The Resolution of Chlorine and Bromine Isotope Shifts in the ^{31}P Nuclear Magnetic Resonance Spectra of PCl_3 and PBr_3

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The isotopomers of PCl_3 and PBr_3 are well resolved in their ^{31}P n.m.r. spectra at very high field (9.4 T) and low temperature (*ca.* 200 K). The isotope shifts of 0.019 ($^{35}Cl/^{37}Cl$) and 0.006 p.p.m. ($^{79}Br/^{81}Br$) fall within the predicted ranges.

THE potential for the observation of isotope shifts in n.m.r. spectra has recently increased with the availability of very high field spectrometers. These shifts are frequently very small but useful both in peak assignment [1] and in chemical and biochemical mechanistic studies.[2] We have recently reported halogen isotope shifts in ^{195}Pt n.m.r. spectra [3] and now report the first example of halogen isotope shifts in ^{31}P n.m.r.

EXPERIMENTAL

Phosphorus tribromide and phosphorus trichloride were neat liquids as supplied by the Aldrich Chemical Co. Ltd., except that [$^2H_6$]acetone was added (5% v/v) to provide the n.m.r. lock.

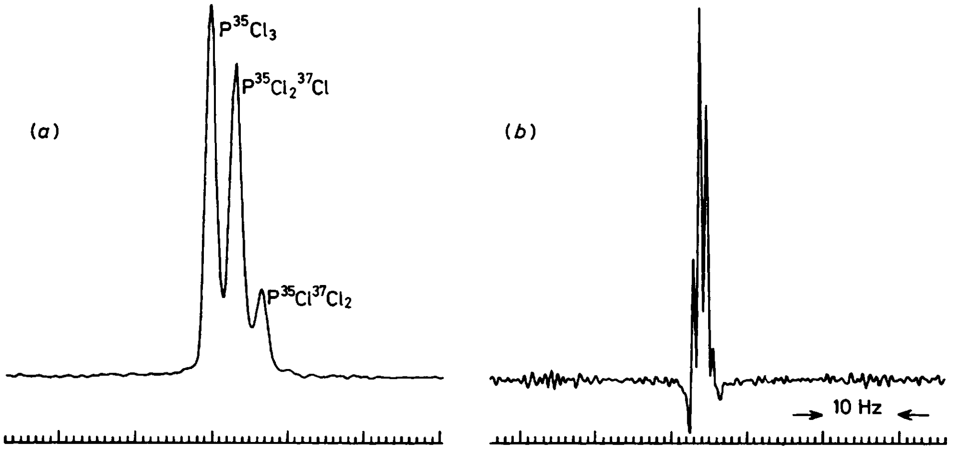
Phosphorus-31 n.m.r. spectra (162 MHz) were recorded using sample tubes (10 mm) on the Bruker WH-400 spectrometer of the U.L.I.R.S. n.m.r. service at Queen Mary College.

RESULTS AND DISCUSSION

The spectra of both PCl_3 and PBr_3 at ambient temperature appeared to be singlets, but on lowering the temperature well resolved fine structure appeared for both PCl_3 (at *ca.* 173 K) and PBr_3 (at 203 K) (see Figure). The intense peaks for PCl_3 are equally spaced by 3.1 Hz (0.019 p.p.m.) and the four for PBr_3 equally spaced by 0.95 Hz (0.006 p.p.m.), resolution enhancement using the Gaussian multiplication technique being essential to reveal the latter. We attribute these splittings to chlorine and bromine isotope shifts.

The expected isotopomer ratios for PCl_3 are 1.0 : 0.99 : 0.33 : 0.036 for $P^{35}Cl_3$: $P^{35}Cl_2{}^{37}Cl$: $P^{35}Cl^{37}Cl_2$: $P^{37}Cl_3$ respectively (natural abundances: ^{35}Cl, 74.5; ^{37}Cl, 24.6%) which are close to the observed peak intensities (1.0, 0.80, 0.23, 0.036). For PBr_3 the calculated ratio of $P^{79}Br_3$: $P^{79}Br_2{}^{81}Br$: $P^{79}Br^{81}Br_2$: $P^{81}Br_3$ are 0.34 : 1.0 : 0.97 : 0.32 respectively (natural abundances: ^{79}Br, 50.6; ^{81}Br, 49.4%), and although the relative intensities of the observed four peaks are severely distorted by the use of resolution enhancement they do confirm that isotopomers are being observed (see Figure).

In common with other isotope shifts the heavier isotopomers resonate at lower frequency. Since the origin of the isotope shift lies in small geometrical (vibrational) differences the shifts decrease in magnitude as the element increases in atomic weight (*i.e.*, Cl > Br); typical values for $^1H/^2H$ and $^{16}O/^{18}O$ isotope shifts in ^{31}P n.m.r. spectra are 0.8 and 0.02 p.p.m. respectively.[4,5] In addition isotope shifts generally increase with increase in chemical shift range of the nucleus observed. Thus the analogous ($^{35}Cl/^{37}Cl$) one-bond isotope shifts for ^{13}C



162-MHz ^{31}P n.m.r. spectra of (*a*) PCl_3 (+5% [$^2H_6$]acetone) at 173 K and (*b*) PBr_3 (+5% [$^2H_6$]acetone) at 203 K are 0.004 [1] and for ^{195}Pt are 0.167 p.p.m.[2] (the chemical shift range for ^{195}Pt being larger than for ^{13}C).

The advantage of a very high field spectrometer for observing these shifts is clear and they can be used as a further assignment aid for resonances. Our success in resolving isotope shifts of PCl_3 and PBr_3 only at low temperature may be attributed to the increase in ^{31}P spin–spin relaxation times (and therefore decrease in linewidths) of these molecules with decrease in temperature. This is because the relaxation mechanism is dominated by spin rotation, the only relaxation rate which normally behaves in this way.[6]

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