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Experimental measurements of the shape and the parameters of the spectral line $J = 0-1$ of HF perturbed by argon and CO₂ (*)

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Résumé. — On présente une étude en spectrométrie par transformée de Fourier de la raie de rotation pure $J = 0-1$ de HF à 41 cm^{-1} , perturbée par l'argon et par CO₂. Par régression non linéaire, on détermine les paramètres du profil de Lorentz corrigé, en tenant compte à la fois du terme de population et de l'influence des raies voisines. Ce profil reproduit correctement celui de la raie expérimentale.

Abstract. — Using Fourier Transform spectroscopy, we study the rotational line $J = 0-1$ of HF (at 41 cm^{-1}) perturbed by argon and CO₂. The parameters of the corrected Lorentz profile are determined by a non-linear regression. The population term and the influence of neighbouring lines are taken into account. This theoretical profile correctly reproduces that of the experimental line.

1. Introduction. — The Lorentz profile is always presumed valid for determining the line shifts and broadening of the spectral lines of diatomic molecules submitted to pressure effects. For low pressure ($\lesssim 1$ bar) this profile, which is given by the Anderson impact theory [1], is exact. But, for intermediate pressure, this is not necessarily the case. To clear up this question, we have studied the profile of the line $J = 0-1$ of HF perturbed by a spherical molecule, argon, and by a molecule having a large quadrupole moment, CO₂.

2. Experimental techniques. — The Fourier Transform spectrometer built in this laboratory [2] has been utilized for this study. It is equipped with a monel cell (two cm thickness) with quartz windows.

Argon and CO₂ are supplied by « l'Air Liquide ». They are purified in a cooled trap filled with activated carbon. HF is supplied by « Matheson ».

The HF concentration is weak enough to avoid pollution by residues.

The maximum optical path difference δ (o.p.d.) of the interferogram has been chosen with the help of the « Dowling criterion » [3, 4], which specifies that the line profile (half width γ) is correctly given

when the interferogram reaches the o.p.d. $1/\gamma$. We verify further that this criterion is too strict in the present case.

3. Comparison method. — A non-linear regression computer program is used in order to optimize the parameters a , b , S , γ , $\Delta\nu$ of the analytic profile

$$A(\nu) = 1 + a + b\nu - \exp \left[- \frac{[f(\nu)/f(\nu_0)] (Sl/\pi\gamma)}{\left(\frac{\nu_0 + \Delta\nu - \nu}{\gamma} \right)^2 + 1} \right]$$

where $f(\nu) = 1 - \exp[-(h\nu)/(kT)]$ and l is the length of the absorbing medium. In this expression, the classical Lorentz formula (for the near infrared) appears. It is corrected by the population term, which is dependent on the frequency.

In order to take account of :

— the influence of the recovery of neighbouring HF lines,

— the spectra induced by CO₂ pressure, we have superimposed an absorption which is linear in frequency.

Such a simple model is justified by the great interval separating the HF lines and by the fact that the line of lower frequency is being studied.

With the intention of verifying the Dowling criterion, we have adjusted the experimental data using

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Fig. 1. — Absorption of HF-Ar mixture : $\square\square\square$ experimental results for an optical path difference δ ; $\blacksquare\blacksquare\blacksquare$ experimental results for an optical path difference $\delta/2$; $\bullet\bullet\bullet\bullet$ recalculated profile without convolution; — recalculated profile with convolution. The second and third plottings have not been drawn when they coincide respectively with the first and the fourth.

the profile $A(\nu)$ and its convolution with the apparatus function $(2\delta \sin 2\pi\delta\nu)/(2\pi\delta\nu)$. These are extracted, by a Fourier Transform, from an interferogram whose δ complies with this criterion.

Both sets of parameters S , γ , $\Delta\nu$ are identical in the two cases.

Fig. 2. — Absorption of the HF-CO₂ mixture. Dotted line, experimental results; full line, recalculated Lorentzian profile.

To take account of the o.p.d. at which the restitution of the experimental line is altered by a truncated interferogram, we divided the number of interferogram points by two, giving an o.p.d. of $\delta/2$.

The results for o.p.d. δ and $\delta/2$ are represented on figure 1. There is no difference between :

- the data
- the convoluted profiles
- the two sets of parameters.

It is only when a value of $\delta/4$ is reached that appreciable differences appear and the line is no longer apodized.

Figure 1 and figure 2 show the very good agreement between our model and the experimental forms.

On table I, the dispersion of the results for HF-Ar-

Table I. — Results for the $J = 0-1$ line of HF perturbed by argon (20 bars).

Exp.	ν (cm ⁻¹)	γ (cm ⁻¹)
1	41.67	1.40
2	41.64	1.42
3	41.74	1.40
4	41.65	1.40
5	41.67	1.34
6	41.68	1.43
7	41.66	1.40
8	41.68	1.365
9	41.66	1.39

20 bars is presented. Agreement between the different experiments is very good.

In figures 3 and 4, the half width of the HF line and its shift are plotted *versus* the argon density. Note that shifts and broadenings increase linearly with pressure.

4. Conclusion. — We have studied the HF $J = 0-1$ line perturbed by pressure effects. The corrected Lorentz profile coincides with experimental data obtained with argon (up to 40 bars) and CO₂ (up to 20 bars). This work will be extended using other lines and for very low densities.

Fig. 3. — Broadening of the HF line *versus* density of Ar or CO₂.

Fig. 4. — Shift of the HF line *versus* density of Ar or CO₂.

References

- [1] ANDERSON, P. W., *Phys. Rev.* **76** (1949) 647;
 TSAO, C. J. et CURNUTTE, J. *Quant. Spectrosc. Radiat. Transfer*
2 (1962) 41.
- [2] BACHET, G., COULON, R., *Infrared Phys.* **17** (1977) 359.
- [3] DOWLING, J. M., U.S.A.-F. Rep. SSDTR 6730 (1967).
- [4] LIGHTMANN, A., *Infrared Phys.* **11** (1971) 125.