convolution product of the Voigt apparatus function described above with the HCl absorption line shape, are adjusted to the observed spectra in a least squares fit procedure in order to determine the different spectroscopic parameters. The absorption line shape is described by $(1 - \exp(-lk(\sigma,P)))$, where l is the absorption path length and $k(\sigma,P)$ is the absorption coefficient at wavenumber σ and total pressure P, which defines the line profile.

When only Doppler effect and simple collision broadening are considered the line profile is roughly described by the convolution of a Gauss (γ_D HWHM) and a Lorentz (γ_c HWHM) functions, producing the usual Voigt function. In fact when the pressure increases the Doppler line is progressively narrowed by the confinement of the molecules in the buffer gas (Dicke effect [9,10]). This effect can be described by the soft [6] or hard [7,8] collision model which are equivalent to the convolution product of a confinement narrowed profile, characterized by the narrowing parameter β^0, with a Lorentz profile. The narrowing parameter can be compared to the dynamic friction, coefficient, β^0_{diff},

$$\beta^0_{diff} = \frac{k_B T}{2\pi c m_1 D_{12}}, \quad (1)$$

where m_1 is the mass of the active molecule and D_{12} the mass diffusion coefficient calculated from the transport properties of gas mixtures [32].

As it is well known, the soft collision model corresponds to a limit case where a significant velocity change of the active molecule needs many individual collisions and is convenient when the perturber mass is much smaller than the absorber mass. The hard collision model corresponds to the opposite limiting case