Line shapes and half widths of pure- and foreign-gas-broadened 2.5-μm HF absorption spectra

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The absorption line shapes of the $R_1(1)$–$R_1(5)$ lines of HF have been measured as a function of pressure for pure HF and with Ar and Kr as buffer gases by means of a cw tunable F_B (II)-type color-center laser operating in the wavelength range from 2.25 to 2.65 μm. Line-broadening coefficients are determined and Einstein A coefficients are evaluated from the line shapes. Collisional narrowing is observed for the $R_1(4)$ line with Kr as the buffer gas.

I. INTRODUCTION

For the understanding of molecular structures and molecular interactions it is desirable to determine the Einstein A coefficients and the line-broadening coefficients for various J values. Comparison with theoretically calculated values allows for modification of the wave functions that are used to describe the molecule. The nature of the electrostatic multipole interactions as well as molecular-rotational energy-transfer dynamics can be understood from the line-broadening behavior.[1] Such measurements are also relevant to the development of molecular lasers, considering that the calculation of small signal gain requires the knowledge of Einstein A and line-broadening coefficients.[2]

Measurements of line-broadening coefficients using incoherent light sources have been reported for many molecules (see, e.g., Ref. 3), however, these measurements are restricted to high gas-pressure values because of the limited resolution of the monochromator. In the special case of *DF*, line-broadening coefficients were determined by use of a *DF* chemical laser in the pressure range from 10^{-3} to 500 mbar.[4] Since the tuning range of the *DF* laser that operates in the pressure range from 5 to 50 mbar is limited by the Doppler width of the transition, the full line shape at high pressures cannot be measured directly.

The use of cw tunable color-center lasers[5,6] allows one to determine the full line shape of the absorption lines with an accuracy of better than 1 MHz. Furthermore the measurements are not restricted to a coincidence between the laser line and the absorption of the molecule to be investigated but fundamental, overtone, and combination bands in the wavelength range from 2.2 to 3.3 μm can be investigated with the presently available cw color-center lasers.[7]

With the high resolution of color-center lasers it is also feasible to investigate foreign gas broadening which is usually one order of magnitude smaller than self-broadening. Results of these measurements can be used to prove the validity of theories for foreign gas broadening.[8] In this paper the line broadening for the $v=1-0$ band of HF in the pressure range of 10^{-3}–1000 mbar is described and first experiments on foreign gas broadening with Ar and Kr as buffer gases are performed.

II. THEORY

The spectral absorption coefficient $\alpha(\nu)$ is defined by

$$I(\nu)=I_0(\nu)\exp[-\alpha(\nu)l], \qquad (1)$$

where I and I_0 are the incident and transmitted light intensities, $\alpha(\nu)$ is the absorption coefficient of the absorber, and l the absorption pass length. The integrated intensity S is related to $\alpha(\nu)$ by

$$S=\int\alpha(\nu)\,d\nu. \qquad (2)$$

For a pure Doppler-broadened absorption line $\alpha(\nu)$ is given by

$$\alpha_D(\nu)=\frac{2S(\ln 2)^{1/2}}{\pi^{1/2}\Delta\nu_D}\exp\left(\frac{4(\nu-\nu_0)^2\ln 2}{\Delta\nu_D^2}\right), \qquad (3)$$

$\Delta\nu_D$ is the full width at half-maximum (FWHM) of

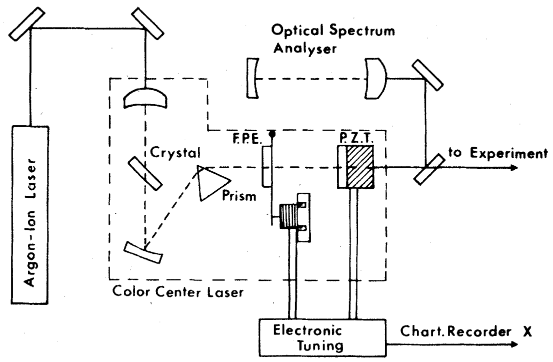

FIG. 1. Single-mode color-center laser.

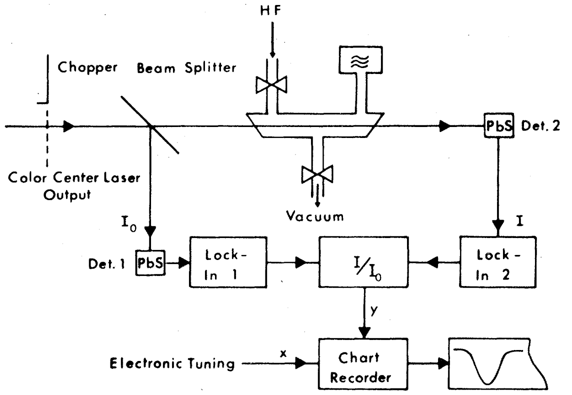

FIG. 2. Experimental setup for absorption measurements.

the absorption line and ν_0 is the center frequency. At higher pressures, where the line shape is predominantly determined by molecular collisions, $\alpha(\nu)$ has a Lorentzian shape with a FWHM $\Delta\nu_L$:

$$\alpha_L(\nu)=\frac{S}{2\pi}\,\frac{\Delta\nu_L}{(\nu-\nu_0)^2+(\frac{1}{2}\Delta\nu_L)^2}\,. \qquad (4)$$

$\Delta\nu_L$ increases linearly with pressure p,

$$\Delta\nu_L=\Delta\nu_L^0 p, \qquad (5)$$

where $\Delta\nu_L^0$ is the line-broadening coefficient.

In a pressure regime between pure Doppler and Lorentzian broadening the spectral absorption coefficient $\alpha(\nu)$ is given by a combination of Eqs. (3) and (4);

$$\alpha(\nu)=\frac{\alpha_D^0}{\pi\Delta\nu_L}\times\int_{-\infty}^{+\infty}\frac{\exp-[(2\nu'/\Delta\nu_D)(\ln 2)^{1/2}]^2}{1+(2/\Delta\nu_L)(\nu-\nu_0-\nu')}\,\delta\nu'\,, \qquad (6)$$

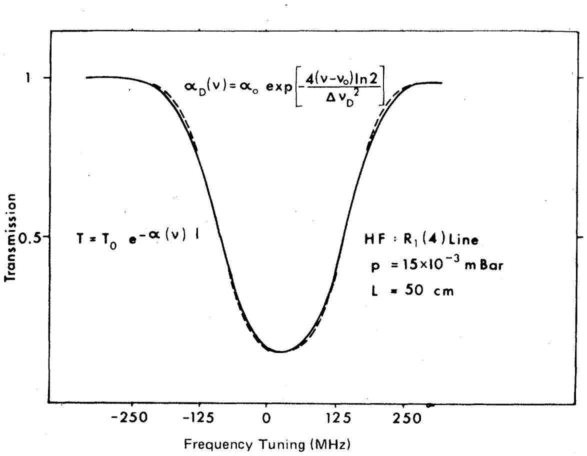

FIG. 3. HF absorption line: ———, experimental curve; -----, fitted curve.

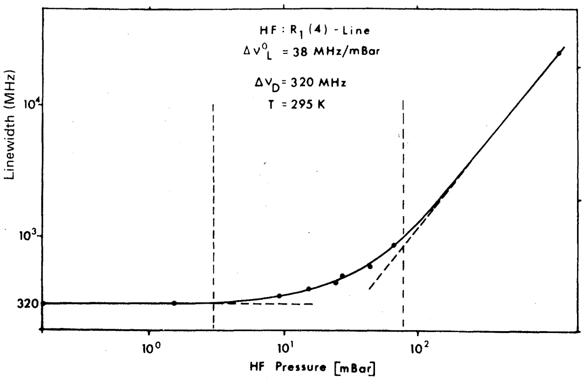

FIG. 4. Linewidth dependence of HF absorption line on pressure.

which is known as the Voigt integral. α_D^0 is the absorption coefficient at the center frequency ν_0 for a purely Doppler-broadened line

$$\alpha_D^0=2S(\ln 2)^{1/2}/(\pi^{1/2}\Delta\nu_D)\,. \qquad (7)$$

In Eq. (6) it is assumed that the natural linewidth of the transition is small compared to the Doppler width. The integrated intensity S is related to the Einstein A_{ul} coefficient by

$$S=\frac{c^2}{8\pi\nu_0^2}N_l A_{ul}\frac{g_u}{g_l}\left[1-\exp\left(\frac{h\nu_0}{kT}\right)\right], \qquad (8)$$

and to the Doppler width $\Delta\nu_D$ by

$$S=\alpha_D^0(\pi/\ln 2)^{1/2}\Delta\nu_D, \qquad (9)$$

where N_l is the number of molecules in the lower level, and g_u and g_l are the degeneracy of the upper and lower level, respectively.[9]

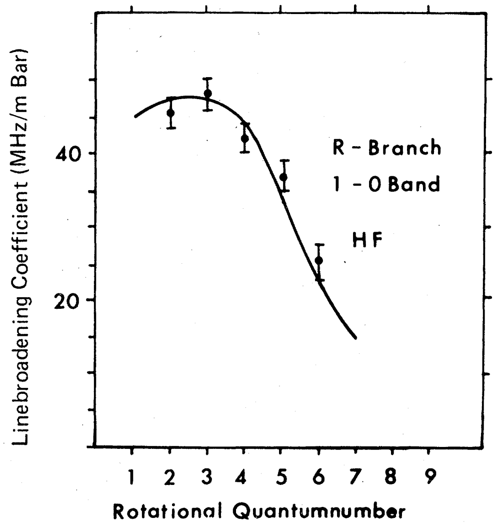

FIG. 5. Dependence of line-broadening coefficient on the rotational quantum number.

TABLE I. Line-broadening and Einstein A_{ul} coefficients.

Transition	$(\Delta\nu_L^0)_{\text{expt}}$ (MHz/mbar)	$(\Delta\nu_L^0)_{\text{theor}}$ [MHz/mbar]	$(A_{ul})_{\text{expt}}$ $[s^{-1}]$	$(A_{ul})_{\text{theor}}$ $[s^{-1}]$
$R_1(1)$	44.2	46	24	32
$R_1(2)$	46.4	46	24	32
$R_1(3)$	42.8	44	22	32
$R_1(4)$	39.4	36	20	32
$R_1(5)$	24.6	22	21	32

From a measurement of $\Delta\nu_D$ at low pressure the Einstein A_{ul} coefficient may be determined. Measurements of $\Delta\nu_L$ at high pressure allow a determination of the line-broadening coefficient $\Delta\nu_L^0$.

The strong dipole moment of HF molecules results in large line-broadening coefficients. Therefore the effect of collisional narrowing of the Doppler line[10] (Dicke narrowing) is masked by collisional broadening. In the case of foreign gas broadening with a line-broadening coefficient which is nearly a factor of 10 smaller and for high J values a reduction of the halfwidth with increasing pressure should be observed. Introducing a hard-sphere-collision cross section the Dicke width can be written[10]

$$\Delta\nu^{\text{Di}} = (1/2\pi)(nv\sigma_H/2\eta^2), \tag{10}$$

where n, v, and η are the number of molecules per cm^3, the mean velocity and the ratio of mean-free path and wavelength of the molecules, respectively.

III. EXPERIMENTAL

The essential part of the experimental setup is a cw single-mode color center laser as shown in Fig. 1.[11] To cover the R-branch absorption lines of HF, $F_B(II)$ centers in KCl:Na crystals are best suited as active material.[6] Using the 514-nm line of a small argon-ion laser as the pump source output power values of several mW tunable from 2.25 to 2.65 μm are available with these crystals. Single-mode operation is achieved with an intracavity etalon (FPE) and results in an emission linewidth of about 100 KHz.[12] Fine tuning is accomplished by varying the cavity length with a piezoceramic (PZT) translator and simultaneously tilting the intracavity etalon with a magnetic system. PZT and magnetic system are controlled by a homemade electronic driver. In this way a tuning range of 2 GHz without mode jumps is attained.

TABLE II. Foreign-gas broadening with Ar and Kr as buffer gas.

Transition	$(\Delta\nu_L^0)_{\text{expt}}$ [MHz/mbar] Ar	Kr	$(\Delta\nu_L^0)_{\text{theor}}$ [MHz/mbar] Ar	Kr
$R_1(1)$	7.0	9.0	6.9	7.6
$R_1(2)$	5.0	5.6	4.0	4.6
$R_1(3)$	4.2	5.0	1.8	3.4
$R_1(4)$	3.0	4.4	1.6	2.8
$R_1(5)$	1.8	3.6	1.5	2.7

The absorption measurements are performed with an experimental set up which is shown schematically in Fig. 2. The output beam of the color-center laser passes through a stainless steel absorption cell with sapphire windows. The total pressure in the cell is measured by use of a capacitance manometer. In order to keep the absorbed power constant, the length of the absorption pass is varied from 0.5–500 mm for HF pressure values between 1000 mbar and 10^{-3} mbar. The infrared intensity behind the absorption cell is measured with a large area (5× 5 mm) PbS infrared detector. The normalized signal I/I_0 is plotted with an x-y chart recorder as a function of the laser frequency.

IV. RESULTS AND DISCUSSION

The result of a typical absorption measurement is shown in Fig. 3. The normalized light intensity behind the absorption cell is plotted versus the detuning of the color-center laser frequency from the center of the absorption line. The dashed line

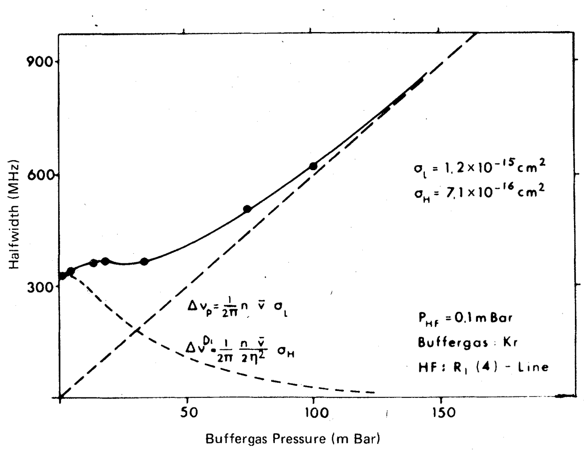

FIG. 6. Collisional narrowing of HF with Kr as buffer gas.

represents the result of a least-squares-fit procedure, varying the four parameters center frequency ν_0, half width $\Delta\nu_D$, maximum absorption constant α_D^0, and maximum transmission I_0. Numerous measurements were performed with increasing HF pressure for the $R_1(1)$ to the $R_1(5)$ line. All curves were fitted to the Voigt integral [Eq. (6)] and half widths and absorption coefficients at center frequency were determined. Figure 4 shows as an example the half width of the $R_1(4)$ line as a function of pressure. The line-broadening coefficient $\Delta\nu_L^0$ can be easily evaluated from these measurements. The dependence of ν_L^0 on the rotational quantum number of the upper level of the transition is shown in Fig. 5. The solid line represents the theoretically expected line-broadening coefficients as calculated by Anderson.[13] The good agreement confirms the Anderson theory of self-broadening of polar diatomic molecules. The Einstein A_{ul} coefficients were determined from the low-pressure measurements. Using Eqs. (8) and (9) A_{ul} can be calculated with the measured values of $\Delta\nu_D$ and α_D^0. Table I gives a summary of the results for the $R_1(1)$ to the $R_1(5)$ line of pure HF in comparison with calculated values for $\Delta\nu_L^0$ and A_{ul}.

The line-broadening coefficients for foreign gas broadening are summarized in Table II. The theory of Anderson is no longer valid for this type of collision. The theoretical values are taken from Jarecki[8] and exhibit still a small difference to the measured data. Figure 6 shows collisional line narrowing of the $R_1(4)$ line of HF with Ar as buffer gas. The reduction of the Doppler width is superimposed by foreign gas broadening, but Dicke narrowing is clearly resolved. From this measurements a hard-sphere cross section of $\sigma_H = 7 \times 10^{-16}$ cm^2 can be determined.

V. CONCLUSION

Line broadening coefficients for self-broadening and foreign-gas broadening have been measured for HF 2.5-μm absorption spectra with an accuracy of better than 1 MHz. Self-broadening coefficients are in good agreement with the Anderson theory. The high resolution of the color-center laser has made it possible to measure collisional narrowing for the $R_1(4)$ line of HF with Kr as buffer gas and to determine the hard-sphere collision cross section.

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