

DENSITY DEPENDENCE OF THE PRESSURE INDUCED SHIFT OF HCl ROTATIONAL LINES PERTURBED BY ARGON

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The density dependence of the pressure induced shift of the HCl pure rotational lines, perturbed by argon, has been measured. The shifts were measured for the rotational transitions $J \rightarrow J+1$, with J from 1 to 9, at a temperature of 162.5 K and argon densities between 39 and 480 amagat. In this density regime, the HCl rotational linewidths are known to depend non-linearly on the density. It is observed that most of the rotational lineshifts show no significant deviation from a linear density dependence. It therefore seemed justified to determine lineshift cross sections from the slopes of the straight lines that fitted the measured shifts best. The magnitude of the cross sections thus determined is significantly larger than has been predicted. The relevance of the lineshift cross sections for the determination of the HCl-Ar intermolecular potential is discussed. A possible explanation for the qualitatively different density dependence of lineshifts and linewidths is indicated.

The width and shift of rotational absorption lines of non-spherical molecules perturbed by foreign gases are very sensitive to the anisotropic part of the rotor-perturber intermolecular potential. For this reason, the experimental determination of rotational line-shapes is a useful tool to study anisotropic intermolecular interactions. Hydrogen chloride perturbed by argon is a system that has been subject to extensive experimental and theoretical investigations. The width of the pure rotational lines of HCl broadened by Ar has been measured at room temperature by Gebbie and Stone [1], Pourcin [2] and Scott [3], and at various temperatures in the range between 125 and 300 K by van Aalst [4]. The pressure induced frequency shift of the $J=0 \rightarrow 1$ transition has been measured by the same authors; for all higher- J rotational transitions, this shift was however too small to be observed. Below, we present rotational lineshift measurements on the HCl-Ar system that differ from the earlier measurements in that a much higher argon pressure was applied.

The far infrared rotational absorption spectra were measured with a Michelson interferometer (RIIC-Beckmann, type FS-720). The HCl-Ar mixture was held in a 15 cm pathlength, stainless steel, variable temperature cell with silicon windows (10 mm in thick-

ness) [5]. The measurements were performed at a temperature of 162.5 K and at Ar densities of 100, 200, 300, 400 and 480 amagat (cf. $\rho_{\text{liq}} = 784$ am); the HCl concentration was always less than 1:1000. Lineshifts of the higher- J rotational transitions ($J \rightarrow J+1$, with $J=6$ to 9) were also measured at an argon density of 39 amagat. The lineshifts were determined by fitting a sum of Lorentzians to the measured spectral intensity; for details see ref. [5]. The sign of the lineshift is defined such that a shift towards higher frequencies is positive. In table I the measured lineshifts are given for the rotational transitions $J=1 \rightarrow 2$ to $J=9 \rightarrow 10$; the shifts of the $J=0 \rightarrow 1$ transitions could not be determined with sufficient accuracy, because the $J=0 \rightarrow 1$ transitions are very broad at the high densities used in these experiments. All data have been corrected for the effect of the isotope splitting of the H^{35}Cl and H^{37}Cl isotopes on the lineshift. Where more than one independent measurement of a given shift was available, the spread in the values of the measured shift was used to estimate the error in the experimental data. The average estimated error in the shifts is approximately 0.12 cm^{-1} ; error estimates that are considerably smaller than this number should be considered accidental. The density dependence of the lineshifts is visualized in fig. 1.

Table 1
Measured lineshifts Δ_J of HCl rotational transitions (cm^{-1})

$J \rightarrow J+1$	$\rho = 39 \text{ am}$	$\rho = 100 \text{ am}$	$\rho = 200 \text{ am}$	$\rho = 300 \text{ am}$	$\rho = 400 \text{ am}$	$\rho = 480 \text{ am}$
1 \rightarrow 2		0.4 ± 0.1	0.55 ± 0.15	2.4	2.3 ± 2.3	4.4 ± 1
2 \rightarrow 3		0.45 ± 0.25	1.45 ± 0.5	1.95	2.45	3.1
3 \rightarrow 4		-0.11 ± 0.04	-0.37	-1.1 ± 0.35	-1.6 ± 0.05	-2.3 ± 0.2
4 \rightarrow 5		-0.20 ± 0.02	-0.70	-1.1 ± 0.03	-1.4 ± 0.2	-2.0 ± 0.25
5 \rightarrow 6		-0.25 ± 0.15	-0.49 ± 0.15	-0.62 ± 0.1	-0.56 ± 0.1	-1.4 ± 0.1
6 \rightarrow 7	-0.09	-0.22 ± 0.13	-0.49 ± 0.03	-0.58 ± 0.05	-0.82 ± 0.15	-0.90 ± 0.03
7 \rightarrow 8	-0.05	-0.22 ± 0.04	-0.40 ± 0.03	-0.50 ± 0.03	-0.71 ± 0.12	-0.73 ± 0.03
8 \rightarrow 9	-0.06	-0.19 ± 0.04	-0.36 ± 0.07	-0.48 ± 0.07	-0.58 ± 0.13	-0.73 ± 0.2
9 \rightarrow 10	-0.05	-0.1	-0.31	-0.54	-0.77	-0.81

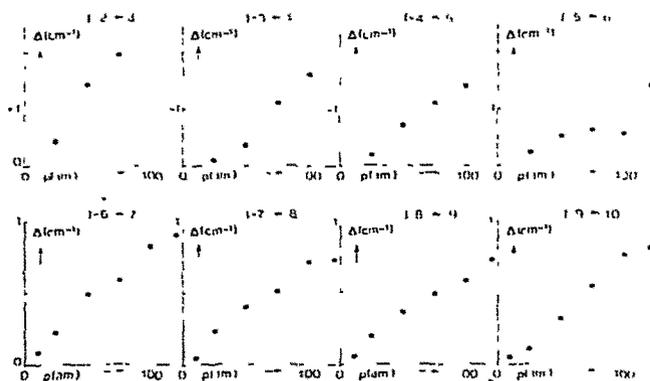


Fig. 1. Shift of the central frequency of the rotational far infrared transitions of HCl dissolved in Ar, as a function of the argon density. The shifts of the transitions with initial $J = 2$ through 9, have been displayed. It should be noted that the shift of the $J = 2 \rightarrow 3$ transition is positive, whereas all other shifts that are displayed are negative. The temperature is 162.5 K.

In an earlier publication [6] we have shown that, at the densities used in these experiments, the relation between the halfwidth of the HCl rotational transitions and the Ar density is no longer linear. Such a deviation from the linear relation between halfwidth and density that is obeyed at low densities, is in fact not surprising. On theoretical grounds one may expect a linear relation between linewidth (-shift) and density if the impact approximation is valid (this is however by no means the only condition that has to be fulfilled [7]). Using the impact approximation, one arrives at a theoretical expression for the lineshift Δ , that is of the following form:

$$\Delta_J = \rho \langle v \rangle \sigma_J / 2\pi c, \quad (1)$$

where σ_J is the cross section for lineshift, ρ is the number density of perturber molecules, and $\langle v \rangle$ is the average relative velocity of rotor and perturber. The impact approximation may be expected to hold as long as the time between collisions is much longer than the duration of a collision, i.e. at low densities. This condition is no longer fulfilled at the densities used in the present measurements. Consequently, there is little reason to expect a linear density dependence of the rotational lineshifts. To investigate whether significant deviations from a linear density dependence did occur, we tried to fit the measured shifts to a linear expression of the form:

$$\Delta(\rho) = a\rho. \quad (2)$$

It was found that, except for the $J=3 \rightarrow 4$ transition, all measured shifts were, within experimental error, compatible with such a linear density dependence. The density dependence of the lineshift of the $J=3 \rightarrow 4$ transition appears to be more or less quadratic. Fitting the frequency shifts of this transition to an expression of the form

$$\Delta(\rho) = a\rho + b\rho^2, \quad (3)$$

yielded a value for the coefficient of the linear term, which did not differ significantly from zero. The accuracy of the measurement of the $J=1 \rightarrow 2$ shift is rather poor. Apart from the observation that the frequency shift of this transition is positive, no quantitative information can be extracted from the experimental data. From the best fits of eq. (2) to the measured lineshifts, cross sections for the lineshifts of the $J=2 \rightarrow 3$ to $J=9 \rightarrow 10$ transitions were estimated (assuming $a = \langle v \rangle \sigma / 2\pi c$). These cross sections are tabulated in

Table 2

$J \rightarrow J+1$	$\sigma_{\text{shift}} (\text{\AA}^2)$
2 \rightarrow 3	$+9.97 \pm 0.95$
3 \rightarrow 4	$+0.03 \pm 0.51$ ^{a)}
4 \rightarrow 5	-6.00 ± 0.35
5 \rightarrow 6	-4.38 ± 0.31
6 \rightarrow 7	-3.26 ± 0.12
7 \rightarrow 8	-2.75 ± 0.12
8 \rightarrow 9	-2.56 ± 0.09
9 \rightarrow 10	-2.92 ± 0.14

^{a)} From quadratic fit.

table 2. One immediately notes that all cross sections for the shift of the rotational transitions $J \rightarrow J+1$ with $J > 3$, are negative. Moreover the magnitude of the cross sections seems to be decreasing more or less monotonically with increasing J , from the $J=4 \rightarrow 5$ transition on. For the higher- J transitions, the estimated error in the cross sections is always less than 10%. Fitting the lineshifts to a non-linear density dependence [eq. (3)], yielded slightly different values for the cross sections (obtained from the coefficient of the linear term). As the quadratic fit was not significantly better than the linear one (except for the $J=3 \rightarrow 4$ transition), there is little reason to prefer the cross sections that were determined from the non-linear fit over the values that resulted from the linear fit. The measured lineshift cross sections are about an order of magnitude smaller than the corresponding cross sections for line broadening [4,5]. This explains why the shift cross sections could not be determined by measuring the pressure induced lineshift at the much lower argon densities that were used in earlier experiments [1-4].

The magnitude and sign of lineshift cross sections may be expected to depend sensitively on the shape of the anisotropic intermolecular potential surface. Neilsen and Gordon [7] did a systematic attempt to determine the HCl-Ar anisotropic potential surface, using all experimental data on the rotational lineshapes (and NMR relaxation times [8]) that were available at the time. To this end, these authors investigated the dependence of computed cross sections (e.g. for line broadening and lineshift) on the parameters that characterize the anisotropic potential surface. In this way it proved possible to select a set of anisotropic potential parameters that did account for the available data,

within experimental accuracy. Apart from the computed cross section for the rotational lineshift of the $J=0 \rightarrow 1$ transition, the magnitude of all cross sections that resulted from these calculations was smaller than the estimated computational accuracy. In view of the great computational effort that a more accurate calculation of the lineshift cross sections would require, Neilsen and Gordon concluded that the experimental determination of these cross sections would not provide material that could easily be used to enhance our knowledge of the HCl-Ar anisotropic potential surface. It seems however that, even with the present accuracy of the Neilsen-Gordon calculations ($\pm 1\%$, which would correspond to about 1\AA^2 in a typical cross section), the cross sections in table 2 differ significantly from the results in ref. [7] ($\sigma_J = 0 \pm 1 \text{\AA}^2$).

A more recent calculation by Dunker and Gordon [9] shows that the "fully optimized" potential, which was proposed by Neilsen and Gordon to account for the far infrared and NMR data, does not account for the observed properties of the Ar-HCl van der Waals molecule [10], and must therefore be rather different from the true HCl-Ar intermolecular potential. Moreover, a recent calculation by Smith and Giraud [11] shows that two quite different anisotropic potentials (i.e. the Neilsen-Gordon potential "52" and a theoretical potential surface obtained by Stevens and Robert) both account reasonably well for the observed line broadening of HCl by Ar at 300 K. It therefore seems probable that, with the present experimental accuracy, rotational line broadening data are compatible with many different anisotropic potential surfaces. Conversely, it is impossible to decide between these potential surfaces on the basis of experimental information on lineshapes (and NMR relaxation times) that is presently available. For this reason we feel that, if one aims at increasing our knowledge of the HCl-Ar interaction, all available experimental information, including the data on the van der Waals molecules [10,12,13] and on the rotational lineshifts must be taken into account, even though the computational effort required to correlate this information with anisotropic potential parameters will be considerable.

The very fact that the density dependence of the HCl rotational lineshifts is more or less linear up to quite high argon densities, whereas the linewidths of the same rotational transitions have a pronounced non-linear density dependence, is, by itself, intriguing. A

possible explanation for this qualitatively different behaviour, may be arrived at, following an approach that has been discussed in some detail in an earlier publication [9]. In this picture, line broadening and shift are directly proportional to the real and imaginary part of the Fourier–Laplace transform of the autocorrelation function of the time dependent perturbation that acts on the rotating molecule. To be more precise, only certain frequency components of this Fourier–Laplace transform contribute to line broadening (-shift). A large contribution to the line broadening comes from the $\omega=0$ part of the power spectrum of the perturbation. Molecular dynamics calculations on Lennard-Jones “argon” [14,5] have shown that this $\omega=0$ component has a pronounced non-linear density dependence, giving rise to a non-linear density dependence of the rotational linewidths. The corresponding contribution to the rotational lineshifts, on the other hand, is zero; hence the lineshifts are exclusively determined by the non-zero frequency components of the perturbing potential. The molecular dynamics calculations indicate that, for the densities used in the present measurements, the relevant non-zero frequency components of the perturbation depend more or less linearly on the density. One would therefore expect a more or less linear density dependence of the rotational lineshifts, as is indeed observed.

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