EXPERIMENTAL AND CALCULATED CROSS SECTIONS FOR PRESSURE BROADENING OF PURE ROTATIONAL RAMAN LINES OF HCl

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The pure rotational Raman transitions $J = 0 \rightarrow 2$ through $J = 5 \rightarrow 7$ of HCl have been measured. Results are presented for HCl without admixture at 1 atm and 300 K, and for HCl with argon at pressures of about 10 and 20 atm. The HCl self-broadening is compared with earlier results. The linewidths of HCl broadened by argon are compared with the result of calculations. Cross sections are calculated based on different potentials which have been suggested for the Ar–HCl system.

1. Introduction

The difficulties that beset the experimental determination of the HCl–Ar potential energy surface are in many respects representative of the problems encountered in the experimental determination of anisotropy in intermolecular interactions in general. It is for this reason that considerable attention has been paid to the physical properties of the HCl–Ar system. The experimental information that is presently available can be divided into four distinct categories: (1) transport properties of the gas mixture (e.g. diffusion coefficients) [1], (2) molecular beam scattering data [2], (3) spectroscopic information on HCl–Ar van der Waals dimers (both, in cold molecular beams [3] and in the bulk gas mixture [4]) and (4) spectroscopic information on rotational relaxation phenomena (e.g. far infrared rotational line broadening [5,6] and NMR measurements of the longitudinal relaxation time of the HCl proton [7]). The experiments in categories (3) and (4) are particularly sensitive to the anisotropy of the intermolecular interaction.

In this paper, we will present still another experimental contribution, namely the broadening of HCl rotational Raman transitions by Ar. We will thereupon

compare the experimental rotational line broadening cross sections with theoretical estimates for these cross sections. We arrive at these theoretical estimates by doing semiclassical trajectory calculations for a number of potential energy surfaces that have been proposed for the HCl–Ar system in the literature. Semiclassical trajectory calculations on the HCl–Ar system were first presented in a paper by Neilsen and Gordon [8] in 1973. Cross sections were computed for a number of rotational relaxation processes, in particular those for infrared and Raman rotational line-broadening, sound absorption and NMR and NQR relaxation. Through comparison of the computed cross sections, for different sets of potential parameters, with the experimental cross sections available at the time, Neilsen and Gordon were able to arrive at a potential energy surface that was compatible with the experimental data. In a subsequent publication Dunker and Gordon [9] used this same potential surface to predict some properties of the HCl–Ar van der Waals dimer. The agreement of the results of this latter calculation with the experimental data of Novick et al. [3] was poor. More recently, Holmgren et al. [10] obtained several potential surfaces that were compatible with the dimer properties, through a non-linear least squares fit of computed dimer properties to the experimental values. For these latter potentials no semiclassical trajectory calculations of the type described by Neilsen and Gordon, have been reported thus far. Consequently,

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it is not known whether these potential surfaces are compatible with the rotational relaxation data.

Since the publication of Neilsen and Gordon's paper, new experimental information has become available on the temperature dependence of the broadening and shift of the HCl far infrared rotational transitions by Ar [6]. Thus far, however, no measurements of the rotational Raman cross sections have been reported. It is the aim of this paper to partly fill this gap.

The outline of the present paper is as follows. First, the experimental determination of the widths of 5 rotational Raman lines of HCl, broadened by argon, will be discussed. We will thereupon present the results of semiclassical trajectory calculations, using as input some of the potential energy surfaces that have been proposed for the HCl—Ar system. The rotational relaxation cross sections thus computed will be compared with the experimental data, in particular the rotational Raman line broadening cross sections to be presented below.

2. Experimental

The HCl rotational Raman spectra were measured using a standard light scattering setup. An Ar-ion laser (Spectra Physics, model 171), operated at the 514 nm transition, was used as a source. At this particular frequency, the laser had a power stabilised output of up to 8 W. The laser was not single moded. The HCl—Ar gas mixture was contained in a stainless steel cell with quartz windows. The laser light was thereupon collimated and focused on the entrance slit of a grating monochromator (Jobin—Ivon, model THR-1500). The output signal from the monochromator was detected by a cooled photomultiplier tube (EMI 9558QA) and processed by standard photon counting equipment. The gases (argon, Matheson 99.998% and HCl, Matheson 99%) were passed through a cold trap, argon in addition through molecular sieve, and finally through a glass filter.

The Stokes rotational Raman transitions $J = 0 \rightarrow 2$ through $J = 5 \rightarrow 7$ of HCl were measured at room temperature (295 K). Measurements were performed at argon pressures of 0, 9.71 and 19.24 atm; the HCl pressure was held constant at 0.99 atm. Even for the HCl rotational transition closest to the laser frequency there was no detectable contribution to the signal due to leak-

age of light at the laser frequency.

To extract rotational Raman linewidths from the experimental scattering data, we proceeded as follows. The instrumental function was determined by measuring the shape of the isotropic Rayleigh scattering of the gas mixture in exactly the same configuration as was used when collecting the rotational Raman scattering data (the resolution, using the monochromator in the single pass mode, was typically 0.26 cm^{-1}). It was assumed that the rotational Raman lineshapes determined in the experiment could be approximated by the convolution of the instrumental function with a lorentzian. In fact, as both $H^{35}Cl$ and $H^{37}Cl$ isotopes contribute to the light scattering, the instrumental function was convoluted with the sum of two lorentzians of equal width at a separation equal to the frequency separation of the rotational Raman transitions of unperturbed $H^{35}Cl$ and $H^{37}Cl$ molecules. This separation varies from ≈ 0.1 cm^{-1} for the $J = 0 \rightarrow 2$ transition to ≈ 0.4 cm^{-1} for the $J = 5 \rightarrow 7$ transition; the ratio of the areas of the two lorentzians was fixed at the ratio of the natural abundances of the ^{35}Cl and ^{37}Cl isotopes (i.e. 3:1). Rotational linewidths were determined by direct comparison of the experimental lineshapes with convoluted lorentzians, for different values of the halfwidths of the lorentzians. Using this procedure, it proved possible to fit all rotational Raman lines within experimental accuracy. In table 1 the halfwidths thus obtained are given as a function of the argon density for the HCl rotational transitions $J = 0 \rightarrow 2$ through $J = 5 \rightarrow 7$.

The width of a given rotational transition is due to both HCl—HCl self-broadening and broadening resulting from the interaction with argon. For the relatively low density gas mixtures studied in the present experi-

Table 1

Experimental linewidths (half width at half height) in cm^{-1} for the pure rotational Raman transitions of HCl (0.99 atm) in a mixture with Ar at a temperature of 295 K

Initial J	$P_{Ar} = 0$ atm	$P_{Ar} = 9.71$ atm	$P_{Ar} = 19.24$ atm
0	0.225 ± 0.008	0.657 ± 0.056	1.333 ± 0.038
1	0.237 ± 0.008	0.561 ± 0.056	0.804 ± 0.019
2	0.263 ± 0.008	0.707 ± 0.056	0.830 ± 0.019
3	0.229 ± 0.008	0.574 ± 0.056	0.826 ± 0.019
4	0.195 ± 0.006		0.760 ± 0.018
5	0.184 ± 0.008		0.606 ± 0.018

Table 2

Experimental line broadening and the cross sections of the HCl rotational Raman lines for HCl–HCl and HCl–Ar at 295 K

Initial J	$\bar{\sigma}_{HCl-HCl}(cm^{-1}/atm)$	$\sigma_{HCl-HCl}(\text{Å}^2)$	$\bar{\sigma}_{HCl-Ar}(cm^{-1}/atm)$	$\sigma_{HCl-Ar}(\text{Å}^2)$
0	0.225 ± 0.008	286 ± 10	0.0513 ± 0.0062	67.7 ± 8.2
1	0.237 ± 0.008	302 ± 10	0.0299 ± 0.0070	39.5 ± 9.2
2	0.263 ± 0.008	335 ± 10	0.0330 ± 0.0070	43.6 ± 9.2
3	0.229 ± 0.008	292 ± 10	0.0317 ± 0.0020	41.9 ± 2.7
4	0.195 ± 0.006	248 ± 8	0.0292 ± 0.0017	38.5 ± 2.2
5	0.184 ± 0.008	234 ± 10	0.0216 ± 0.0017	28.5 ± 2.2

ments, the total linewidth may be written as the sum of these two contributions:

$$\Delta\nu_{1/2} = \rho_{HCl} \langle v \rangle_{HCl-HCl} \, \sigma_{HCl-HCl}$$

$$+ \rho_{Ar} \langle v \rangle_{HCl-Ar} \, \sigma_{HCl-Ar} , \qquad (1)$$

where $\rho_{HCl}(\rho_{Ar})$ are the HCl(Ar) number densities, $\langle v \rangle_{HCl-HCl}, \langle v \rangle_{HCl-Ar}$ are the average relative velocities of an HCl–HCl(HCl–Ar) pair and $\sigma_{HCl-HCl}, \sigma_{HCl-Ar}$ are the cross sections for self-broadening and broadening due to argon respectively. According to eq. (1), the halfwidth of a given rotational transition depends linearly on the argon density. From the slope of the line $\Delta\nu_{1/2}$ versus ρ_{Ar}, the cross section σ_{HCl-Ar} may be determined. $\sigma_{HCl-HCl}$ can be obtained from the intercept of this line of $\rho_{Ar=0}$. Straight lines were fitted to the experimental points of table 1, for all rotational transitions. The cross sections σ_{HCl-Ar} and $\sigma_{HCl-HCl}$ as determined from the slopes and intercepts of these lines are given in table 2, together with error estimates. In fig. 1 the line broadening, $\bar{\sigma}$, for pure HCl for the different rotational Raman transitions, is displayed. In the same figure, values for the same line broadening, as determined previously by other investigators [11–13] have been indicated. Also shown are theoretical estimates by Gray [14]. As can be seen, the present results are in fair agreement with the data of Fabre [11] and Perchard [12]. It is not clear why the cross sections given by Rich and Welsh [13] are considerably smaller than the results of any of the other groups. The theoretically predicted cross sections are in qualitative agreement with the present results and the data of refs. [11, 12], though all calculated cross sections are seen to be about 10% too large.

In fig. 2 the experimental cross section σ_{HCl-Ar} for the rotational Raman transitions $J = 0 \rightarrow 2$ through $J = 5 \rightarrow 7$ are displayed. No attempt was made to de-
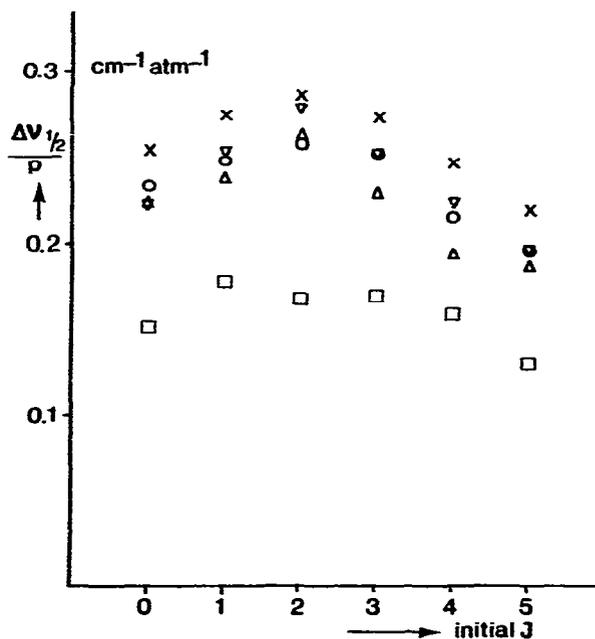

Fig. 1. The self-broadening of rotational Raman lines of HCl at 300 K. × theoretical, ref. [14]; ○ experimental, ref. [11]; ▽ experimental, ref. [12]; △ experimental, this work; □ experimental, ref. [13]. The values given are the half width at half height for one atmosphere.

termine the pressure induced frequency shift of the HCl rotational Raman lines.

3. Calculations

In this section we present the results of semiclassical trajectory calculations for a number of potential surfaces that have been proposed for the HCl–Ar system. As has been mentioned in section 1, Neilsen and
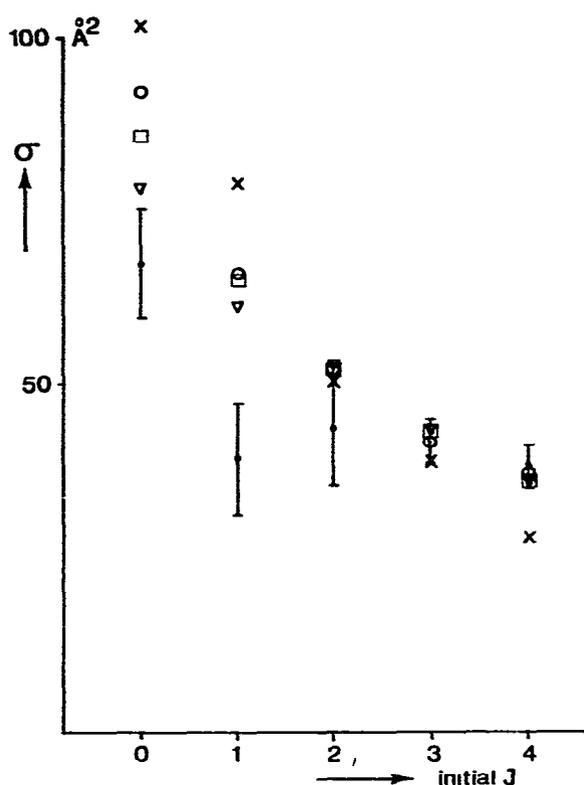
Fig. 2. The experimentally determined cross sections for broadening of rotational Raman lines of HCl in argon compared with values calculated using: o potential "e", ref. [8]; X potential "747", ref. [10]; □ potential "52", ref. [8]; and ∇ with values given in ref. [8].

Gordon [8] did such semiclassical trajectory calculations to investigate the dependence of cross sections for a number of relaxation processes upon the parameters that characterize the HCl—Ar potential energy surface. Making the assumption that, for not too large variations of the parameters, the change in the cross sections is linear in the change of the parameters, these authors determined a set of potential parameters that supposedly fitted all available data within experimental accuracy. Unfortunately, Neilsen and Gordon never actually published the results of semiclassical trajectory calculations for this "fully optimized" potential (designated potential "e" in ref. [9]). Below we present line broadening cross sections computed for this potential "e". We also present the results of semiclassical trajectory calculations for a potential that is designated as potential "52" in ref. [8]. Potential 52 was

used by Neilsen and Gordon as an initial estimate of the HCl—Ar potential energy surface. Because the results of the calculations for potential 52 have been given in great detail, we did calculations for the same potential in order to be able to compare the results. The parameters characterising these potentials are given in table 3. Also included is potential "747" which corresponds with a potential of a form suggested for the ArHCl complex by Holmgren et al. [10] with parameter values $\epsilon_0 = 187$ K, $\epsilon_1 = 81$ K, $\epsilon_2 = 30$ K; $\alpha_0 = 14.9$, $\alpha_1 = 10.2$, $\alpha_2 = 12.9$; and $r_{m0} = 3.83$ Å, $r_{m1} = 4.13$ Å, $r_{m2} = 4.28$ Å. Such a potential seems to give a fair reproduction of the angular and radial properties of the ArHCl complex measured in molecular beam experiments [3, 15].

In the semiclassical trajectory calculations, the translational degrees of freedom are treated classically, whereas the internal degrees of freedom of the HCl molecule are treated quantum mechanically. In the actual calculations, we followed the procedure outlined in ref. [8]. Our choice of the set of relative kinetic energies for which we did the trajectory calculation was slightly different from the set chosen by Neilsen and Gordon. Furthermore we used a basis set for the HCl molecule of rigid rotor eigenfunctions with $J \leqslant 7$. The effect of expanding the basis set to include all states with $J \leqslant 10$ was checked but no significant effect on the values of the cross sections for the five lowest rotational transitions was found. As a check, we compared our results obtained with potential 52 with those given by Neilsen and Gordon for the same potential. The comparison is shown in table 4. One notes that for all but the lowest two transitions, the agree-

Table 3

Potential parameters for the potentials used in the semiclassical calculations (see ref. [8])

Parameter	Pot 52	Pot e	Pot A₁	747 [a]
ϵ (K)	202	202	189.9	187.04
r_m (Å)	3.805	3.805	3.883	3.828
α	13.5	13.5	14.5	14.9
$P_1 A$	0.30	0.32	0.61	0.32
$P_1 R$	0.35	0.51	0.55	0.35
$P_2 A$	0.09	0.24	0.39	0.14
$P_2 R$	0.65	0.76	0.22	0.31

[a] These coefficients correspond with the values of the potential parameter given.

Table 4
Experimental and calculated line broadening cross sections (A^2) for rotational Raman lines of HCl broadened by Ar and for the far infrared pure rotational absorption lines of HCl broadened by Ar at 295 K

Initial J	Experimental [a]	Pot 52		Pot e	Pot A_1	Pot 747
		this work	ref. [8]			
Raman						
0	67.7 ± 8.2	85.8	77.9	92.1	105.9	101.5
1	39.5 ± 9.2	65.0	61.5	65.9	96.9	78.7
2	43.6 ± 9.2	53.5	51.6	51.7	51.6	51.1
3	41.9 ± 2.7	43.0	42.8	42.3	32.9	38.7
4	38.5 ± 2.2	36.5	35.7	37.1	26.7	28.2
5	28.5 ± 2.2					
Far infrared						
0	89.90 ± 5.85	80.4	74.0	89.5	102.4	111.6
1	54.48 ± 7.81	61.4	59.2	63.2	94.2	75.9
2	45.52 ± 2.44	49.0	47.4	49.3	42.4	49.6
3	32.02 ± 3.71	37.9	38.4	49.0	27.1	38.2
4	29.30 ± 5.85	29.4	31.5	33.0	23.8	28.5
5	29.14 ± 6.20	26.5	25.4	27.3	21.7	20.0

[a] Experimental far infrared results were published in ref. [6].

ment is good. For the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ transitions, the cross sections computed by Nielsen and Gordon are somewhat smaller than the values we obtain.

The cross sections for the low J transitions are quite large (≈ 70 A^2 for $J = 0 \rightarrow 2$). Consequently, collisions with large impact parameters contribute appreciably to these cross sections. Since there is only a discrepancy for low J transitions, it seemed appropriate to test our computing method for large values of the impact parameter. To this end we computed the σ-matrix for a collision in which the perturber follows a straight trajectory at a large impact parameter ($b = 6.76$ Å). For this value of the impact parameter, the anisotropic interactions are very weak and perturbation theory should be applicable. Comparing our results with the analytic expression derived from the Anderson theory [16], we found good agreement.

Considering the above mentioned differences in approach and the checks made, we come to the conclusion that the differences in the final results must have a computational origin. The slightly different trajectories may be the source, or possibly the manner in which the finite steps in the time evolution have been calculated. This confronts us with the limitations of such calculations.

Fig. 2 shows a comparison of the experimental rotational Raman cross sections that have been computed for the different potential surfaces. In table 4 these cross sections and the experimental and computed cross sections for far infrared rotational line broadening are given. It is observed that the Neilsen and Gordon potential 52 gives the best overall agreement with experiment; the "fully optimized" potential "e" is slightly worse. Potential "747" yields cross sections that differ appreciably from the experimental results. It is somewhat surprising that potential 52 which was introduced in ref. [8] as an initial estimate of the HCl—Ar potential surface, yields better results than the supposedly fully optimized potential "e". The fact that potential "747" does not agree with the line broadening data, is not surprising since this potential was designed to fit the properties of cold HCl—Ar dimers. These properties depend almost exclusively on the shape of the anisotropic potential energy surface about its absolute minimum in contrast to rotational line broadening which depends also on the steep repulsive part of the potential. From the work of Dunker and Gordon [9] it is clear that the potential "e" and 52 are not compatible with the properties of the HCl—Ar dimers. Consequently, we are forced to conclude that, as yet, no potential energy surface is available

that correctly predicts both the rotational line broadening and the dimer properties of the HCl—Ar system.

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