Effect of centrifugal distortion and anharmonic vibration on the chemical shielding of ^{31}P in PH_3 and PD_3

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(Received 5 January 1978)

The observed temperature dependence of ^{31}P NMR chemical shift and the sign of the ^{31}P isotope shift in the PH_3–PD_3 system are found to be inconsistent with the thermal average of $\Delta\alpha$ which can be calculated using approximate cubic force constants for PH_3 and PD_3 [K. Kuchitsu, J. Mol. Spectrosc. 7, 399 (1961)]. By using a reasonable estimate for k_{222} and k_{244}, and keeping all other cubic force constants the same as Kuchitsu's, the observed temperature dependence of the ^{31}P NMR signal is reproduced within experimental error.

^{31}P NMR studies of PH_3 gas have revealed some very interesting results.[1] The most striking feature of this system is that the temperature dependence of the chemical shielding of ^{31}P in the isolated PH_3 molecule is in the opposite direction to that observed in every other molecule for which it is known. In an isolated molecule the chemical shielding σ_0 usually decreases with increasing temperature.[2–4] In an isolated PH_3 molecule however, the ^{31}P chemical shielding was found to increase with increasing temperature, i.e., $d\sigma_0/dT$ is positive. In this paper we will examine the conditions which can give rise to such a behavior and attempt to reconcile this with isotope shifts and the temperature dependence of σ_0 observed in other isolated molecules. In order to understand the unusual behavior of the PH_3 system, let us consider the conditions under which it is possible for $d\sigma_0/dT$ to be positive.

The theory of the shift of the NMR signal of a nucleus in an isolated molecule with increasing temperature has been considered in earlier papers.[5–8] The chemical shielding of a nucleus in an isolated molecule is a function of temperature due to the anharmonicity of vibrations and the centrifugal distortion of the molecule. When expanded in terms of the normal coordinates of a molecule, σ_0 may be written as

$$\sigma_0(T) = \sigma_e + \sum_i (\partial\sigma/\partial q_i)_{eq} \langle q_i \rangle^T + \cdots \quad .$$

For a diatomic molecule,

$$\sigma_0(T) = \sigma_e + \langle \Delta r \rangle^T (\partial\sigma/\partial\Delta r)_{eq}$$
$$+ \text{quadratic and higher order terms.}$$

For a nucleus in an atom bonded to only one other atom in a polyatomic molecule, the most significant Δr_i is that of the bond involving the nucleus in question. For diatomic molecules we see that the shift depends essentially on the linear term which is a product of two quantities, the thermal average of Δr and the derivative of the NMR chemical shielding with respect to Δr. This has been found to be the case for many polyatomic molecules as well. There are also higher order terms which have been considered unimportant for the systems studied, and in some molecules there are linear terms in $\langle \Delta\alpha \rangle^T$ in addition to the linear term in $\langle \Delta r \rangle^T$.

$\langle \Delta r \rangle$ is generally expected to be positive and to monotonically increase with temperature. Observations and theoretical arguments supporting this have been given by Herschbach and Laurie as well as others.[9–12] Since $\langle \Delta r_i \rangle^T$ is expected to increase with temperature, the direction of the temperature dependence of chemical shielding will be uniformly decreasing with temperature, provided that $(\partial\sigma/\partial\Delta r)_{eq}$ is negative. The empirical value of $(\partial\sigma/\partial\Delta r)_{eq}$ has indeed been found to be negative in all the systems which have been investigated so far. Examples are ^1H in HCl and HBr, ^{19}F in F_2, ClF, SiF_4, CF_4, SF_6, and BF_3, and ^{13}C in CO.[5–8] However, in all these systems the nucleus is a peripheral one and it is not unusual to find that the chemical shielding of a nucleus decreases with the extension of the one bond with which it is attached to the rest of the molecule. In every system of this type in which theoretical values of σ have been calculated at the equilibrium configuration and also at configurations away from equilibrium, it has been found that deshielding accompanies bond extension. Examples are ^1H in H_2^+ ion,[13] ^1H in various isotopomers of H_2,[5,14–16] ^1H and ^{19}F in HF,[17] ^1H in LiH,[18] ^{13}C and ^{17}O in CO,[19] and ^{14}N in N_2.[20] The only known exception appears to be ^3Li in LiH.[18] $d\sigma_0/dT$ can be positive if $(\partial\sigma/\partial\Delta r)_{eq}$ is positive, unlike empirical and theoretical values mentioned above.

There is one other observable which is related to $d\sigma/d\Delta r$. Since $\langle \Delta r \rangle^T$ is usually found to be larger for the lighter isotope than for the heavier isotope, the sign of $d\sigma/d\Delta r$ also determines the sign of the isotope shift, $(\sigma_{\text{heavy}} - \sigma_{\text{light}})$.[21] Experimental values of the latter are nearly always positive.[22] This is consistent with the nearly always negative experimental values of $d\sigma_0/dT$. If $d\sigma_0/dT$ is due entirely to $\langle \Delta r \rangle^T$, the sign of the isotope shift will be the opposite of the sign of $d\sigma_0/dT$. Thus, the positive sign of $d\sigma_0/dT$ in PH_3 implies a negative sign of the isotope shift as well, so long as only $\langle \Delta r \rangle^T$ is considered.

Some molecules have bond angles that cannot change without destroying the symmetry of the molecule. Examples are CO_2, BF_3, and CH_4-type molecules. In such cases the changes in the bond angles during vibration are not all independent of one another, that is, they are

J. Chem. Phys. **69**(2), 15 Jul. 1978 0021-9606/78/6902-0615$01.00

related by a redundancy condition.[23,24] For example, the changes in the bond angles of BF_3 are related by $\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 = 0$. For these molecules the thermal average of $\Delta\alpha_i$, where α_i is any one of the bond angles, is zero. Thus, in such molecules the linear term in $\sigma_0(T)$ includes only $\langle\Delta r\rangle^T$, no $\langle\Delta\alpha\rangle^T$ appears. "Bent" molecules such as AX_3-type molecules with C_{3v} symmetry (of which PH_3 is an example) and AX_2-type molecules with C_{2v} symmetry, do not have a redundancy condition relating changes in the bond angles, so they have a nonzero thermal average of $\Delta\alpha_i$. Therefore, in all bent molecules we have to consider the linear contribution to $\sigma_0(T)$ due to $\langle\Delta\alpha_i\rangle^T$, as well as $\langle\Delta r_i\rangle^T$. While $\langle\Delta r_i\rangle^T$ is normally expected to increase with temperature, there is no physical reason why $\langle\Delta\alpha\rangle^T$ has to increase with temperature. The PH_3 molecule provides a good test case for the behavior of $\langle\Delta\alpha\rangle^T$ with temperature and its effect on the temperature dependence of σ_0.

THE THERMAL AVERAGE OF Δr AND $\Delta\alpha$

PH_3 has four normal modes: two are totally symmetric and two are doubly degenerate. The set of symmetry coordinates that we will use are the ones used by Kuchitsu[25] for PH_3, the same ones used by Morino, Kuchitsu, and Yamamoto for NH_3[26]:

$$\begin{aligned} S_1 &= 3^{-1/2}(\Delta r_1 + \Delta r_2 + \Delta r_3), \\ S_2 &= 3^{-1/2} r(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3), \\ S_{3a} &= 6^{-1/2}(2\Delta r_1 - \Delta r_2 - \Delta r_3), \\ S_{4a} &= 6^{-1/2} r(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3), \\ S_{3b} &= 2^{-1/2}(\Delta r_2 - \Delta r_3), \\ S_{4b} &= 2^{-1/2} r(\Delta\alpha_2 - \Delta\alpha_3), \end{aligned} \tag{1}$$

where $\Delta r_i = \Delta r(P\text{–}H_i)$, $\Delta\alpha_i = \Delta\alpha(H_j\text{–}P\text{–}H_k)$, and $r = r_e(P\text{–}H)$. These symmetry coordinates are related to the normal coordinates Q_i by

$$S_1 = L_{11}Q_1 + L_{12}Q_1, \tag{2}$$

$$S_2 = L_{21}Q_1 + L_{22}Q_2,$$

in which the elements of the L matrix are obtained from the eigenvectors in the solution of the normal coordinate problem for PH_3 molecule. We need to consider only the totally symmetric coordinates S_1 and S_2 since the nontotally symmetric ones lead to a zero contribution to the thermal average of Δr or $r\Delta\alpha$:

$$\Delta r_1 = \Delta r_2 = \Delta r_3 = 3^{-1/2}(\bar{L}_{11}q_1 + \bar{L}_{12}q_2), \tag{3}$$

$$r\Delta\alpha_1 = r\Delta\alpha_2 = r\Delta\alpha_3 = 3^{-1/2}(\bar{L}_{21}q_1 + \bar{L}_{22}q_2), \tag{4}$$

where

$$q_i = (4\pi^2 c\omega_i/h)^{1/2} Q_i, \tag{5}$$

$$\bar{L}_{si} = (h/4\pi^2 c\omega_i)^{1/2} L_{si}. \tag{6}$$

The thermal average of chemical shielding of any nucleus in this molecule is given by a Taylor series expansion

$$\langle\sigma\rangle^T = \sigma_e + \langle\Delta r_1\rangle^T \left\{\left(\frac{\partial\sigma}{\partial\Delta r_1}\right)_{eq} + \left(\frac{\partial\sigma}{\partial\Delta r_2}\right)_{eq} + \left(\frac{\partial\sigma}{\partial\Delta r_3}\right)_{eq}\right\} + \langle r\Delta\alpha_1\rangle^T \left\{\left(\frac{\partial\sigma}{\partial r\Delta\alpha_1}\right)_{eq} + \left(\frac{\partial\sigma}{\partial r\Delta\alpha_2}\right)_{eq} + \left(\frac{\partial\sigma}{\partial r\Delta\alpha_3}\right)_{eq}\right\} + \text{quadratic and higher order terms.} \tag{7}$$

If σ is to be determined for the ^{31}P nucleus which is at the threefold axis of the molecule, then the following relations hold:

$$\left(\frac{\partial\sigma_P}{\partial\Delta r_1}\right) = \left(\frac{\partial\sigma_P}{\partial\Delta r_2}\right) = \left(\frac{\partial\sigma_P}{\partial\Delta r_3}\right) \tag{8}$$

and

$$\left(\frac{\partial\sigma_P}{\partial r\Delta\alpha_1}\right) = \left(\frac{\partial\sigma_P}{\partial r\Delta\alpha_2}\right) = \left(\frac{\partial\sigma_P}{\partial r\Delta\alpha_3}\right). \tag{9}$$

On the other hand, if σ is to be determined for the ^1H nuclei, then

$$\frac{\partial\sigma_{H1}}{\partial\Delta r_2} = \frac{\partial\sigma_{H1}}{\partial\Delta r_3} \neq \frac{\partial\sigma_{H1}}{\partial\Delta r_1} \tag{10}$$

and

$$\frac{\partial\sigma_{H1}}{\partial r\Delta\alpha_2} = \frac{\partial\sigma_{H1}}{\partial r\Delta\alpha_3} \neq \frac{\partial\sigma_{H1}}{\partial\Delta\alpha_1}. \tag{11}$$

In order to obtain σ as a function of temperature, we need to determine the thermal average of Δr_1 and $r\Delta\alpha_1$ as functions of temperature. These are obtained from the anharmonic vibration and centrifugal distortion contributions to $\langle q_1\rangle^T$ and $\langle q_2\rangle^T$ which are given in terms of the molecular constants by Toyama *et al.*[27] The $\langle q_i\rangle^T$ take the following particular forms for the PH_3 molecule:

$$\langle q_1\rangle^T_{\text{anh}} = -\frac{1}{2\omega_1}\left[3k_{111}\coth(hc\omega_1/2kT) + k_{122}\coth(hc\omega_2/2kT) + 2k_{133}\coth(hc\omega_3/2kT) + 2k_{144}\coth(hc\omega_4/2kT)\right], \tag{12}$$

$$\langle q_1\rangle^T_{\text{cent}} = \frac{kT}{4\pi c\omega_1}\left(\frac{1}{hc\omega_1}\right)^{1/2} \sum_{\alpha=x,y,z} \frac{a_1^{\alpha\alpha}}{I^{(e)}_{\alpha\alpha}}, \tag{13}$$

$$\langle q_2\rangle^T_{\mathrm{anh}} = -\frac{1}{2\omega_2}\,[3k_{222}\coth(hc\omega_2/2kT) + k_{211}\coth(hc\omega_1/2kT) + 2k_{233}\coth(hc\omega_3/2kT) + 2k_{244}\coth(hc\omega_4/2kT), \tag{14}$$

$$\langle q_2\rangle^T_{\mathrm{cent}} = \frac{kT}{4\pi c\omega_2}\left(\frac{1}{hc\omega_2}\right)^{1/2} \sum_{\alpha=x,y,z} \frac{a_1^{\alpha\alpha}}{I^{(e)}_{\alpha\alpha}} \,. \tag{15}$$

The inertial constants for PH$_3$ are given by Nielsen as follows[28]:

$$a_1^{(xx)} = a_1^{(yy)} = 2\{\beta_1(I^{(e)}_{xx} - \tfrac{1}{2}I^{(e)}_{zz})^{1/2} + \tfrac{1}{2}\beta_3 I^{(e)\,1/2}_{zz}\}, \tag{16}$$

$$a_1^{(zz)} = 2\beta_3 I^{(e)\,1/2}_{zz}\,, \tag{17}$$

$$a_2^{(xx)} = a_2^{(yy)} = 2\{\beta_3(I^{(e)}_{xx} - \tfrac{1}{2}I^{(e)}_{zz})^{1/2} - \tfrac{1}{2}\beta_1 I^{(e)\,1/2}_{zz}\}\,, \tag{18}$$

$$a_2^{(zz)} = -2\beta_1 I^{(e)\,1/2}_{zz}\,, \tag{19}$$

where β_1 and β_3 are dimensionless constants. The latter have been derived by Morino, Kuchitsu and Yamamoto for the pyramidal AX$_3$ molecule using the same set of symmetry coordinates as in Eq. (1):

$$\beta_1 = -(\tfrac{1}{3}\mu)^{1/2}\{2L^{-1}_{21}\sin(\tfrac{1}{2}\alpha) + L^{-1}_{22}\,[3\cos(\tfrac{1}{2}\alpha) - \sin^2(\tfrac{1}{2}\alpha)/\cos(\tfrac{1}{2}\alpha)]\}\,, \tag{20}$$

$$\beta_3 = (\tfrac{1}{3}\mu)^{1/2}\{2L^{-1}_{11}\sin(\tfrac{1}{2}\alpha) + L^{-1}_{12}\,[3\cos(\tfrac{1}{2}\alpha) - \sin^2(\tfrac{1}{2}\alpha)/\cos(\tfrac{1}{2}\alpha)]\}\,, \tag{21}$$

where $\mu = 1/m_{\mathrm{H}}$ in PH$_3$ and α = the equilibrium HPH angle. L^{-1}_{ij} are the elements of the inverse of the same L matrix referred to in Eqs. (2) and (6). The equilibrium moments of inertia were obtained from the rotational constants in the microwave spectrum of this molecule. For the isotopic molecule PD$_3$ for which they were not all available, the equilibrium moments of inertia were calculated as follows:

$$I_{zz} = 3mh^2\tan^2\beta,$$

$$I_{xx} = I_{zz}/2 + (3mM/(3m+M))\,h^2\,,$$

where $m = m_{\mathrm{H}}$ or m_{D}, $M = m_{\mathrm{P}}$, $h = r\cos\beta$, using the following molecular dimensions[29]:

$$h = 0.764\ \text{Å}, \quad \beta = 57°\,30', \quad \text{and } \alpha = 93°\,50'\ .$$

The $a_1^{\alpha\alpha}$ and $a_2^{\alpha\alpha}$ constants for PH$_3$ were calculated using Eqs. (16)–(20).[30]

The molecular constants required in the calculation of the anharmonic vibration contribution to $\langle\Delta r\rangle^T$ and $\langle r\Delta\alpha\rangle^T$ in PH$_3$ were obtained from Kuchitsu.[25] Since the harmonic frequencies of PH$_3$ and PD$_3$ are not experimentally known, they were obtained by using Dennison's rule[31] on the series of molecules of the type AH$_3$ and AD$_3$ involving Group V elements. The cubic force constants [Set (ii)] were calculated by Kuchitsu and the F matrix obtained using these harmonic frequencies and also from the F matrices given by Sundaram *et al.*,[32] Set (i).

Both sets were used in our calculations. Table I summarizes the molecular constants for PH$_3$ and PD$_3$ which we used.

Some properties of the $\langle\Delta r\rangle^T$ and $\langle r\Delta\alpha\rangle^T$ functions for PH$_3$ and PD$_3$ are shown in Table II, in which they are compared with the corresponding values for NH$_3$ and ND$_3$ which were given by Toyama *et al.*[27] The $\langle\Delta r\rangle^T$ functions for PH$_3$ and PD$_3$ are essentially identical for the two sets of constants which Kuchitsu obtained from the two sets of F matrices. The anharmonic vibration contribution to the $\langle r\Delta\alpha\rangle^T$ function is somewhat different for the two sets. The total change in $\langle r\Delta\alpha\rangle$ from 200 to 400 K is virtually the same for both sets. The $\langle\Delta r\rangle^T$ function is nearly identical for both sets at 300 K although the change over the 200 deg range is somewhat larger for Set (ii) than for Set (i). However, since there are no substantial differences in the $\langle\Delta r\rangle^T$ and $\langle r\Delta\alpha\rangle^T$ obtained using Sets (i) and (ii), only the full results based on Kuchitsu's F matrix [Set (ii)] will be given here.

The temperature dependence of the thermal average of Δr and $r\Delta\alpha$ for PH$_3$ and PD$_3$ are tabulated in Tables III and IV and are shown in Figs. 1 and 2. Note that while $\langle\Delta r\rangle^T$ is fairly linear for both molecules, there is a rather large curvature in $\langle r\Delta\alpha\rangle^T$. The thermal average of any observable such as σ of ^{31}P which depends on the molecular configuration will be a combination of two linear terms:

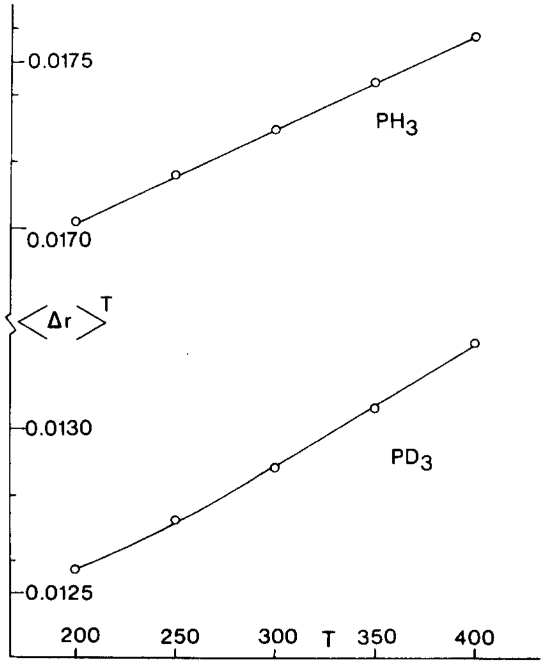

FIG. 1. The thermal average of Δr for PH$_3$ and PD$_3$ based on cubic force constants from Ref. 25.

TABLE I. Molecular constants for PH_3 and PD_3.

	PH_3[a]		PD_3[a]	
ω_1[b] cm^{-1}	2436	(2448)	1743	(1760)
ω_2	1061	(1045)	774	(759)
ω_3	2437	(2390)	1751	(1720)
ω_4	1151	(1153)	821	(822)
k_{111}[b] cm^{-1}	− 131	(− 139)	− 78	(− 84)
k_{122}	22	(48)	8	(27)
k_{133}	− 377	(− 384)	− 229	(− 234)
k_{144}	16	(41)	4	(20)
k_{211}	− 84	(− 9)	− 56	(− 11)
k_{222}	51	(44)	32	(28)
k_{233}	− 39	(27)	− 24	(16)
k_{244}	274	(266)	166	(163)
L_{11}[b] $amu^{-1/2}$	1.009		0.724	
L_{12}	− 0.049		− 0.029	
L_{21}	0.008		− 0.042	
L_{22}	1.409		1.027	
r_e[b] Å	1.415		~ 1.411	
α_e[c] deg	93.5		93°10′	
$I_{xx}^{(e)}$[d] 10^{-40} $g cm^2$	6.285		12.076	
$I_{zz}^{(e)}$[c,d]	7.23		(14.4485)[e]	
β_1[e]	− 0.5181		− 0.5472	
β_3	0.8555		0.8381	
$a_1^{(xx)}$ $amu^{1/2}\cdot$Å	3.0992		4.3433	
$a_1^{(zz)}$	3.5728		4.9433	
$a_2^{(xx)}$	− 1.0857		− 1.2529	
$a_2^{(zz)}$	2.1638		3.2275	

[a] Values in parentheses are based on F matrix of Sundaram *et al*. (Ref. 32).

[b] Reference 25.

[c] Reference 29.

[d] C. A. Burrus, A. Jache, and W. Gordy, Phys. Rev. 95, 706 (1954).

[e] This work.

TABLE III. Temperature dependence of the thermal average of Δr and $r\Delta\alpha$ for PH_3 based on Kuchitsu's cubic force constant.[a]

	$10^2\langle\Delta r\rangle$			$10^2\langle r\Delta\alpha\rangle$		
T (K)	Cent	Anh	Tot	Cent	Anh	Tot
200	0.05695	1.66548	1.72243	− 0.01266	− 3.67375	− 3.68640
220	0.06264	1.66554	1.72818	− 0.01392	− 3.67689	− 3.69082
240	0.06834	1.66563	1.73397	− 0.01519	− 3.68200	− 3.69719
260	0.07403	1.66576	1.73980	− 0.01645	− 3.68958	− 3.70603
280	0.07973	1.66595	1.74568	− 0.01771	− 3.70009	− 3.71781
300	0.08542	1.66621	1.75164	− 0.01898	− 3.71388	− 3.73286
320	0.09112	1.66655	1.75767	− 0.02025	− 3.73122	− 3.75147
340	0.09681	1.66698	1.76379	− 0.02151	− 3.75231	− 3.77382
360	0.10251	1.66751	1.77002	− 0.02278	− 3.77723	− 3.80001
380	0.10820	1.66815	1.77636	− 0.02404	− 3.80600	− 3.83004
400	0.11390	1.66892	1.78282	− 0.02531	− 3.83861	− 3.86392

[a] Reference 25.

$$\langle\sigma_P\rangle^T = \sigma_e + 3\,(\partial\sigma/\partial\Delta r)_{eq}\langle\Delta r\rangle^T + 3\,(\partial\sigma/\partial r\Delta\alpha)_{eq}\langle r\Delta\alpha\rangle^T + \text{quadratic and higher order terms.} \qquad (22)$$

The factor of 3 comes from Eqs. (8) and (9). It can be seen that the curvature in the theoretical $\langle\sigma_P\rangle^T$ will be determined by the curvature in $\langle r\Delta\alpha\rangle^T$, since $\langle\Delta r\rangle^T$ is close to linear. Conversely, determination of the two parameters, $(\partial\sigma/\partial\Delta r)_{eq}$ and $(\partial\sigma/\partial r\Delta\alpha)_{eq}$, will depend to a large extent on the precision with which the curvature in the experimental $\sigma_0(T)$ can be obtained. The quadratic terms in Δr and in $\Delta\alpha$ in Eq. (22) should be considered. The $\langle(\Delta r)^2\rangle^T$ term has been shown to have a negligible temperature dependence in the case of a diatomic molecule.[7] It is to be expected that in polyatomic molecules as well, the $(\Delta r)^2$ terms are effectively constant over the temperature range of the experiment. The temperature dependence of the $(\Delta\alpha)^2$ terms cannot be so easily dismissed. The only evidence we have for neglecting it is the lack of temperature dependence of the ^{31}P isotope shift, to which $(\Delta\alpha)^2$ is expected to make a contribution.

COMPARISON WITH EXPERIMENT

The spectroscopic value r_0 of the P–H distance in PH_3 is 1.419 Å.[29] The difference between r_0 and r_e for PH_3 has not been measured but on the basis of available

TABLE II. Summary of results on AX_3 molecules using Kuchitsu's cubic force constants.

	At 300 K						Slope			
	Anharmonic		Centrifugal		Total (anh + cent) (Å)		centrifugal		Total change 10^4 Å	
Molecule	$\langle\Delta r\rangle$(Å)	$\langle\Delta\alpha\rangle$(deg)	$\langle\Delta r\rangle$(Å)	$\langle\Delta\alpha\rangle$(deg)	$\langle\Delta r\rangle^{300}$	$r\langle\Delta\alpha\rangle^{300}$	$10^6\langle\Delta r\rangle/$ A/deg K	$10^6\langle\Delta\alpha\rangle$ rad/deg K	$(\langle\Delta r\rangle^{400} - \langle\Delta r\rangle^{200})$	$(r\langle\Delta\alpha\rangle^{400} - r\langle\Delta\alpha\rangle^{200})$
PH_3[a]	0.01666	− 1.5038	0.000854	− 0.007687	0.0175164	− 0.0373286	2.012	− 0.447	6.039	− 17.752
PD_3	0.1204	− 1.1365	0.0008495	0.001745	0.0128871	− 0.0279444	2.007	0.1015	6.83	− 36.68
PH_3[b]	0.01645	− 2.0192	0.000846	− 0.00793	0.0172967	− 0.0500623	1.993	− 0.4616	5.583	− 17.376
PD_3	0.01173	− 1.5241	0.000833	0.001933	0.0125628	− 0.0374856	1.968	0.1125	5.799	− 36.729
NH_3[c]			0.00067	− 0.054	(0.0120)[d]	(+ 0.0109)[d]	2.22	− 3.12		
ND_3[c]			0.00063	− 0.030	(0.0102)[d]	(+ 0.0093)[d]	2.09	− 1.74		

[a] Using Kuchitsu's data [Set (ii)].

[b] Using Sundaram's data [Set (i)].

[c] Reference 27,

[d] Calculated using cubic force constants from Ref. 26.

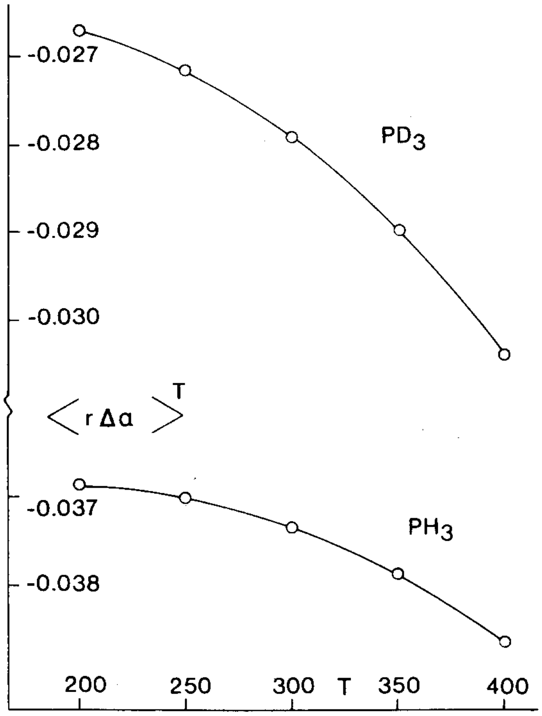

FIG. 2. The thermal average of $r\Delta\alpha$ for PH_3 and PD_3 based on cubic force constants from Ref. 25.

data for other molecules it has been estimated at approximately 0.005 Å.[25] The electron diffraction value r_g of the P–H distance is 1.437 ± 0.004 Å,[33] which is 0.023 Å larger than the estimated r_e for P–H. Our value of $\langle\Delta r\rangle^{300} = +0.0175$ Å accounts for most of the 0.023 Å difference. On the other hand, there is no experimental value of $\langle\Delta\alpha\rangle$ to be compared with. We get $\langle\Delta\alpha\rangle^{300} = -1.51°$ for PH_3 and $-1.14°$ for PD_3. Calculations which we have carried out on NH_3 and ND_3 based on the cubic force constants of Morino *et al.*[26] give the opposite sign for $\langle\Delta\alpha\rangle^{300}$, $+0.67°$ and $0.53°$, respectively. Kuchitsu has pointed out that while Δr is relatively unaffected by the value chosen for the force constant H_3 which represents the anharmonicity of the bond-bending interaction, the $\Delta\alpha$ values are very sensitive to this quantity.[25] Although stretching anharmonicities are now quite well understood, virtually no generalities have been established for bending anharmonicities. The value of H_3 on which Kuchitsu's cubic force constants are based is $+1.7$ mdyn/Å, which was a somewhat arbitrary choice. A value of $H_3 = 0$ would lead to positive thermal averages for $\Delta\alpha$ such as those observed for NH_3 and ND_3, rather than the negative values obtained here. Since there is no *a priori* reason why the thermal average of $\Delta\alpha$ for PH_3 and PD_3 should be radically different from that of NH_3 and ND_3, we must view the $\Delta\alpha$ listed in Tables III and IV with some skepticism.

If we accept the theoretical $\langle\Delta r\rangle^T$ and $\langle\Delta\alpha\rangle^T$ calculated here for PH_3 using $H_3 = 1.7$, then we see from Eq. (22) that there are certain constraints that are imposed on the parameters $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$ by the observed temperature dependence of the ^{31}P chemical shift. The observed resonance frequency of ^{31}P in the isolated molecule was found to (a) decrease with increasing temperature, and (b) be concave upward. Since there is no curvature in the $\langle\Delta r\rangle^T$ function for PH_3 shown in Fig. 1, then the experimental curvature in the ^{31}P resonance frequency must be entirely from the curvature of the $\langle\Delta\alpha\rangle^T$ function. Observation (a) necessitates that the sign of

$$\partial\sigma/\partial\Delta r + \frac{\langle\Delta\alpha\rangle^{380} - \langle\Delta\alpha\rangle^{270}}{\langle\Delta r\rangle^{380} - \langle\Delta r\rangle^{270}}\,\partial\sigma/\partial\Delta\alpha$$

be positive. Observation (b) necessitates that the sign of $\partial\sigma/\partial\Delta\alpha$ be positive. Since $\langle\Delta\alpha\rangle^{380} - \langle\Delta\alpha\rangle^{270}$ shown in Table III is negative while $\langle\Delta r\rangle^{380} - \langle\Delta r\rangle^{270}$ is positive, the signs of both $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$ are necessarily positive if the $\langle\Delta\alpha\rangle^T$ functions calculated from Kuchitsu's cubic force constants are correct. However, there is also the isotope shift for ^{31}P in PH_3 and PD_3. The NMR isotope shift has been found to be uniformly positive, i.e., $\langle\sigma\rangle^T_{\text{heavy}} - \langle\sigma\rangle^T_{\text{light}} > 0$.[22] But if indeed $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$ are both positive, then the ^{31}P isotope shift in the PH_3–PD_3 system will be unique, i.e., negative! Therefore, a reasonable test to see if the $\langle\Delta\alpha\rangle^T$ functions obtained for PH_3 and PD_3 are wrong is to measure the ^{31}P isotope shift. If the isotope shift is found to be the usual sign, i.e., positive, then the $\langle\Delta\alpha\rangle^T$ functions given in Tables III and IV are wrong. If the isotope shift is found to be negative, then the $\langle\Delta\alpha\rangle^T$ functions obtained here are not necessarily wrong, even though they have the opposite signs to the $\langle\Delta\alpha\rangle^T$ for NH_3 and ND_3.

We measured the ^{31}P isotope shift between PH_3 and PD_3. We obtained $\langle\sigma_{^{31}P}\rangle_{PD_3} - \langle\sigma_{^{31}P}\rangle_{PH_3} = +2.5$ ppm, with the usual sign. Therefore, the $\langle\Delta\alpha\rangle^T$ functions shown in Tables III and IV are wrong.

Having eliminated the $\langle\Delta\alpha\rangle^T$ functions in Tables III and IV, we now proceed to estimate a new set of $\langle\Delta\alpha\rangle^T$ functions. The cubic force constants for NH_3 and ND_3 are roughly related to those given by Kuchitsu. The k_{1ss} for the stretching modes of NH_3 and ND_3 are approximately twice those of PH_3 and PD_3, respectively. The cubic force constants which determine the temperature dependence of the $\langle\Delta\alpha\rangle^T$ function are k_{222} and k_{244}. These are -126.6 and -36.1 cm^{-1}, respectively, in NH_3.[26] Since there is no other set of cubic force constants in

TABLE IV. Temperature dependence of the thermal average of Δr and of $r\Delta\alpha$ for PD_3 based on Kuchitsu's cubic force constants.[a]

	$10^2\langle\Delta r\rangle$			$10^2\langle r\Delta\alpha\rangle$		
T (K)	Cent	Anh	Tot	Cent	Anh	Tot
200	0.05664	1.20078	1.25742	0.002865	−2.67563	−2.67276
220	0.06230	1.20108	1.26338	0.003151	−2.68984	−2.68669
240	0.06796	1.20150	1.26947	0.003438	−2.70909	−2.70565
260	0.07363	1.20207	1.27570	0.003724	−2.73364	−2.72992
280	0.07929	1.20282	1.28210	0.004011	−2.76355	−2.75954
300	0.08495	1.20376	1.28871	0.004297	−2.79874	−2.79444
320	0.00062	1.20492	1.29554	0.004584	−2.83901	−2.83443
340	0.00628	1.20635	1.30263	0.004870	−2.88411	−2.87924
360	0.10194	1.20806	1.31001	0.005157	−2.93374	−2.92858
380	0.10761	1.21009	1.31769	0.005443	−2.98757	−2.98212
400	0.11327	1.21245	1.32572	0.005730	−3.04529	−3.03956

[a] Reference 25.

TABLE V. Temperature dependence of the thermal average of Δr and $r\Delta\alpha$ for PH_3 using Kuchitsu's cubic force constants, with the exception that $k_{222} = -20$ and $k_{244} = -8$ cm^{-1}. The centrifugal distortion contributions are unchanged from Table III.

T (K)	$10^2\langle \Delta r \rangle$ (Å)	$10^2\langle r\Delta\alpha \rangle$ (Å)
200	1.538	1.6263
220	1.543	1.6254
240	1.549	1.6249
260	1.554	1.6247
280	1.560	1.6249
300	1.565	1.6254
320	1.571	1.6265
340	1.576	1.6280
360	1.581	1.6300
380	1.586	1.6325
400	1.591	1.6354

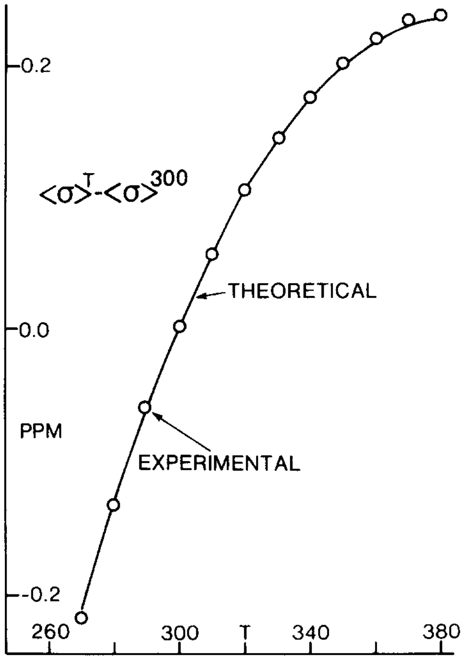

FIG. 4. Comparison of the calculated $(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})$ for ^{31}P in PH_3 with the experimental values.

the literature for PH_3 and PD_3, we assumed initially that k_{222} and k_{244} (2 and 4 are bending modes) are, like k_{1ss} for the stretching modes, roughly half the values for NH_3, i.e., -65 and -17 cm^{-1}, respectively. These still gave the wrong sign for the isotope shift. The second choice of -20 and -8, respectively, gave the results shown in Table V and Fig. 3. We used this $\langle\Delta\alpha\rangle^T$ function to calculate $\langle\sigma\rangle^T$ for PH_3 using $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$ as parameters. The results are shown in Fig. 4. The values of $\partial\sigma/\partial\Delta r$ and $\partial\sigma/\partial\Delta\alpha$ are obtained by a least squares fitting procedure. They are $+1050$ ppm/Å and -50 ppm/deg, respectively.

The ^{31}P chemical shielding in three-coordinate phosphorus has been considered as a function of a small variation in bond hybridization accompanying a small variation in the valence angles.[34] Using a $\Delta\alpha$ of $-0.62 \pm 0.2'$ by analogy with the microwave spectroscopy value for PH_2D and PHD_2,[35] Borisenko *et al.* reproduced a chemical shift of $+1.20 \pm 0.04$ ppm between (C_6H_5) PHD and $(C_6H_5)PH_2$.[36] This is equivalent to a shift of -36 ppm/deg accompanying a simultaneous increase in all three bond angles. The agreement with our $\partial\sigma/\partial\Delta\alpha = -50$ ppm/deg is probably fortuitous, but it does indicate that our value of $\partial\sigma/\partial\Delta\alpha$ is not unreasonable.

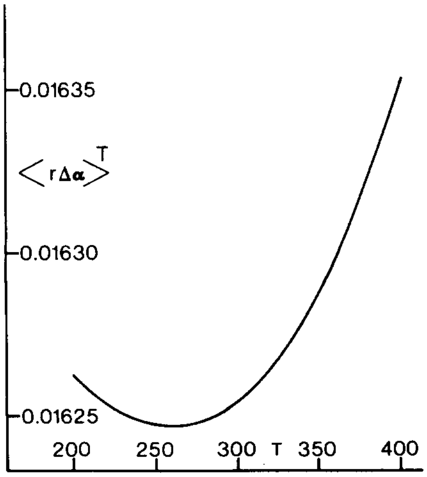

FIG. 3. The thermal average of $r\Delta\alpha$ for PH_3 based on cubic force constants from Ref. 25 with the exceptions of $k_{222} = -20$ and $k_{244} = -8$ cm^{-1}.

CONCLUSIONS

We have found that a combination of NMR observables (temperature dependence of resonance frequency in the isolated molecule and the isotope shift) may be used as a check on the validity of a set of cubic force constants. In this particular case, the result was unequivocal. The estimated values of the cubic force constants involving the bending modes are found to be inconsistent with this combination of NMR observations.

The derivative $\partial\sigma/\partial\Delta r$ for ^{31}P in PH_3 is found to be positive, i.e., deshielding accompanies bond contraction rather than bond extension. However, this is not an entirely surprising result for ^{31}P in PH_3. The bond contraction must be accompanied by some redistribution of the lone pair electrons on the P atom. If, as expected, the lone pair electrons move further out from the ^{31}P nucleus as the P–H bond contracts, some deshielding will accompanying bond contraction.

It will be of interest to compare the $\partial\sigma/\partial\Delta\alpha$ of -50 ppm/deg for ^{31}P in PH_3 to that for ^{15}N in NH_3 and ^{77}Se in H_2Se. PH_3 is the first system that has been studied in which $\langle\Delta\alpha\rangle^T$ gives a significant contribution to the temperature dependence of chemical shielding in the isolated molecule. Other examples are necessary in order to find the general trends in $\partial\sigma/\partial\Delta\alpha$ and $\langle\Delta\alpha\rangle^T$ functions such as are now known for $\partial\sigma/\partial\Delta r$ and $\langle\Delta r\rangle^T$.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation in grants to the University of Illinois at

Chicago Circle (CHE74-12100) and Loyola University (CHE74-12098).

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