The temperature dependence of chemical shielding in diatomic molecules: CO, F_2, ClF, HBr, and HCl

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The temperature dependence of chemical shielding in CO, F_2, ClF, HBr, and HCl gas has been measured. The functions $\sigma_0(T)$ and $\sigma_1(T)$ in the virial expansion of chemical shielding $\sigma = \sigma_0(T)+\sigma_1(T)\rho+\cdots$ are reported here for ^{13}C, ^{19}F, and ^{1}H nuclei. The largest shifts with temperature are observed for F_2.

INTRODUCTION

In the gas phase the chemical shift of a nucleus in a molecule depends on both density and temperature. If the experimental conditions are such that only binary collisions contribute to changes in chemical shielding, then only the terms in $\sigma_0(T)$ and $\sigma_1(T)$ need be considered in the virial expansion of the chemical shielding in terms of density:

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \cdots .$$

Any diatomic or polyatomic molecule has rotational and vibrational degrees of freedom as well as the usually inaccessible electronic degrees of freedom. Each rovibrational state can be expected to have a different chemical shielding. The NMR time scale is such that the observed signal is an ensemble average over all the rovibrational states of the molecule. In the limit of nearly zero pressure there will still be enough collisions for collisional averaging over all these states. Hence, an "isolated" molecule has a temperature dependent chemical shielding $\sigma_0(T)$.

In a recent paper we reported $\sigma_0(T)$ for several polyatomic molecules, BF_3, CF_4, SiF_4 and SF_6.[1] Theoretical analysis of the temperature dependence of the chemical shielding in an isolated molecule would be simplest for the diatomic case. However, the only ones which have been measured experimentally so far are those of ^{1}H in HCl and HBr.[2,3] Unfortunately the ^{1}H shifts are very small so that the relative errors in the measured values are fairly large. In particular, the unknown frequency shifts due to the temperature dependence of the reference substance used (in this case, acetone) is probably of the same order of magnitude as the quantity being sought. Since we expected ^{19}F and ^{13}C shifts to be larger than ^{1}H shifts, we have made measurements of the temperature dependence of the ^{19}F and ^{13}C shielding in isolated diatomic molecules: F_2, ClF, and CO. CO is of particular interest since theoretical values already exist for its temperature dependence.[4]

EXPERIMENTAL

The experimental procedures are as described earlier except for a number of complicating details in dealing with the molecules reported here.[5] ClF was degassed and vacuum distilled to eliminate some high boiling substances. No indication of high levels of impurities was found when vacuum distillation was used. F_2 and ClF are very reactive, hence we found it necessary to use an all-metal vacuum line which was well passivated with F_2 or ClF. A section of line was calibrated and a calibrated Bourdon gauge was used to measure the pressure at room temperature. Some of the gas was frozen out into calibrated sample tubes (< 4.0 mm o.d., ~2.2 mm i.d.). The amount of gas removed was determined from the difference in Bourdon gauge readings. In the case of ClF a small amount of solid NaF (~1 mg) was placed in the bottom of our borosilicate sample tubes in order that any HF formed be removed and reaction of ClF with tube walls be minimized.[6] Once made the samples were kept under liquid nitrogen until spectra were obtained. We believe our densities to be accurate to a relative error on the order of 5%. We usually observed the signal due to a small amount of SiF_4 (~1% or less) in the ClF samples. Even though we observed ^{19}F in ClF at temperatures as high as 350 K, the chemical shifts were reproducible within experimental error when spectra were again observed as samples were taken down in temperature. Hence, we are confident that decomposition did not systematically distort the results obtained.

^{13}C labeled CO was used as obtained from Stohler Isotopes. Even though CO has a substantial vapor pressure when transfers are made under liquid nitrogen, our samples are prepared in such a manner that the dead volume is less than 1 ml. This would have led to a small systematic error had it not been corrected. With an approximate correction we estimate our measured densities to be accurate to 2% maximum relative error.

For many molecules chemical shift determination is further complicated by broad lines. Such a complication was observed for F_2 and ClF, CO having a smaller linewidth on the order of 50–100 Hz wide. Our F_2 samples had widths of 300–1100 Hz depending on density and temperature (10–40 amagat and 220–380 K) while ClF was somewhat narrower, being 125–300 Hz wide under similar conditions. In such situations the peak top is rather flat and phase adjustments after performing the Fourier transform on the FID can cause substantial errors in determination of the peak center. To handle this problem the Fourier Transform software package for the Nicolet 1080 computer was modified by adding two subroutines,

TABLE I. Frequency shifts in the limit of zero density for ^{19}F in ClF and F_2 at 84.7 MHz.

	F_2		ClF	
T	$\Delta\nu_0$, Hz	SD	$\Delta\nu_0$, Hz	SD
230	−144.6	3.5		
240	−132.0	3.2		
250	−116.3	4.5		
260	−97.7	4.8		
270	−76.4	4.1	−10.2	6.1
280	−52.8	2.8	−10.7	2.2
290	−26.8	1.4	−7.2	0.5
300	0	1.6	0	1.5
310	30.7	2.8	10.3	1.8
320	61.8	3.7	23.4	1.7
330	94.3	4.1	38.8	1.3
340	127.7	4.8	56.1	1.1
350	162.0	7.8	74.9	1.5

one to calculate a Lorentzian line shape in one portion of memory, the second subroutine to subtract the calculated Lorentzian from the measured spectrum. We then can save the residual from one set of parameters (linewidth and position) to visually compare with the residual from a second set of parameters. The visual difference can be observed on the CRT by switching quickly from one portion of memory to another. This procedure yielded satisfactory results. We can confidently determine line centers to within one cursor position when the line width is well over 100 points wide at half height. In situations in which we observed very broad lines, determining the peak center had been the dominant contribution to error. After we developed the line fitting procedure the dominant contribution to the error once again became inaccuracies in densities, as we have always observed in the past.

TABLE II. Second virial coefficient of chemical shielding, $\sigma_1(T)$, for ^{19}F in ClF and ^1H in HCl and HBr, in Hz/amagat.[a]

	^{19}F in ClF		^1H in HBr		^1H in HCl	
T	σ_1	SD	σ_1	SD	σ_1	SD
240			1.109	0.069		
250			1.032	0.055		
260			0.965	0.047		
270	6.131	1.054	0.906	0.043	0.829	0.075
280	6.201	0.612	0.855	0.047	0.770	0.070
290	6.153	0.430	0.810	0.063	0.721	0.065
300	6.008	0.393	0.773	0.061	0.682	0.066
310	5.788	0.370	0.741	0.060	0.650	0.058
320	5.513	0.325	0.714	0.058	0.626	0.063
330	5.204	0.278	0.692	0.055	0.608	0.066
340	4.884	0.261	0.673	0.051	0.595	0.070
350	4.573	0.299	0.658	0.006	0.586	0.049
360			0.646	0.030	0.580	0.052
370			0.636	0.050	0.575	0.058
380			0.627	0.065	0.570	0.063
390			0.619	0.075	0.565	0.068
400			0.612	0.082	0.558	0.070
410			0.604	0.084	0.548	0.071
420			0.595	0.084	0.535	0.069
430			0.584	0.082	0.516	0.066
440			0.571	0.081	0.491	0.059

[a]Observed at 84.679 MHz for ^{19}F and 90.00 MHz for ^1H.

TABLE III. Summary of temperature dependence of chemical shielding in terms of the functional form $a_0+a_1(T-300)+a_2(T-300)^2$; $\sigma=\sigma_0(T)+\sigma_1(T)\rho+\cdots$.

	$\sigma_0(T)-\sigma_0(300\text{ K})$, ppm			σ_1, ppm/amagat		
Nucleus	10^2a_1	10^3a_2	10^2a_0	10^4a_1	10^5a_2	10^8a_3
^{19}F in F_2	−3.400	−0.1029	−0.547 ± 0.077			
^{19}F in ClF	−1.0415	−0.1878	−7.053	1.833	3.218	
^{13}C in CO	−0.03133 ± 0.0211		−0.4348 ± 0.017			
^1H in HBr			−0.8587	0.3867	−0.3228	0.1149
^1H in HCl			−0.7469	0.4102	−0.5366	0.2491

Our experiment consists of several steps. Samples of known density are made in the manner we have previously described.[5] The NMR spectrum of each constant density sample is taken as a function of temperature using an external lock substance with a known temperature dependence to stabilize the field.[7] The data are analyzed and line fit in a manner which has become relatively routine—extracting $\sigma_0(T)$ as well as $\sigma_1(T)$.

RESULTS

In the course of analyzing our results we obtained both $\sigma_0(T)$ and $\sigma_1(T)$ for each of five molecules: F_2, ClF, CO, HCl, and HBr. The range of values and the relative contributions of σ_0 and σ_1 to the observed shifts were extremely variable. Results for $\sigma_0(T)$ for F_2 and ClF are shown in Table I while $\sigma_1(T)$ is shown in Table II for ^{19}F in ClF and ^1H in HCl and HBr. Table III consists of the coefficients of least squares polynomial fits of the functions

$$\sigma_0(\tau)=a_1\tau+a_2\tau^2,$$

$$\sigma_1(\tau)=a_0+a_1\tau+a_2\tau^2,$$

where $\tau=T-300$ K. Of about 20 systems studied so far (involving ^1H, ^{19}F, ^{15}N, ^{13}C, ^{11}B) ^{19}F in F_2 has the largest temperature dependence observed, approximately 2.5

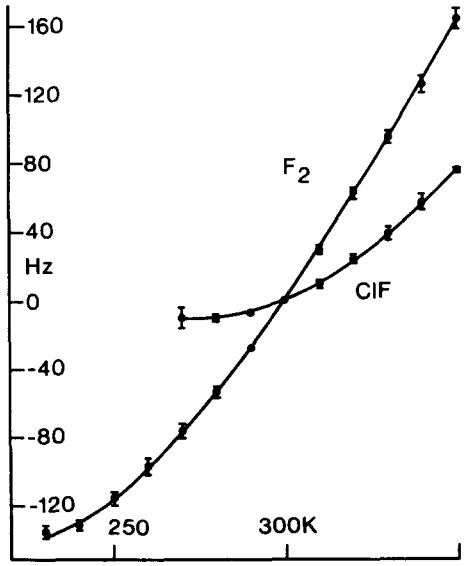

FIG. 1. Frequency shifts with temperature for the ^{19}F in the isolated F_2 and ClF molecules at 84.7 MHz.

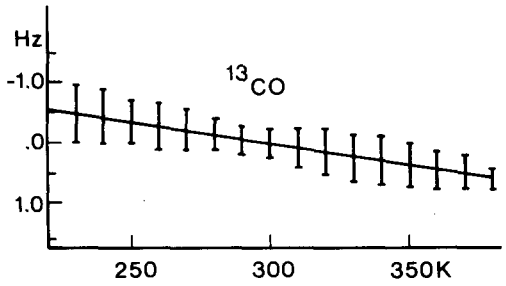

FIG. 2. Frequency shifts with temperature for ^{13}C in the isolated CO molecule at 22.6 MHz.

Hz/deg (0.03 ppm/deg). The F_2 data are almost completely dominated by the temperature dependent chemical shielding of the isolated molecule. This, coupled with the very broad lines make it very difficult to determine the small temperature dependence of σ_1. We obtain a value, $(-5.47 \pm 0.77) \times 10^{-3}$ ppm/amagat, which is constant (within our experimental error) over the entire temperature range studied.

The ClF system has some experimental features which make the data simpler to analyze than F_2—narrower lines and not nearly so large a variation of σ with temperature. In this case we could obtain both σ_0 and σ_1 as a function of temperature from 260 to 350 K. Below about 260 K we observed the presence of a dimer of ClF, longlived on the NMR time scale. Hence, we were unable to obtain meaningful data on monomer temperature and density dependence in this temperature range. The dimer data and interpretation are being reported separately.[8]

^{13}C in CO turned out to be a particularly frustrating case because its temperature dependence is small. The resonance peaks were narrower than either ClF or F_2 but broad enough that, even with our line fitting procedures, we could not determine the centers to the especially high precision required in this case. σ_1 is small $(-4.35 \pm 0.17) \times 10^{-3}$ ppm/amagat and the temperature dependence of only σ_0 could be determined. Even here the observed shift is only about three times as large as that of the reference shift. As can be seen from Fig. 2 the temperature dependence of σ_0 for CO is very small with a substantial relative error.

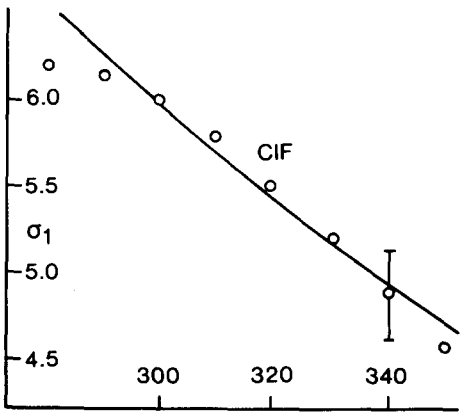

FIG. 3. Second virial coefficient of ^{19}F chemical shielding in ClF, in Hz/amagat.

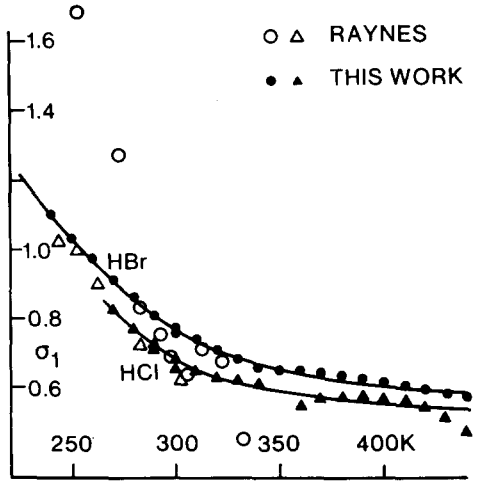

FIG. 4. Second virial coefficient of ^{1}H chemical shielding in HCl and HBr, this work and that of Raynes and Chadburn (Refs. 2 and 3).

We were able to obtain reliable values for $\sigma_1(T)$ for ^{1}H in HBr and HCl. However, since $\sigma_0(T)$ proved to be so nearly temperature independent, when coupled with the experimentally known uncertainty in the lock substance temperature dependence, we could extract no meaningful information about $\sigma_0(T)$.

Raynes and Chadburn measured the chemical shielding of gaseous HBr and HCl earlier using acetone as a secondary external reference.[2,3] They ultimately used ethane as the primary reference, assuming the C_2H_6 isolated molecule to have no temperature dependence. Our results for σ_1 of HCl are completely consistent with those of Raynes and Chadburn as can be seen in Fig. 4. However, they found that HBr gave an unusual curve for $\sigma_1(T)$ as can also be seen in Fig. 4. In the context of the Raynes, Buckingham, and Bernstein theory they were unable to fit their data with parameters that were physically realistic and suggested that the existing theory needed revision.[9] However, our results for HBr differ substantially from those of Raynes and Chadburn and appear quite similar to the data for HCl. Insofar as its density dependence is concerned, HBr does not appear to have any unusual behavior.

The ^{19}F shifts in F_2 and ClF are very large; the relative errors are 1.3 and 2.3% of the total observed shift, respectively. In these cases the relative errors are sufficiently small so that the nonlinear behavior of $\sigma_0(T)$ can be observed. For ^{13}C in CO the errors in the measurements compounded with the reported uncertainty of the reference shifts lead to absolute errors which are smaller than those in F_2 and ClF. These are shown by the error bars in Fig. 2. However, the shifts in CO are much smaller than in F_2 and ClF so that the relative error is 30% of the observed shift in CO. This precludes the observation of any nonlinear behavior in $\sigma_0(T)$.

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