THE EFFECT OF PRESSURE ON THE VIBRATIONAL FREQUENCY OF BONDS CONTAINING HYDROGEN *

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Using a technique described earlier, measurements have been of the effect of pressure on the vibrational frequency of a series of chemical bonds mostly containing hydrogen. The systems were studied in CS_2 and $CFCl_3$. The shifts vary from the " red shifts " resulting from van der Waals' forces in OH to a definite " blue shift " for the antisymmetric CH_2 vibration. In general the repulsive forces are effective at lower relative densities in $CFCl_3$ than in CS_2. While the data are not yet extensive, certain regularities are noted which should have theoretical significance. A possible application of the pressure coefficient of the frequency to the identification of molecular structure is noted.

In previous papers [1,2] a method for studying infra-red spectra in solutions under pressures to 12,000 atm, has been described and applied to the OH stretching vibration of *n*-butanol in a series of solvents. A " red-shift " (to lower frequencies) was obtained which varied approximately as ρ^2/r^6 and which was roughly proportional to the polarizability of the most polarizable bond in the solvent. This shift seems clearly due to the attractive interaction between the solvent, or at least the more polarizable bonds of the solvent, and the hydrogen in the OH bond. At some density the controlling interaction must become repulsion rather than attraction. Since this critical density should be different for different bonds, we have extended our investigation to include a series of other bonds mostly involving hydrogen.

The apparatus used was essentially the same as described in the previous papers. The spectrometer was a Perkin-Elmer single-beam double-pass type, employing LiF optics. The systems studied are shown below.

TABLE 1

bond	molecule	solvent	concentration	vibration
NH	$C_6H_5NH_2$	$CFCl_3$	0·4 %	νNH stretch (*s* and *a*)
SH	*n*-C_3H_7SH	CS_2	5 %	νSH stretch
CH	$CHCl_3$	CS_2	3 %, 5 %	νCH stretch
CH	$CHCl_3$	$CFCl_3$	6 %	νCH stretch
CH_2	CH_2Cl_2	CS_2	5 %	νCH stretch (*s* and *a*)
CH_2	CH_2Cl_2	$CFCl_3$	5 %	νCH stretch (*s* and *a*)
OH	*n*-C_4H_9OH	$CFCl_3$	0·7 %	νOH stretch
OH	C_6H_5OH	CS_2	0·6 mg/ml	νOH stretch
CF	$CFCl_3$	$CFCl_3$	100 %	3νCF stretch

The chemicals used were generally the best available commercially, in some cases purified further by distillation. The runs were made in a room maintained at constant temperature and each point was re-run 3 or 4 times and the average shift taken. While the accuracy varied with the dispersion and with other factors, the shifts were reproducible generally to a fraction of a wave number.

No density data were available for $CFCl_3$ as a function of pressure. We have made some crude p, v, t measurements at 24-25° C and supplemented these from Bridgman's data on CCl_4 and $CHBr_3$. The relative densities used in the plots were:

3 ν CF stretch
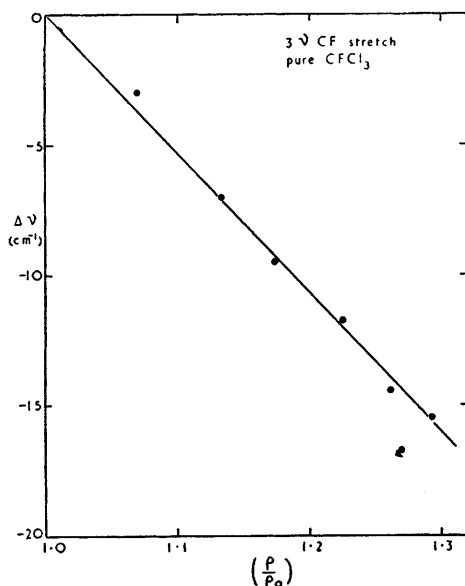pure $CFCl_3$

$\Delta \nu$ (cm^{-1})

$\left(\frac{\rho}{\rho_0}\right)$

FIG. 1.

TABLE 2.—RELATIVE DENSITY OF $CFCl_3$

p (atm)	ρ/ρ_0
1	1·000
500	1·053
1,000	1·092
2,000	1·151
4,000	1·215
6,000	1·255
8,000	1·285
10,000 (extrapolated)	1·305

The results are shown in fig. 1-6. A really satisfactory theoretical analysis was not possible before the deadline for papers, but the salient features will be indicated.

From fig. 1 and 2 it can be seen that the CF and OH stretching frequencies shift to lower frequencies ("red shift") with a roughly linear density dependence. A somewhat better correlation is obtained by plotting against ρ^2. If only interaction with nearest neighbours is considered a ρ^2/r^6 dependence would be predicted. If the surroundings are treated as a continuum, a ρ/r^3 dependence is predicted. The experimental results lie between, but nearer the former case. The magnitude of the shift for n-C_4H_9OH in $CFCl_3$ is consistent with the polarizability of the CCl bond (see Fishman and Drickamer [1]). The red shift for phenol in CS_2 is very close to that obtained previously for n-C_4H_9OH and CH_3OH in CS_2 for all except the two highest pressures.

This is apparently due to phenol freezing out at these pressures. In general for these dilute solutions there seems to be very little effect of the size of the group attached to the OH, although there was some indication in our earlier data for t-C_4H_9OH of shielding of the OH by the adjacent CH_3 groups.

It is relatively easy to show that the magnitude of the shift should be proportional to the number of quantum jumps between the initial and the final state, i.e. to the number of the overtone. Since we measured the second overtone (3ν) for CF, the fundamental would show a maximum shift of about five wave numbers at the highest density. This is consistent with the relatively weak attractive forces in fluorocarbons, as evidenced by low cohesive energy and large molar volume.

In fig. 3-5 we show the shifts with pressure of the CH and CH_2 stretching vibrations for $CHCl_3$ and CH_2Cl_2 in CS_2 and in $CFCl_3$. Here, for the first time, one obtains "blue shifts", i.e. to higher frequency, with increasing density at pressures well below 10,000 atm.

The CH stretching vibration in $CHCl_3$ and the symmetrical CH_2 stretching vibration in CH_2Cl_2 behave in a qualitatively similar manner. Both are of the same symmetry type (A_1). In CS_2 they both give a red shift throughout the entire pressure range. In $CFCl_3$ both show a small red shift at low pressures followed by a small but distinct blue shift at high density. Apparently the

repulsive forces become significant at lower relative densities in $CFCl_3$ than in CS_2. Of course, since the molar volumes and other parameters are not identical for the two solvents at 1 atm, we are not measuring our relative densities from the same fiducial conditions for the two solvents.
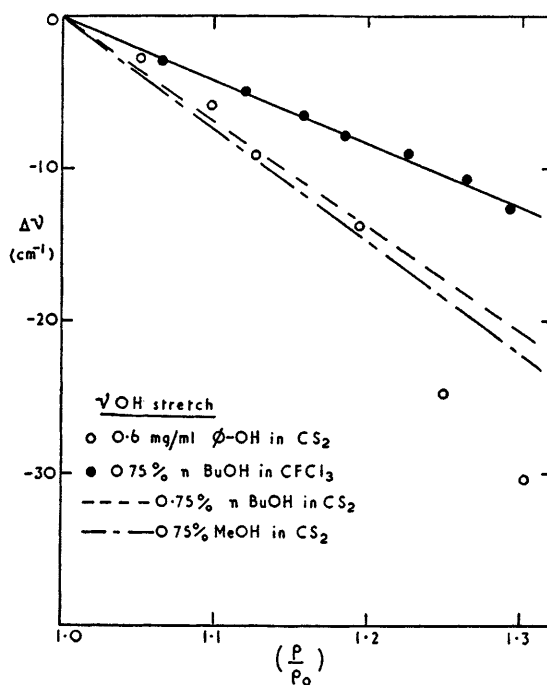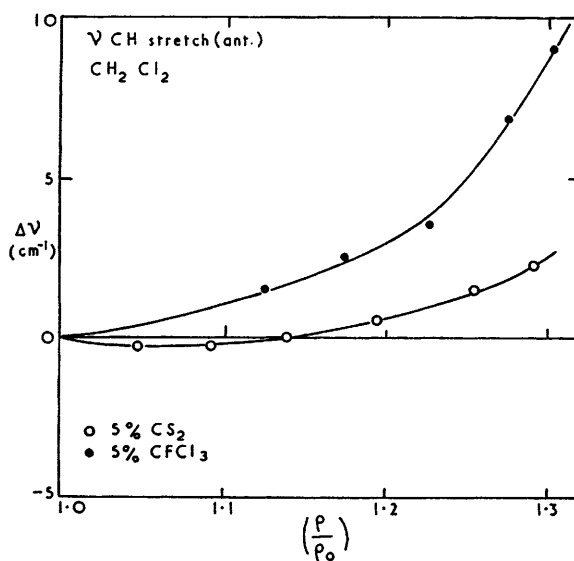

FIG. 2.

FIG. 3

The antisymmetric (type B_1) CH_2 vibration in CH_2Cl_2 shows a greater importance for repulsive forces at any given density than does the symmetric vibration. This is true in both solvents. It is interesting to note that the difference between the shifts for the symmetric and antisymmetric vibrations are nearly the same at the same relative density in each solvent. For this vibration also repulsive effects are more important in $CFCl_3$ than in CS_2.
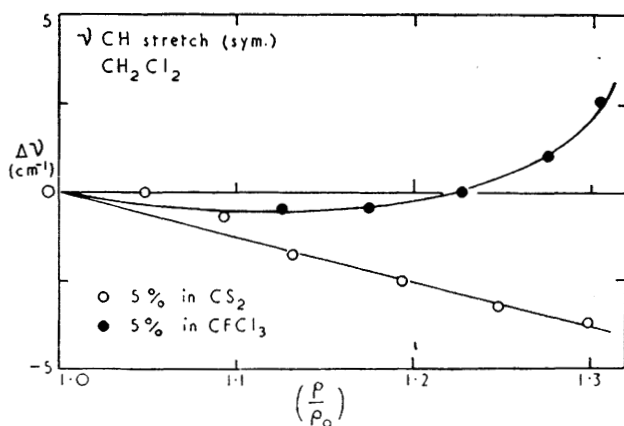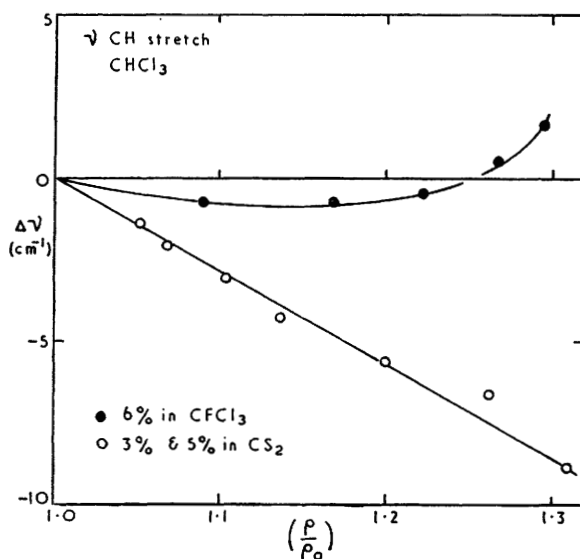

FIG. 4.

FIG. 5.

It should be noted that the CF stretching vibration shows no apparent effect of repulsive forces even at the highest pressures, whereas the CH stretch in $CHCl_3$ shows a distinct blue shift. One might expect that the electrons clustered on the fluorine would lead to repulsion at relatively low densities. Apparently the attractive potential for CF is rather shallow, but the repulsive potential rises steeply only at quite small intermolecular distances.

Fig. 6 shows the results for the NH_2 vibrations of aniline in $CFCl_3$ and for the SH vibration of n-C_3H_7SH in CS_2. The NH_2 vibrations show somewhat less effect of repulsion in the pressure range than do the CH_2 vibrations. As might be expected, the effect lies between that for OH and for CH_2. It may be noted that there is no significant difference between the symmetric and antisymmetric NH_2 vibrations such as was found for CH_2. This point requires further investigation.
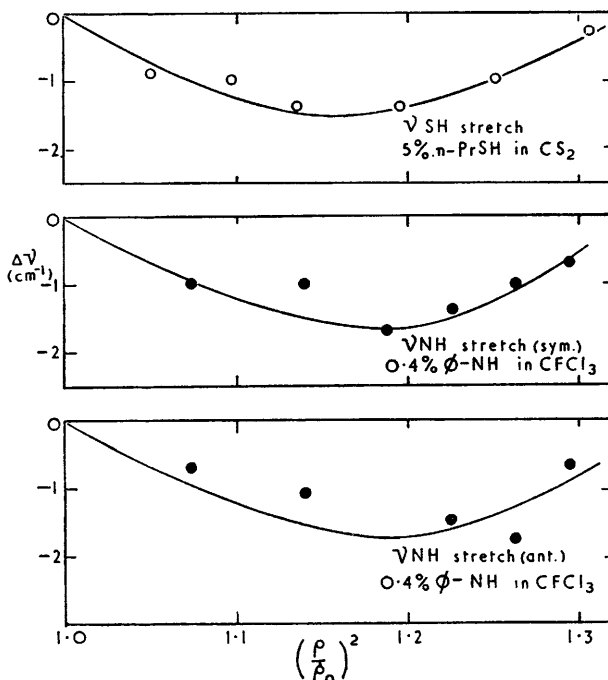

FIG. 6.

The SH stretching vibration shows the effect of repulsion at somewhat lower pressures than does the OH, as might possibly be expected.

The results obtained to date raise several interesting theoretical questions which we plan to treat, along with more extensive results, in a future paper, One interesting possible application of the work [3] lies in the field of identification of molecular structure. If each vibration has not only a characteristic frequency but also a characteristic pressure coefficient, by running spectra at several pressures, it might be possible to resolve many ambiguities which arise in the usual 1-atm spectrum.

[1] Fishman and Drickamer, *J. Chem. Physics*, in press.
[2] Fishman and Drickamer, *Anal. Chem.*, May, 1956.
[3] Douglas Applequist, private communication.