

CASE FILE

Line Shifts in the First Overtone of DF Broadened by HF¹

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ABSTRACT

The self-shifts of the lines in the fundamental of HF from P(7) to R(8) and the line shifts in the first overtone band of DF when perturbed by HF were measured from P(7) to R(6). Pressure-induced shifts in the HF fundamental were studied at room temperature and at pressures of HF varying from 37.5 cm of Hg to 113.5 cm of Hg. The shifts agreed with those observed by Herget, but the estimated error $0.5 \times 10^{-4} \text{ cm}^{-1}/\text{cm Hg}$ for the present study was about one-third of that of Herget. The partial pressures of DF ranged from 5.48 cm of Hg to 22 cm of Hg, and total pressure of mixed gases ranged from 36.12 cm of Hg to 121.8 cm of Hg. Temperatures of reference and sample cells were 110°C, 120°C, 150°C, and 134°C. The shifts oscillate with a period of one in J and with increasing amplitude in the wings from R(1) to R(6) and P(3) to P(7). The direction of the shifts is the same as that found for the DC1-HCl system and is opposite to that predicted by the simple near-resonant dipole theory. The magnitude of the shifts in the present study are considerably larger than those found from the DC1-HCl study.

Index Headings: Absorption; Atmospheric optics; Infrared; Spectra.

One of the most interesting studies of line shifting reported in the recent literature is that of Jaffe, et al.,² who reported on the pressure-induced shifts of DC1 due to HCl and also on the shifts of HCl due to DC1. They observed in the first overtone band of DC1 broadened by HCl not only the expected J-dependence of the line shifts, but also a striking oscillation from line to line of the magnitude of the shift. They suggest this phenomenon is due to near-resonant dipolar interaction between DC1 and HCl. In HCl-DC1 they found no oscillations in the shifts. Another example of oscillating line shifts has been discovered in HF broadened by HCl.³

The authors decided to study DF-HF, to see if the large oscillations would occur that were found in DC1-HCl and, if so, if the simple theory of near-resonant dipolar interaction would correctly predict the directions of the oscillations. The results of our study would indicate that the shifts do occur, are large, compared to the DC1-HCl case, are linear with pressure of broadener gas, and are opposite to the direction predicted by theory.

EXPERIMENTAL METHOD

The spectrometer, the cells, and the method of handling of the gases used in this study are basically as reported for earlier studies.⁴ However, several modifications of the instrument have since been made. A 600-Hz chopper incorporating a tuned reference signal is used in conjunction with a phase-sensitive Princeton Applied Research Amplifier, model HR-8, and a Texas Instruments model FWS recorder. A Nernst-type filament is used as the source and the detector is an uncooled lead sulphide photoconductor made to order by the Santa Barbara Research Corporation. The resolution of the spectrometer may be estimated from the measured instrumental slit half width of 0.14 cm^{-1} . The signal to noise ratio varied from fifty to one to five to one.

A two-cell method of measuring line shifts was employed to reduce error due to instrumental drift. An elevator inside the vacuum housing brought the reference cell and then the sample cell into the beam. By this means the time between runs was considerably reduced from that of the single cell method. The reduction in error in the measurement as compared to the one-cell method is illustrated in Fig. 1 which compares the line shifts measured by Herget, et al.⁵ in self-broadened HF (a one-cell method) with those measured by the authors for the same gas. The shifts measured by the authors are reported in Table I. The reference cell (17.8 cm) contained a trace of HF. The pressures and lengths in the sample cell were 37.5 cm Hg (17.8 cm), 76 cm Hg (1.62 cm), and 113.5 cm Hg (0.047 cm). Both cells were held at room temperature, $24^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The mean deviation calculated for this study, $0.5 \times 10^{-4} \text{cm}^{-1}/\text{cm Hg}$, is about one third of that reported by Herget. The agreement of the results of the two studies is quite good, however.

Gas, whether DF or HF, was admitted to the cell open to the manifold at room temperature. The cell-manifold pressure was then read on a Bourdon gauge. Subsequently, the cell was closed, heated to temperature, and a run was made. The pressure of the gas at the higher temperatures was calculated by the ideal gas approximation. It was feared that because of possible polymer formation and non-ideality of the gases that this approximation would not be good enough. A check on these measurements was made by method devised to read the cell pressure directly.⁶ A pressure transducer was mounted

in the cell body and calibrated in the desired pressure range. The pressure transducer used was a type M6S, Model No. SA-SA manufactured by the Cornyel Corporation. It is temperature-compensated from 23°C to 150°C for the range of pressure from 0 - 6 atm. It was read when the cell was at the proper temperature and its reading checked against the ideal gas approximation. The readings differed at most by 5 cm Hg at the highest pressure readings. This difference led to a possible error in the line shift measurement of about fifteen percent of the average shift observed.

RESULTS

Five sets of data were recorded for the line shifts in the first overtone of DF broadened by HF. The temperatures, cells and path lengths are given in Table II. The line shift per unit pressure is presented in Table III for each line measured. The measured line shifts are plotted in Figures 2 and 3 as a function of the difference in pressure of the sample and reference. It appears that with the exception of a few points there is good evidence for the linearity of the shifts with pressure. It is also significant that the straight lines which have been drawn as the lines of best fit pass reasonably well through the origin. This result would indicate that no large systematic error in pressure measurements exists.

The measured shifts as a function of J-number are displayed in Fig. 4. The points plotted are the averages of the five sets of data taken. The results of Jaffe, et al. for the DCl-HCl system are also reproduced for comparison. The average deviations are indicated by the error bars. It can be seen from the graph that large amplitude oscillations occur in the R-branch and from P(3) outward in the P-branch. These oscillations are in

phase with those in the DC1-HCl system but are considerably larger in amplitude. In the wings, e.g., for the R(6) line the value of the shift is comparable to the value found for HF shifted by Xenon.⁷ This value of $5.6 \times 10^{-4} \text{ cm}^{-1}/\text{cm Hg}$ is indicated at R(6) on the graph.

ERRORS

The error bars in Fig. 4 represent the averaging of the scattered points. It is illuminating to consider the sources of error in the experiment to see how the estimated error compares with measured error. The major sources of error are in the pressure measurement, in instrumental drift and in determination of line peak.

Instrumental drift was checked by running and rerunning a line. For example, for the R(1) line the magnitude of the maximum frequency difference in three runs was 0.002 cm^{-1} which is about 0.4 of the minimum shift observed.

The problems associated with the measurement of line centers and gas impurity are related. Even after all the possible precautions were taken in the handling of the DF, a considerable amount of DF, perhaps about 50 percent of it, was converted into HF. This conversion created a two-fold problem. First, it was not possible to know the exact pressure of DF inside the cell, and second it required a considerably larger amount of gas inside the reference cell. If the gas were pure, a trace of DF would be sufficient to produce a sharply peaked line--at least near the band center. However, it was found that the converted HF had a strong effect upon the peak heights, tending sharply to reduce the line peak. It was this effect that prevented us from studying the lines beyond P(7) and R(6) and, moreover, led to a larger amount of DF being required to obtain measurable intensities of the lines near the band center. At the low pressures of DF a line in the wing is very weakly absorbing. Amplification of the signal only increased the

noise level, making it difficult to find the line peak precisely. The same line at a high pressure of DF is quite flat. The conversion of DF to HF also prevented us from reporting on the line shifts of HF perturbed by DF. First, because it was not possible to take a trace of HF and large amounts of DF, and second, because flattening of line peaks also occurred. Along this line it is interesting to note that the most scatters in the points are found for the lines further away from the band center. Those lines were weakly absorbing and hence the peaks were not sharply defined. In these cases a larger error in determining line peak was rather natural. The mean error estimated by adding the errors due to drift and pressure measurements is about $\pm .9 \text{ cm}^{-1}/\text{cm Hg} \times 10^{-4}$. The mean scatter found is $\pm .7 \text{ cm}^{-1}/\text{cm Hg} \times 10^{-4}$. In all the cases the magnitude of scatter was considerably less than the shift observed.

CONCLUSIONS

A qualitative approach to the origin of the line shifting in this molecular system is given by the theory of the near-resonant dipolar interaction. Jaffe, et al.¹ have given the expression for the energy change due to the dipolar interaction as derived from second order perturbation theory. When the molecular parameters for HF and DF are substituted into this expression, the calculated energy shifts are such as to lead to large oscillating line shifts. However, just as in the DCl-HCl case, the predicted shifts are exactly opposite to those observed. The shifts not only oscillate but increase in magnitude toward the red in the R-branch and the blue in the P-branch.

1. The work was supported by the National Aeronautical and Space Administration, Grant NGL-43-001-006.
2. J.H. Jaffe, M.A. Hirshfeld and A. Ben-Reuven, J. Chem. Phys., 40, 1705 (1964).
3. Private communication to the authors from Arieh Rosenberg, Institute of Chemistry, Tel-Aviv University.
4. Herndon, J.A., W.E. Deeds, N.M. Gailar, W.F. Herget, R.J. Lovell and A.H. Nielsen, J. Optical Society, 52, 1108 (1962).
5. Herndon, J.A., W.E. Deeds, N.M. Gailar, W.F. Herget, R.J. Lovell and A.H. Nielsen, J. Optical Society, 52, 113 (1962).
6. This direct-reading method was not available until near the end of this study. The measurements could not be more extensively redone because of time commitments for the spectrometer.
7. J.H. Jaffe, A. Rosenberg, M.A. Hirshfeld, and N.M. Gailar, J. Chem. Phys., 43, 1525 (1965).

Table I

observed line shifts per unit pressure in HF

Line	Line Shift per Unit Pressure*
	$\frac{\Delta\nu}{\Delta\rho} \times 10^{-4} \text{ cm}^{-1} / \text{cm Hg}$
R(0)	+ 3.9
R(1)	+ .91
R(2)	+ .53
R(3)	- 3.24
R(4)	- 3.44
R(5)	- 3.99
R(6)	- 3.54
R(7)	- 2.66
P(1)	- 2.86
P(2)	+ 1.79
P(3)	+ .91
P(4)	- .66
P(5)	- .36
P(6)	+ 1.47
P(7)	+ 1.15

*Averages of measurements at pressures of
37.5 cm Hg, 76 cm Hg, and 113.5 cm Hg

Table II
 temperatures, pressures and cells

Set of Data	Temperature	Pressure in the Sample Cell P_1 - cm Hg	Pressure in the Reference Cell P_2 - cm Hg	ΔP $P_2 - P_1$ cm Hg	Cells Used cms
First	110°C	42.07	5.95	36.12	17.33 17.80
Second	120°C	52.23	5.80	46.43	17.33 17.80
Third and Fourth	150°C	115.46	6.50	108.96	17.33 1.62
Fifth	134°C	131.58	9.70	121.88	17.33 1.62

Table III

line shifts per unit pressure in DF broadened by HF

Line	$\Delta P = 36.12 \text{ cm}$ $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$	$\Delta P = 46.43 \text{ cm}$ $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$	$\Delta P = 108.96 \text{ cm}$ $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$	$\Delta P = 108.96 \text{ cm}$ $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$	$\Delta P = 121.88 \text{ cm}$ $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$	Average Deviation $\frac{\Delta \nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$
R(0)	+ 2.71	+ 3.16	+ 2.41	+ 2.52	+ 2.41	+ 2.64
R(1)	+ 7.36	+ 6.56	+ 7.78	+ 7.91	+ 6.96	+ 7.21
R(2)	+ 1.38	+ 1.20	+ 1.25	+ 1.31	+ 1.68	+ 1.36
R(3)	+ 2.76	+ 2.79	+ 3.19	+ 3.13	+ 3.20	+ 3.01
R(4)	- 3.80	- 4.03	- 4.75	- 3.31	- 3.36	- 3.82
R(5)	+ 2.78	+ 2.16	+ 2.31	+ 2.21	+ 2.87	+ 2.46
R(6)	- 6.09	- 5.94	- 5.90	- 5.92	- 5.89	- 5.94
P(1)	- 6.64	- 6.20	- 6.20	- 6.23	- 6.40	- 6.33
P(2)	- 3.32	- 3.12	- 3.05	- 3.19	- 3.16	- 3.16
P(3)	- 1.32	- 1.61	- 1.28	- 1.60	- 1.97	- 1.55
P(4)	- 5.26	- 6.30	- 5.89	- 4.94	- 4.92	- 5.46
P(5)	+ 2.50	+ 3.11	+ 2.08	+ 2.20	+ 2.18	+ 2.41
P(6)	- 6.36	- 4.93	- 4.90	- 6.08	- 5.28	- 5.51
P(7)	+ 7.70	+ 6.89	+ 6.61	+ 6.72	+ 6.82	+ 6.94

Figure Captions

1. Figure 1. Line Shifts per unit pressure in the 1-0 band of HF.
O - Herget et al, O - Desai et al, ——— revised curve using
the results of both studies.
2. Figure 2. Measured Line shifts for the R-branch lines.
3. Figure 3. Measured line shifts for the P-branch lines.
4. Figure 4. A comparison of the pressure-induced shifts of lines
in the 2-0 bands of DF-HF and DC1-HCl. -----DF-HF, ——— DC1-HCl,
----- these lines as they appear in Jaffe et al.¹ The arrow ← in-
dicates the value measured by Jaffe et al⁴ for the shift of R(6)
in the 2-0 band of HF-Xe.

Line Shift, $\frac{\Delta\nu}{\Delta P} \frac{\text{cm}^{-1}}{\text{cmHg}} \times 10^{-4}$

Error Bars
Desai et al



Error Bars
Herget et al







