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Correlation of Linestrength and Linewidth in Highly-Resolved Infrared Spectroscopy**

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Abstract: Rotational-vibrational spectra found in even excellent textbooks show a wrong ratio for the $H^{35}Cl/H^{37}Cl$ rotational-vibrational lines. Distortion is a common problem encountered when spectral resolution is insufficient to measure the true shape of a line. Unfortunately deconvolution with the apparatus function is not always possible. In this paper the correlation of the Lorentz linewidth and linestrength in case of a Voigt profile is studied and some consequences are explained.

The natural linewidth of a (1–0) rotational-vibrational transition of e.g. HCl molecules is of the order of 10^{-8} to 10^{-7} cm^{-1}. At a pressure of 133.32 Pa (1 torr) the lineshape can be described by a Voigt profile and the linewidth is about $7 \cdot 10^{-3}$ cm^{-1}[1]. A resolution better than the linewidth is necessary to measure the true shape of such a line and that is often not available. For this reason all rotational-vibrational spectra found in even excellent textbooks show a wrong ratio for the $H^{35}Cl/H^{37}Cl$ rotational-vibrational lines[2]. The problem of unresolved narrow spectral lines was first treated by *Ladenburg* and *Reiche*[3]. They introduced the idea of the equivalent width which was used by *Benedict* et al.[4] in a careful analysis to determine (1–0) rotational-vibrational oscillator strengths of $H^{35}Cl$ and $H^{37}Cl$. Because of computational problems at that time it was necessary to apply an approximation developed by *Plass* and *Fivel*[5].

The strength of a line can be measured by determining the integrated absorption S of a line, defined by the relation

$$S = \int_0^\infty k_\nu \mathrm{d}\nu \qquad (1)$$

where k_ν is the absorption coefficient in cm^{-1}. k_ν of a gas at a path length l is given in terms of the transmission $T = I_\nu / I_\nu^0$, where I_ν is the intensity of the light transmitted by the sample, according to *Lambert*'s law,

$$-\ln T = \varepsilon_\nu = k_\nu \cdot l \qquad (2)$$

where ε_ν is the extinction. For gases at sufficiently low pressure, the integrated absorption S is directly proportional to the

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number of absorbing molecules in the optical path:

$$S = S^0 \cdot P \tag{3}$$

P is the pressure of the absorber. The equivalent width W is defined by the relation

$$W = \int_0^\infty (1 - T)\mathrm{d}\nu \tag{4}$$

which is the integral of the fractional energy removed from the incident radiation. The range in equation (4) should be large enough to include all frequencies at which $(1 - T)$ is different from zero. If this range covers a single line and no others, then we may meaningfully speak of the equivalent width of that particular line. If shape and strength of a line are known, its equivalent width may be calculated from equations (1)–(4).

Correlation of Linestrength and Linewidth in Case of a Voigt-Profile

When both the Doppler effect and Lorentz collision damping contribute to the linewidth, the expression for the line absorption coefficient is

$$k(\nu,a) = \frac{k_0 \cdot a}{\pi} \int_0^\infty \frac{\exp(-x^2)}{a^2 + (\omega - x)^2}\mathrm{d}x \tag{5}$$

In this expression a is proportional to the ratio of the Lorentz and the Doppler linewidths:

$$a = \sqrt{\ln 2} \cdot \frac{\gamma_L}{\gamma_D} \tag{6}$$

with γ_L being by definition a linear function of the sample pressure, $\gamma_L = \gamma_L^0 \cdot P$, and γ_D for a given molecule and temperature depending linearly on the frequency:

$$\gamma_D = \sqrt{2 \cdot \ln 2 \cdot \frac{N_A \cdot kT}{M}} \cdot \nu \tag{7}$$

ω is a measure of the spectral offset from resonance absorption ν_0:

$$\omega = \sqrt{\ln 2} \cdot \frac{\nu - \nu_0}{\gamma_D} \tag{8}$$

and k_0, finally, is proportional to the linestrength S^0:

$$k_0 = \sqrt{\frac{\ln 2}{\pi}} \cdot \frac{S^0 \cdot P_i}{\gamma_D} \tag{9}$$

P_i designates the partial pressure of the absorbing species.

For a given molecule S^0 and γ_L^0 are the parameters a priori unknown. By assuming values for these two parameters, the integral (5) can be evaluated numerically at a given frequency and sample pressure. The corresponding transmission is given by equation (2) for each value of the absorption coefficient (5). If all transmission values for one line are calculated this way the equivalent width (4) can be determined by numerical integration.

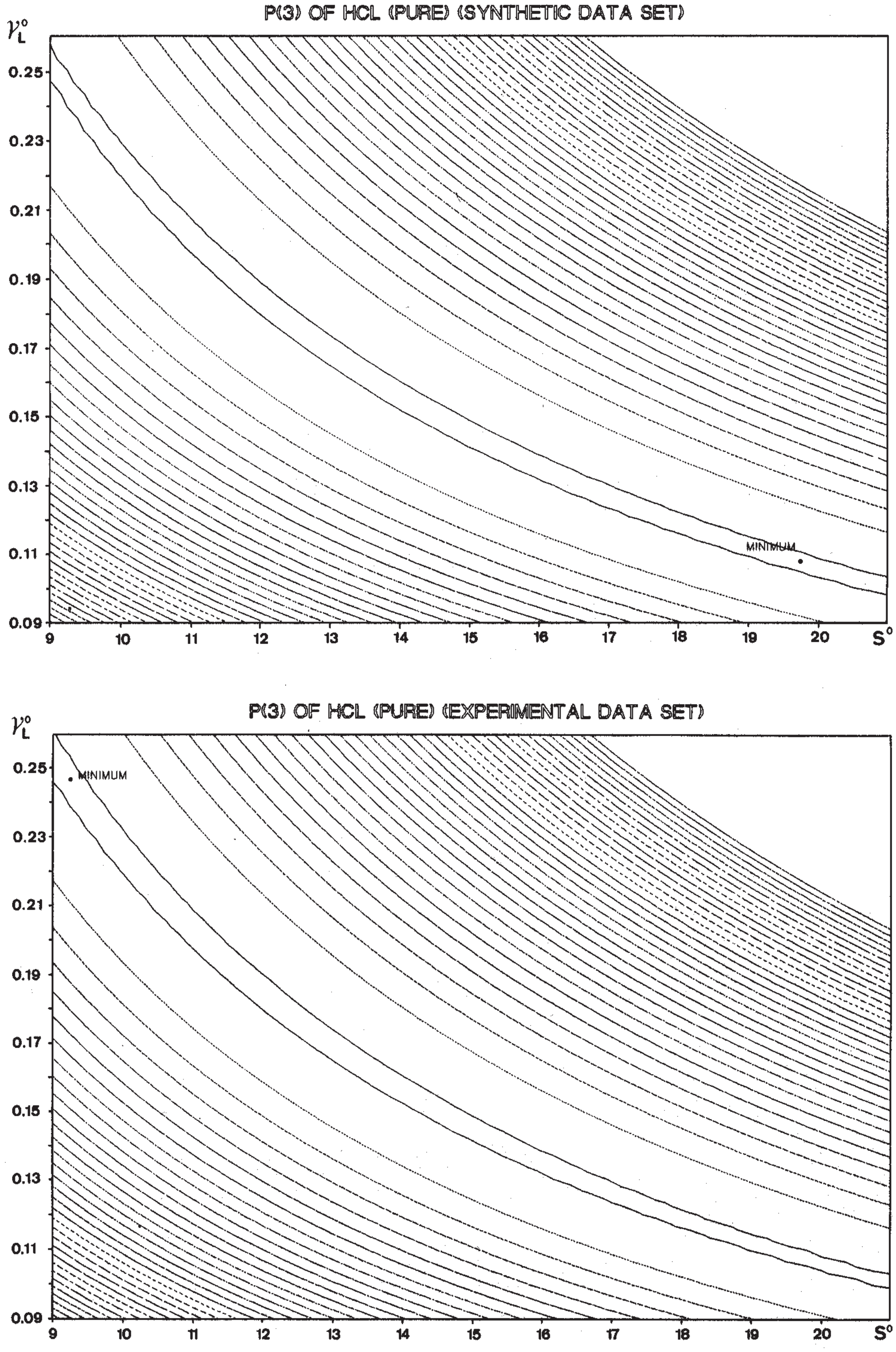

Fig. 1. Sum of squared residuals contour plot of the $P(3)$ line of $H^{35}Cl$ for a synthetic data set (above) with synthetic scatter and for an experimental data set (below). The deepest contour represents $\chi^2 = 6.7$ and the equidistance is 39.

Since the equivalent width is also an experimental quantity, its measured and calculated values can be compared, and the initial guesses for S^0 and γ_L^0 can be optimized by a nonlinear least squares fit. The advantage of this procedure over methods developed in pre-computer decades, all relying on analytical approximations of equations (4) and (5), is that no assumptions on the ratio of the unknown parameters S^0 and γ_L^0 have to be made. A most general treatment of the linestrength determination appears to be possible within the domain of the Voigt-profile (5).

In order to study possible correlation between S^0 and γ_L^0, a set of equivalent width data for $H^{35}Cl$ was generated using equations (4) and (5) with $S^0 = 8.18$ cm^{-2}atm^{-1}, $T = 20\,^\circ C$, and $\gamma_L^0 = 0.379$ cm^{-1}atm^{-1} matching the experimental data set described below. White noise of $3.57 \cdot 10^{-3}$ cm^{-1} standard deviation was superimposed to the artificial data set and a least squares fit was carried out using the simplex algorithm[6]. A contour plot of the resulting sum of squared residuals plane is shown in

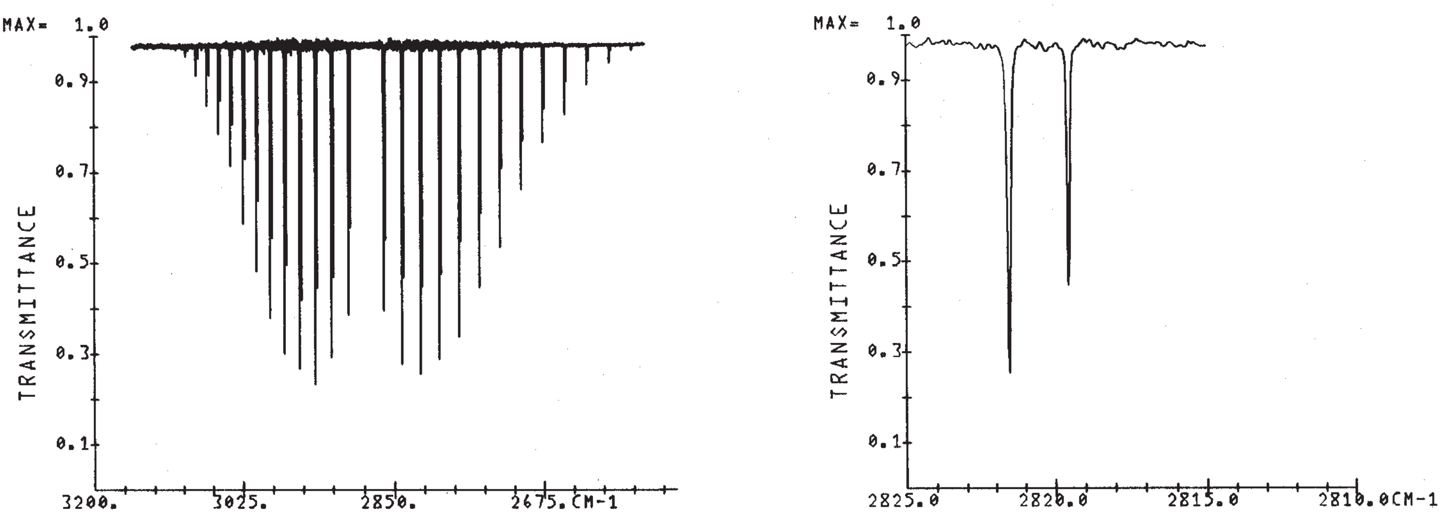

Fig. 2. Rovibrational spectrum of HCl of a natural $H^{35}Cl/H^{37}Cl$ mixture at 10 torr (left) and the magnified P(3) $H^{35}Cl$ and $H^{37}Cl$ lines of the spectrum (right); resolution 0.074 cm^{-1}.

Table 1.

Line	$H^{35}Cl$ S^0 [$cm^{-2}atm^{-1}$]	$H^{35}Cl$ γ_L^0 [$cm^{-1}atm^{-1}$]	$H^{35}Cl$ σ[c] [cm^{-1}]	$H^{37}Cl$ S^0 [$cm^{-2}atm^{-1}$]	$H^{37}Cl$ γ_L^0 [$cm^{-1}atm^{-1}$]	$H^{37}Cl$ σ[c] [cm^{-1}]
P(1)[a]	8.41	0.163	$1.73 \cdot 10^{-3}$	1.77	0.930	$1.19 \cdot 10^{-3}$
P(2)[a]	6.60	0.401	$3.50 \cdot 10^{-3}$	2.59	1.156	$2.26 \cdot 10^{-3}$
P(3)[a]	8.18	0.379	$3.57 \cdot 10^{-3}$	2.75	1.298	$2.80 \cdot 10^{-3}$
P(4)[a]	8.69	0.309	$3.71 \cdot 10^{-3}$	2.63	1.207	$2.51 \cdot 10^{-3}$
P(3)[b]	18.66	0.017	$2.38 \cdot 10^{-3}$	18.02	0.016	$1.71 \cdot 10^{-2}$

[a] Pure HCl; [b] HCl/He mixture; [c] σ of fitted function.

Fig. 1. This plot reveals significant negative correlation between the two parameters to be determined. The topography of the sum of squared residuals is almost identical to the one resulting from the fit of experimental data discussed below. Please note that the minimum has shifted very much from the starting values.

To compare these results with experiments, we have recorded equivalent width data of the (1–0) rovibrational transition of HCl of 0.074 cm^{-1} on a BOMEM DA3.01 interferometer with a variable length (1–10 cm) stainless-steel cell and KBr windows. Pure HCl of natural isotopic composition was measured at the pressures of 2, 5, 10, 15, 20, 25, 30, 35, and 40 torr at 20 °C, while HCl/He mixtures of atmospheric pressure and HCl partial pressures corresponding to those of the pure samples were treated in an analogous way. The least squares fits with 7 degrees of freedom were performed on an IBM 3083 mainframe computer and required typical CPU times of 10 to 15 min. As an illustration, Fig. 2 shows the complete (1–0) rovibrational spectrum of a natural $H^{35}Cl/H^{37}Cl$ mixture as well as the P(3) line of both isotopes.

Table 1 shows the result of the least squares fits of the first four lines of the P-branch of pure HCl and of the P(3) line of the HCl/He mixtures. The large scatter in both S^0 and γ_L^0 is a direct consequence of the correlation between these two parameters. From this follows that S^0 and γ_L^0 cannot be determined independently unless further information is available. There are several ways to obtain the information needed, some of them being described in the literature mentioned and discussed in a recent article by *Pine* et al. The aim of this paper is, however, to point out the correlation between linestrengths and linewidths present, although not always realized, in highly, not fully resolved infrared spectroscopy.

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