Variation of chemical shielding with intermolecular interactions and rovibrational motion. III. ^{31}P nucleus in PH_3

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The functions $\sigma_1(T)$ and $\sigma_0(T)$ have been determined for the ^{31}P nucleus in PH_3. The former is a measure of the intermolecular effects on chemical shielding whereas the latter is a property of the isolated molecule and is due to centrifugal distortion and anharmonic vibration. The PH_3 molecule is of special interest since it is a good test case for the contributions to $\sigma_0(T)$ from the thermal average of bond angle deformation. It is also of interest that the observed temperature dependence of σ_0 is in a direction opposite to that observed for other isolated molecules.

In gas-phase NMR spectroscopy one observes the chemical shifts due to both intermolecular and intramolecular interactions. The former is observed in the dependence of nuclear resonance frequencies on density. Using a general virial theorem one may write the nuclear magnetic shielding in terms of density as follows:

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

The chemical shift due to intermolecular interactions can be characterized by the second virial coefficient σ_1 provided that samples of sufficiently low densities are used such that the higher order terms are negligible. The chemical shift due to intramolecular interactions is obtained by extrapolation of the data to zero pressure. The changes of σ_0 with temperature can be determined from this provided that the temperature dependence of the external heteronuclear reference is precisely known.

Several nuclei have been used for the study of intermolecular effects. ^1H and ^{19}F were the first probes used in a variety of solutes and solvents due to their very high sensitivity in NMR measurements.[1] ^{129}Xe has also been found to be a good probe due to spherical symmetry of the molecule and the very large shifts characteristic of this nucleus.[2,3] Another nucleus which has received some attention in the study of intermolecular effects is ^{13}C.[4] While the range of ^{13}C chemical shifts is reasonably large, the shifts due to intermolecular interactions is not as large as might be expected due to the rather protected location of a carbon nucleus in a molecule. Whereas ^1H, ^{19}F, and ^{129}Xe are exposed to collisions by being located on a peripheral atom, ^{13}C nuclei are not, except in CO.

Another very suitable nucleus for study of intermolecular effects on chemical shielding is ^{31}P. For example, in solutions of P_4 in several nonpolar solvents at 30 °C the chemical shift is found to vary linearly with the concentration (% by weight) of phosphorus by -0.460 ppm/%.[5] The only measurements of ^{31}P shifts with temperature in the gas phase is the study of P_4 gas by Heckmann and Fluck.[6] The vapor was studied in equilibrium with liquid phosphorus. By varying the temperature the density of the vapor could be changed. The data therefore reflects a combination of the density and temperature effects. From the gas to liquid shift data of Heckman and Fluck, Rummens estimates a σ_1 at room temperature equal to about -0.266 ppm/amagat.[1] If we attribute the temperature dependence of the chemical shift of the liquid entirely to the linear term σ_1, then we can make an estimate of σ_1 from the temperature dependence of the chemical shift of the liquid. Landolt-Bornstein gives the density of liquid phosphorus as a function of temperature from 319 to 354 K.[7] It is a linear function with a temperature coefficient of 7.42121×10^{-6} mole $\mathrm{cm}^{-3}\,\mathrm{deg}^{-1}$. From the temperature coefficient of the chamical shift of the liquid from 60 to 140 °C, 4.3×10^{-2} ppm/deg,[6] the average σ_1 for the liquid is found to be -0.259 ppm amagat^{-1}, which is very close to the value obtained by Rummens from the gas to liquid shift. This value of σ_1 is rather large, comparable to the shifts of ^{129}Xe in the presence of some molecules.[2,3]

The theoretical interpretation of σ_1 of nuclei in molecules with structure is difficult. At best, this can be done only in a qualitative fashion. The spherical part of the intermolecular potential between molecules with structure is not well known and the dependence on orientation of the molecules is even less well known. In addition, the intermolecular effects on magnetic shielding of nuclei in molecules with structure are complicated by what may qualitatively be described as site effects.[8] The interpretation of σ_1 for ^1H and ^{19}F nuclei has been done in terms of various contributions such as bulk susceptibility, van der Waals, anisotropic, and repulsive contributions, and effects due to electrical moments.[9] The Raynes, Buckingham, and Bernstein model on which this interpretation is based was found to be moderately successful in interpreting trends in σ_1 in a

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broad way.[1] However, the model has been less successful in quantitative prediction of σ_1 differences between specific systems. It has been found that different values of the parameters are sometimes found for the same solute molecule. In addition, the observed temperature dependence of σ_1 in molecules with structure is not explained satisfactorily by any model. While the interpretation of the magnitudes and the temperature dependence of intermolecular effects on chemical shielding is attended with these difficulties, the interpretation of the temperature dependence of the intramolecular effects is somewhat more promising.

The variation of chemical shielding with rovibrational motion is obtained by studying the temperature dependence of the NMR resonance frequency in the limit of zero pressure. In this limit one is effectively observing the thermal average of the NMR spectrum of the isolated molecule. The temperature dependence of the NMR chemical shielding of a nucleus in an isolated molecule has been studied for several ^1H and ^{19}F systems.[10–13] The ^1H shift with temperature in isolated HCl and HBr molecules, the ^{19}F shift in CF_4, SiF_4, BF_3,[14] F_2, ClF[15], and the ^{13}C shift in CO[15,16] have been interpreted in terms of the centrifugal distortion and the anharmonic vibration contributions to the thermal average of Δr and thus to the NMR chemical shielding σ. In some cases, nearly all of the temperature dependence is due to centrifugal distortion (as in HCl, HBr, and CO)[10,11,15] and in other cases a combination of both centrifugal distortion and anharmonic vibration account for the temperature dependence of σ.[14,15] Most of the systems which have been studied involve nuclei of atoms which are bonded to only one other atom in the molecule. The $\langle\Delta r\rangle$ of greastest significance in these cases are the $\langle\Delta r\rangle$ of the one bond linking the nucleus under study to the rest of the molecule. In the cases in which anharmonic vibration plays an important role, the changes in σ with temperature are sufficiently large to allow the empirical determination of $d\sigma/d(\Delta r)$ (or $d\sigma/dR$ in our notation).[15] It also turns out that in these cases $d\sigma/d(\Delta r)$ is rather large.[14,15]

Some other gas-phase NMR studies have involved centrally located nuclei, such as ^{13}C in CO_2, and CH_4,[4,17,18] ^{11}B in BF_3,[18] ^{15}N in $N^{15}NO$.[17] In all these studies the experimental NMR shifts are found to be rather small and therefore accompanied by large relative errors. The determination of a reliable $d\sigma/dR$ then becomes very difficult. For example, for ^{11}B in BF_3, only an estimate of the upper limit of $d\sigma_B/dR$ is possible because the shift with temperature of the ^{11}B NMR signal in the gas at nearly zero pressure is very small.[18] It might also be expected that $d\sigma/dR$ is somewhat smaller in these cases from the example of ^{11}B in BF_3.[18]

All the systems studied so far have involved only $d\sigma/dR$ in the linear term in the Taylor series expansion of the chemical shielding. Thus, we have information about the contribution of bond stretching to the temperature dependence of chemical shielding. No parameters of the type $\partial\sigma/\partial\Delta\alpha$ have been involved due to the symmetry of the molecules studies (T_d, D_{3h}, O_h, $D_{\infty h}$, and $C_{\infty v}$). For these cases, the thermal average of the change in the bond angle α is zero. Thus, angular contributions are involved only in second order or higher order terms. In other cases, such as AX_3-type molecules of C_{3v} symmetry and AX_2-type molecules of C_{2v} symmetry, the thermal average of $\Delta\alpha$ is not zero. Thus, some information may be obtained about $\partial\sigma/\partial\Delta\alpha$ in these molecules. Of these systems, the AX_2 type is the simplest. The molecular constants (e.g., cubic force constants) which are necessary for the interpretation of the temperature dependence of σ are available for many AX_2-type molecules, e.g., H_2O, D_2O, H_2S, D_2S, H_2Se, D_2Se, SO_2, OF_2, NO_2, O_3, ClO_2, SeO_2.[19–22] However, the properties of these triatomics for which the anharmonic force constants are known are not the ideal ones for NMR measurements. The nuclei in the molecules of interest are in the following order of relative sensitivity for NMR measurements and separated by approximately one order of magnitude in sensitivity:

$$(^1H \text{ and } ^{19}F),\ ^{31}P,\ (^2D \text{ and } ^{77}Se),\ ^{15}N\,.$$

^1H has a high sensitivity but the ^1H shifts are very small. ^{19}F would be an ideal nucleus for NMR study in terms of the size of its shifts; however, OF_2 is an unstable compound. ^{31}P is a favorable nucleus to study because of its high sensitivity and large shifts. None of the AX_2-type molecules listed above have ^{31}P nuclei, however. ^2D, like ^1H has very small NMR shifts. ^{77}Se would be a possible candidate for study in the H_2Se molecule. The difficulties associated with studying this gas are related to its relatively high boiling point. Observations of the temperature and density dependence of the chemical shielding have to be carried out in samples of reasonably high density such as to have a sufficient number of nuclei in the receiver coil. The substance should remain in the gas phase at densities of about 5 to 40 amagat for a fairly sizable portion of the temperature range in which NMR measurements are feasible (200–400 K). A sample of H_2Se with a density of 1 amagat condenses at 230 K. Premature condensation of H_2Se samples of the desired density would shorten the range of temperatures at which the NMR data can be obtained. Since a wide range of temperatures is desirable for the determination of the effect of anharmonic vibration and centrifugal distortion on σ, premature condensation of H_2Se samples makes it a less than ideal system for this study. ^{15}N in NO_2 would be a favorable nucleus but unfortunately NO_2 is paramagnetic, a property which would lead to broadening of the ^{15}N signal such that it cannot be observed even with FT techniques. In addition, there would be an overwhelming $1/T$ Curie type shift due to the unpaired electron density at the ^{15}N nucleus which would swamp out the effects of vibration–rotation.

Of the next simplest molecular types with $\langle\Delta\alpha\rangle^T \neq 0$, ^{15}N in NH_3 and ^{31}P in PH_3 are the most likely candidates. Like H_2Se, the NH_3 system is plagued with condensation problems at one end of the temperature range. It is also complicated by decomposition to $N_2 + H_2$ at the other end of the temperature range. The results on ^{15}N in NH_3 will be reported later.[23] ^{31}P in PH_3 appears to be the best system for study to illustrate the angular contributions to the shift. First, the cubic force constants

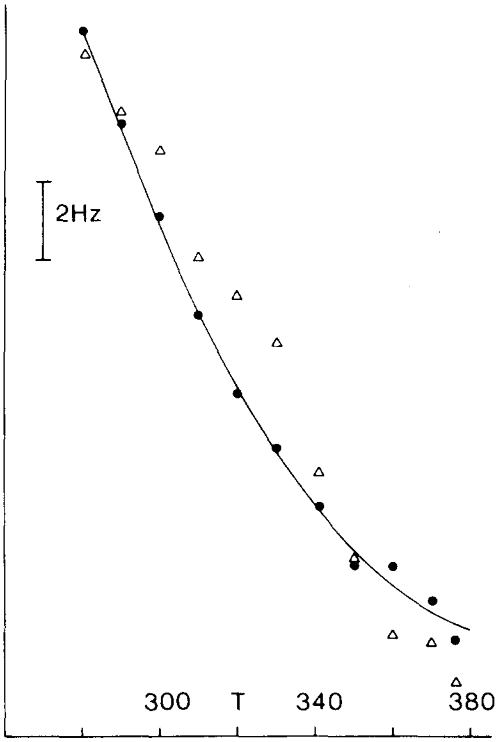

FIG. 1. Typical raw data obtained for ^{31}P NMR in PH_3. This is for a sample of density equal to 29.895 amagat. Triangles show frequencies of peak centers estimated visually, filled circles are frequencies of the peak centers determined by the curve fitting procedure described in the text. The solid curve shows a polynomial function chosen to represent the data (i.e., the filled circles).

for PH_3 and PD_3 have been calculated by Kuchitsu.[24] PH_3 is one of very few molecules with four or more atoms for which even estimates of cubic force constants are available. The other such molecules are C_2H_2,[25] CH_3F,[26] NH_3 and ND_3,[27] CH_4,[28] and SO_3.[29] Second, ^{31}P shifts are generally sizable so that a large shift with temperature is expected. Due to its favorable sensitivity, the availability of cubic force constants, the expectation of sizable shifts with small relative error, and the absence of other complicating factors the ^{31}P chemical shift in PH_3 has been chosen as the test case for the estimation of the importance of the angular contributions to the temperature dependence of the chemical shielding.

EXPERIMENTAL

PH_3 gas was frozen out with liquid nitrogen and degassed in a conventional vacuum system. Expansion upon warming into an accurately known volume at a pressure of less than 300 torr provides a known number of moles of gas. This gas can then be swept with mercury into a sample tube held under liquid nitrogen and then sealed off. Sample tubes of borosilicate tubing, nominally 5 cm long, 3.9 mm o.d., 2.2 mm i.d., 0.2 ml, were previously calibrated with mercury and the volume is accurately known at about 1% relative error. The PH_3 samples were limited to less than 30 amagats density (1 amagat $= 2.68 \times 10^{19}$ molecules cm^{-3}) in order that the vapor temperature range be upwards of 300 K in all samples.

TABLE I. Second virial coefficient of ^{31}P chemical shielding σ_1 in PH_3, Hz amagat^{-1} at 36.42 MHz.

T, K	σ_1	S.D. Hz amagat^{-1}
270	3.052	0.103
280	3.051	0.063
290	3.046	0.067
300	3.039	0.092
310	3.029	0.112
320	3.015	0.123
330	2.999	0.125
340	2.980	0.120
350	2.958	0.115
360	2.933	0.120
370	2.905	0.149
380	2.874	0.204

^{31}P spectra in PH_3 were obtained at 36.42 MHz on a Bruker spectrometer operating in the pulsed Fourier transform mode using a quadrature detection system. A $\pi/4$ rf pulse with a duration of 13 μsec and a recycle time of 2.2 sec was used. A Nicolet 1080 data system was used to accumulate the free induction decays. The multiplet spectrum first observed by Gutowsky, McCall, and Slichter[30] was reduced to a single peak with 2 W of decoupling power. 4 K data points collected in a sweep width of 1000 Hz provided adequate definition. A satisfactory signal-to-noise ratio was acheived by collecting 1000–2000 transients. The field was stabilized by time-shared lock using the high field sideband of the CD_3 group of toluene-d_8. Regulation of the temperature of the spinning 5 mm sample assembly, i.e., the gas sample tube together with the lock substance in the annular region, is provided by a Bruker B-ST 100/700 variable temperature system. With this unit the temperature can be set to the nearest degree and a meter indicates deviations from this in units of 0.1 deg. Calibration and other details of temperature regulation are given in Ref. 31.

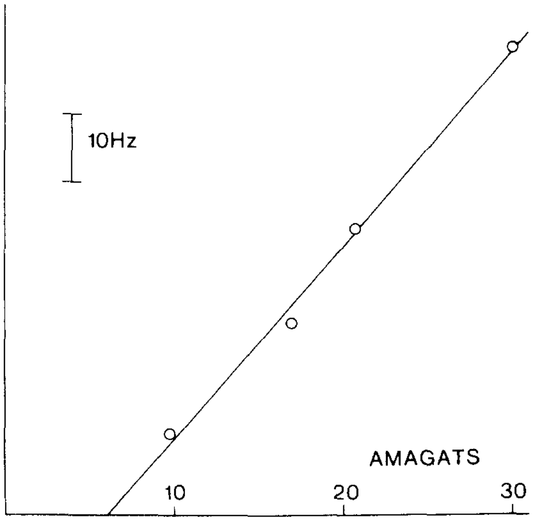

FIG. 2. A typical frequency vs density plot at a given temperature. This one is for $T = 370$ K. The slope is the value of σ_1 for ^{31}P in a PH_3 molecule interacting with another PH_3 molecule.

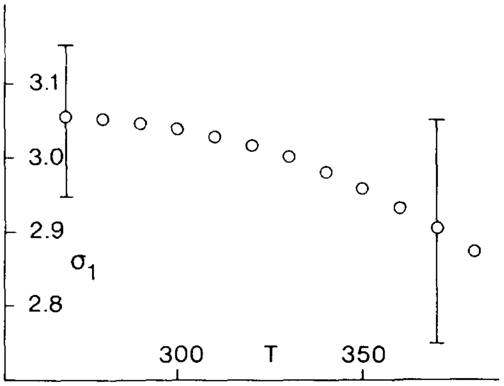

FIG. 3. The temperature dependence of σ_1 for ^{31}P in a PH_3 molecule interacting with another PH_3 molecule.

The lower density samples of PH_3 exhibited broad lines especially at higher temperatures. The linewidths varied depending on density and temperature. For the broader peaks, the location of the peak centers are accompanied by substantial errors because phase adjustments on the Fourier transformed signals cannot be done adequately. In such cases, the peak center is determined by subtracting a calculated Lorentzian peak from the measured spectrum. The residuals from one such subtraction can be visually compared with the residual from another one using a slightly different set of peak parameters. From the appearance of the residuals the need for a phase adjustment on the measured peak can also be determined. This line fitting procedure which was developed earlier[12] reduced the inaccuracies of determining the peak center sufficiently so that the spectrometer error is reduced to the statistical error and errors in temperature regulation. A detailed discussion of sources of error is given in Ref. 32.

The ^{31}P NMR resonance frequency was determined over the range 270–380 K for six samples ranging in density from 9.8 to 29.9 amagat. The frequencies for each sample are least-squares fitted to a polynomial of degree 2 in $(T-300\ \text{K})$. The lock solvent temperature dependence which is known from previous work[33] is subtracted from each sample. The linear fit of the resulting frequencies at each temperature vs density gives σ_1. The $\sigma_1(T)$ function so obtained is used to remove the effect of the density dependence from each sample, leaving several independent measures of $\sigma_0(T)$. These are combined to determine σ_0 and the standard deviation of σ_0 at each temperature.[33]

TABLE II. Temperature dependence of the chemical shielding of ^{31}P in an isolated PH_3 molecule in terms of frequency shifts relative to 300 K at 36.42 MHz. Standard deviation is 1.05 Hz.

T, K	$\Delta\nu$, Hz
270	7.81
280	4.93
290	2.32
300	0.0
310	−2.04
320	−3.81
330	−5.29
340	−6.49
350	−7.41
360	−8.06
370	−8.42
380	−8.50

TABLE III. Summary of the temperature and density dependence of the chemical shielding of ^{31}P nucleus in PH_3, in ppm;

$$\sigma(T,\rho)=\sigma_0(T)+\sigma_1(T)\rho\ ,$$

$$\sigma_0(T)-\sigma_0(300)=a_1(T-300)+a_2(T-300)^2\ ,$$

$$\sigma_1(T)=a_0+a_1(T-300)+a_2(T-300)^2\ .$$

	$\sigma_0(T)-\sigma_0(300)$	$\sigma_1(T)$
a_0	0	-0.08344
a_1	$+5.9935\times10^{-3}$	$+2.4166\times10^{-5}$
a_2	-3.8432×10^{-5}	$+4.035\times10^{-7}$

RESULTS

Typical raw data are shown in Fig. 1 and the linearity of the frequency vs density plots obtained at each temperature is illustrated by Fig. 2. It is clear that terms involving $\sigma_2\rho^2$ and higher order need not be included. The slopes obtained from plots like Fig. 2 are tabulated in Table I from 270 to 380 K. Below 270 K condensation of the higher density samples occurred. Samples with densities much lower than 9 amagat remained in the vapor phase at lower temperatures. However, broadness of the peak obtained at densities below 9 amagat precluded accurate measurements of the resonance frequency. The σ_1 values obtained are rather large compared to ^{1}H and ^{19}F. They are about $\frac{1}{3}$ the values found for P_4 gas. The temperature dependence of σ_1 is very small, unlike ^{129}Xe, with which it is comparable in magnitude. A plot of σ_1 with temperature is shown in Fig. 3.

The temperature dependence of σ_0 is more pronounced than that of σ_1. Moreover, it is unusual in that it is in a direction which is opposite that observed for all other systems. Table II shows the $\sigma_0(T)$ function and the estimated error associated with it. Figure 4 shows that this function certainly cannot be fitted with a temperature dependence in the usual direction. The unusual direction of the temperature dependence appears to be real, definitely outside the errors in the measurement. Table III gives a summary of the $\sigma_1(T)$ and the $\sigma_0(T)$ functions for ^{31}P in PH_3.

CONCLUSIONS

The ^{31}P NMR shifts in PH_3 gas as a function of density and temperature have been measured with sufficient precision to allow the determination of both the $\sigma_0(T)$ and the $\sigma_1(T)$ functions. The precision of the $\sigma_0(T)$ function is sufficient to indicate definitively a temperature dependence which is opposite to that observed for other systems such as ^{1}H in HCl and HBr,[10,11] ^{19}F in F_2, ClF,[12] CF_4, SiF_4, BF_3, SF_6,[13] ^{13}C in CO[12] and CO_2,[17] and ^{15}N in $N^{15}NO$

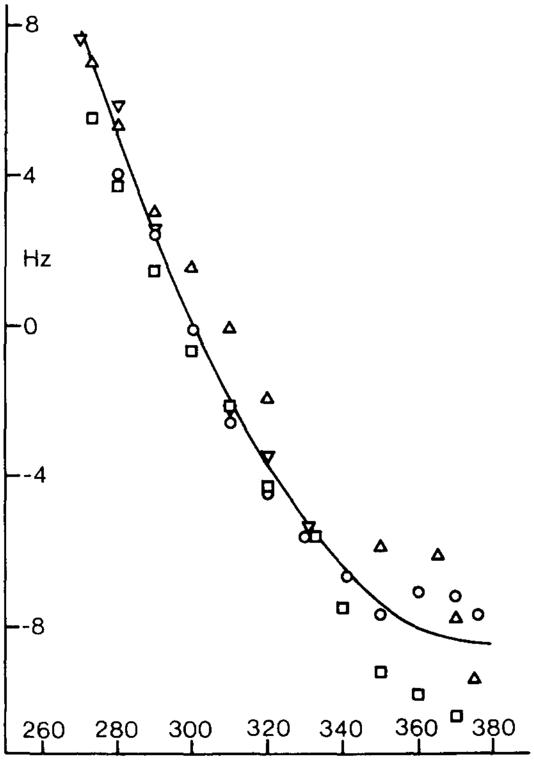

FIG. 4. The temperature dependence of the resonance frequency of ^{31}P in an isolated PH_3 molecule.

and ^{15}NNO.[17] This $\sigma_0(T)$ function should be a good test case for the angular contributions to the temperature dependence of the chemical shielding of an isolated molecule. It is unfortunate that the temperature range in which the measurements could be carried out is not any wider than it is. The curvature of the $\sigma_0(T)$ function would be more easily established with a wider range of values for which the thermal average of Δr and $\Delta\alpha$ can be calculated and compared with the experimental results. Nevertheless the opposite direction of the temperature dependence of the $\sigma_0(T)$ function for ^{31}P in PH_3 is established. The ^{15}N in NH_3 also appears to show the same unusual $\sigma_0(T)$, but the complications in the interpretation of the results for this system do not allow this to be established unequivocally as yet.[23]

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