Super Lorentzian effects on the wings of self-broadened HCl and of HCl diluted in Ar

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Abstract. Super-Lorentzian effects in the troughs between HCl lines were observed long time ago [Varanasi et al., J Quant Rad Transfer, Vol. 12, pag. 857, 1972]. The observed spectral shape was then modelled by using an empirical law and there was no explanation about the mechanisms underlying these super-Lorentzian effects. In this work, new spectra of pure HCl and HCl diluted in Ar have been measured using a high resolution Fourier Transform spectrometer, for pressure from 6 to 10 bars. Spectra of pure HCl and HCl in Ar have been also computed using classical molecular dynamics simulations (CMDS). First comparisons between CMDS-calculated spectra and measured ones, for regions at the troughs between HCl lines, show that the observed super-Lorentzian behaviour is correctly reproduced by the calculations. These results thus open the paths for the determination of the origin of these super-Lorentzian effects.

1. CMDS calculations and experimental spectra

Detailed description of our classical molecular dynamic simulations for HCl can be found in [1], thus only the main features are recalled here. In our CMDS calculations, a large number of molecules ($>10^6$) are treated. They are placed in cubic boxes with periodic boundary conditions [2]. Their initializations are perfomed as follows: the center of mass position and molecular axis orientation are randomly initialized. For the translational and angular velocity, their orientations are randomly initialized while Maxwell-Boltzmann distributions are used for their modulus. The time evolution of the system is then computed using the classical equation, i.e. for the molecule i :

$$m\dot{\vec{v}}_i = \vec{f}_i \quad \text{and} \quad I\dot{\vec{\omega}}_i = \vec{\tau}_i \tag{1}$$

Where the force f and the torque τ are computed from the potential gradient summed over all nearby collision partners $\sum_{j \neq i} \vec{\nabla} V_{i,j}$. The intermolecular potential is taken from Refs. [3,4]. These calculations thus provide the center of mass positions and velocities as well as the orientations and angular velocity of all molecules at all times. The auto-correlation function of the dipole moment carried by the

molecular axis and thus the corresponding spectrum can thus be computed using the Fourier-Laplace transform. Note that the same requantization procedure as in Ref. [1] has been used in order to associate a rotational quantum number J_m to a value of ω_m, i.e. $\frac{1}{2}I\omega_m^2 \approx \frac{\hbar^2}{2I}J_m(J_m+1)$.

Spectra of pure HCl and HCl diluted in Ar in the 2-0 band have been measured at room temperature at pressures ranging from 6 to 10 bars, using a Fourier transform spectrometer. The detailed description of the experimental setup can be found in [5]. Spectra of HCl diluted in Ar in the 1-0 band, measured at room temperature and pressures up to 350 bars of Ref. [6] are also used for the comparison with our calculations.

2. First results and discussions

In order to analyze both measurements and CMDS-calculated spectra, different following steps have been carried: (i) at low pressure range, line parameters such as line position, line integrated intensity and line broadening have been retrieved from fits of measured (or calculated) spectra using the Voigt profile, (ii) using these data, we then calculate the corresponding spectra at higher pressure (more than 6 bars) using the Lorentzian profile. From these spectra, we determine the absorption at the troughs between HCl P and R branches lines, which will be denoted $a_{Lorentz}$. Absorption at the same regions but determined from measured (CMDS-calculated) spectra are denoted a_{obs} (a_{CMDS}). The super-Lorentzian effect is then determined by calculating the ratio $a_{obs}/a_{Lorentz}$ ($a_{CMDS}/a_{Lorentz}$).

Figure 1 show the $a_{obs}/a_{Lorentz}$ ratio obtained for three pressures: 6, 8 and 10 bars for pure HCl in the 2-0 band. We can observe that this ratio is constant with pressure as expected since absorption in the wings is proportional to the squared pressure [7]. The same analysis procedure has been performed for all measured and CMDS-calculated spectra.
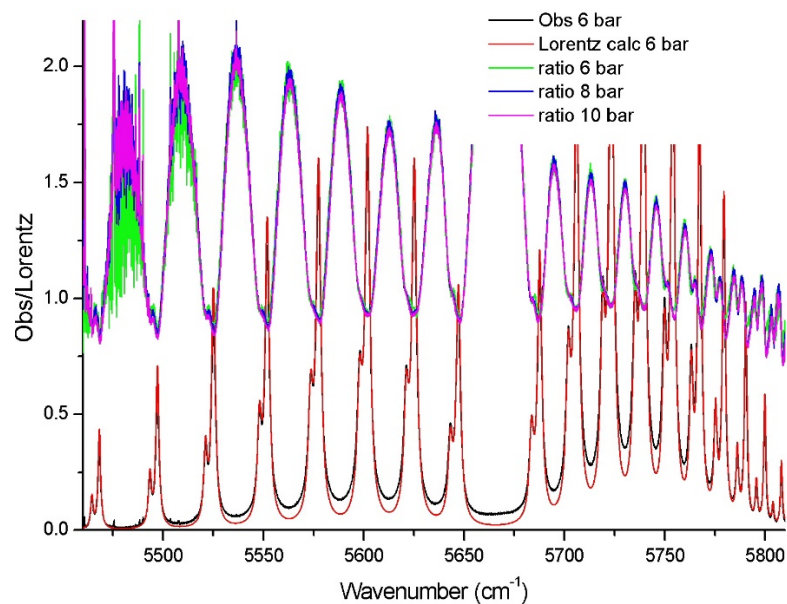

Figure 1: Comparison between spectra calculated using the Lorentz profile and measurements at 6 bars and the $a_{obs}/a_{Lorentz}$ ratio at various pressures for pure HCl.

Figure 2 shows the comparison between the measured and CMDS-calculated results for HCl diluted in Ar in the 1-0 band where a very good agreement can be observed. Work is now in progress for the 2-0 band region and for self-broadening HCl. We also plan to perform similar study for HCl in

CO_2 for which the observed super-Lorentzian effect is much larger. Finally, the different physical mechanisms contributing to this super Lorentzian behavior will be determined and analyzed using CMDS.
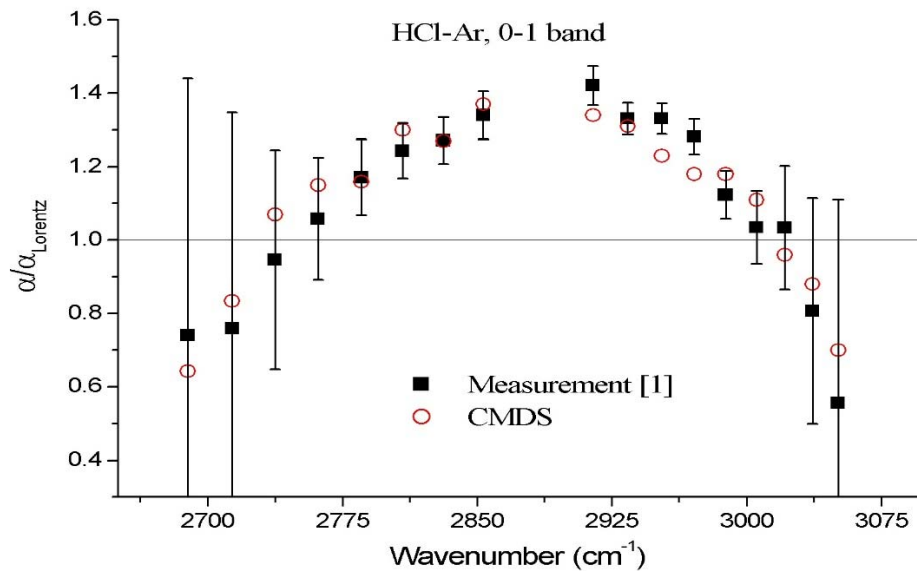

Figure 2: Comparison between measured and CMDS-calculated results

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