Chlorine Kinetic Isotope Effect Models. I. Isotopic Dependence in Nominal C–Cl Stretching Vibrations of Aliphatic Chlorides and Vibrational Analysis of the *tert*-Butyl Chloride Ground State

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Abstract: The infrared isotopic shift of the C–Cl stretching frequencies of methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, and *tert*-butyl chloride have been determined, using isotopically labeled chlorine-35 and chlorine-37 compounds synthesized in this laboratory. Detailed high-resolution studies of *tert*-butyl chloride skeletal modes show at least three other important isotopic shifts, in addition to the nominal C–Cl mode. A point mass-methyl-group skeletal model of *tert*-butyl chloride used for vibrational analysis reproduces the experimental spectrum to within 0.051% and confirms isotopic splitting in more than one mode. The frequencies have also been obtained as a function of solvent, and the isotopic shifts estimated from the methyl chloride shift, measured in methanol-d_1. Geometric factors influencing the size of the isotopic shift are discussed, and the implications for chlorine kinetic isotope effect calculations are enumerated.

Knowledge of the vibrational modes of a molecule in general, and of any isotopic shifts in particular, is required for the calculation of kinetic isotope effects.[1,2] Chlorine kinetic isotope effect (KIE) studies in progress in this laboratory[3–5] require knowledge of the frequencies and isotopic shifts of *tert*-butyl chloride and several other aliphatic chlorides. Nominal carbon–chlorine stretching bands have previously been identified in many aliphatic chlorides[6–16] and the position of these bands has been correlated with molecular geometry.[6,7] Unfortunately, these studies have usually not reported the individual isotopic bands, either because of low resolution, or because the physical state of the sample caused sufficient band broadening to obscure isotopic fine structure. In cases where there is sufficient resolution, the lack of labeled compounds often prevents determination or confirmation of isotopic shifts. When it has been possible to determine chloride isotopic shifts, often only the "C–Cl stretch" has been studied. Because of this, simplified chlorine KIE calculations commonly neglect other vibrational modes and solvent effects.[1,2,17] Work was therefore initiated: (1) to develop a general method of synthesizing labeled aliphatic chlorides, and to determine the nominal isotopic shifts and C–Cl stretching frequencies of methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, and *tert*-butyl chloride; (2) to evaluate the influence of solvent on vibrational frequencies and associated isotopic shifts; (3) to search for possible isotopic effects in other modes of *tert*-butyl chloride; and (4) to create a model for *tert*-butyl chloride, which could be used for chlorine KIE calculations in both gas and solution phase.

Experimental Section

High-resolution spectra of bands above 550 cm^{-1} were taken on a Perkin-Elmer Model 421 (Grating) spectrophotometer; a somewhat lower resolution Perkin-Elmer Model 457 (Grating) spectrophotometer was used for all scans below 550 cm^{-1}. Both instruments were operated in the double beam mode, and spectra were calibrated with as many of the following lines as were applicable: polystyrene 1181.4, 1154.3, and 906.7; CO_2 667.3; and indene 590.8 and 381.4 cm^{-1}. Linear interpolation and extrapolation from calibration lines were used. High resolution spectra were taken using expanded abscissa mode, at 0.25 or 0.125 cm^{-1}/mm on the Model 421, and 0.5 cm^{-1}/mm on the Model 457. Calibration on the Model 457 was only possible for the normal abscissa mode of 5.0 cm^{-1}/mm. Liquid samples were in either 0.1- or 0.05-mm cells, with silver bromide windows. A 10-cm cell with cesium iodide windows and a 1-m folded-path cell with KBr windows were used on the gaseous samples, with compensation for the 1-m cell provided by an evacuated 10-cm cell, also with KBr windows. To remove atmospheric interference, the respective spectrometer and sample area were purged continuously with dry nitrogen, before and during operation. Vapor-phase samples were purified by preparative gas chromatography, and their purity checked spectroscopically. Except for methyl chloride, chemicals in the liquid-phase studies were used as received from commercial sources, after full range (4000–250 cm^{-1}) scans showed them to be free of appreciable impurities. Vibrational assignments were confirmed by reference to the literature,[6–16] and by their isotopic shifts. Isotopic shifts were determined by comparison of normal abundance spectra with 99% ^{35}Cl and/or 96% ^{37}Cl labeled compounds synthesized in this laboratory.

The methyl chloride solution was prepared by vacuum distilling

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0.75 ml of methanol-d_1 onto 0.35 mmol of frozen methyl chloride. This mixture was then melted, refrozen, vented with nitrogen, melted again, and used immediately. Unused portions were stored under a slight positive pressure of nitrogen to inhibit methyl chloride degassing.

Synthesis. Synthesis was achieved by utilization of the method previously employed for methyl chloride:[18] sealed-tube reaction of the appropriate aliphatic iodide (onefold mole excess) with labeled or natural abundance silver chloride, followed by gas chromatographic purification of the resultant chloride. At the same column temperature, approximate elution times relative to methyl chloride were 1.8, 5.7, 18.5, 3.5, and 5.3, for ethyl, *n*-propyl, *n*-butyl, isopropyl, and *tert*-butyl chloride, respectively. All iodides were commercially available and, except for *tert*-butyl, were used as received. The *tert*-butyl iodide was purified using a procedure similar to Stone and Shechter,[19] by shaking with two equivalent volumes of cold, 10% sodium thiosulfate solution, then washing with two volumes of cold, saturated potassium nitrate solution. The resultant *tert*-butyl iodide was dried over magnesium sulfate for 15 min, purified gas chromatographically, and immediately vacuum distilled into the reaction flask. Labeled silver chloride was prepared from 99.32 ± 0.05% $Na^{35}Cl$ and 96.05 ± 0.10% $Na^{37}Cl$, purchased from Oak Ridge National Lab.

Results

General Synthesis Technique. The sealed-tube reaction technique previously used to synthesize methyl chloride[18] was successfully adapted to prepare labeled ethyl, *n*-propyl, *n*-butyl, isopropyl, and *tert*-butyl chloride. Maximum observed yields were greater than 90% of theoretical, except for *tert*-butyl, whose lower yield is probably caused by the competing elimination reaction to produce isobutylene.[5] These data indicate that this synthesis technique may be successfully used to synthesize primary, secondary, or tertiary aliphatic chlorides of moderate molecular weight, although low volatility chlorides may require some variation in the isolation procedure.

C–Cl Peak Positions. The measured frequencies and isotope shifts of the bands which are predominantly C–Cl stretch are summarized in Table I. Although the instrumental limitations prevent determining the absolute frequencies to much better than 0.3 wave number, isotopic shifts could be measured considerably more accurately, particularly when it was possible to resolve both isotopes in the scan of a normal abundance sample. Shipman, Folt, and Krimm have shown that rotationally isomeric molecules possessing distinctly different geometric conformations may have a different absorption band for each conformation.[6] Of the compounds studied here, only *n*-propyl and *n*-butyl chloride fit this criterion; each of them has two distinct bands, corresponding to configurations where either carbon or hydrogen is trans to chlorine, using the observation plane along the bond between C_1 (attached to chlorine) and C_2. These configurations are designated P_C and P_H, respectively, following the notation of Mizushima, *et al.*[12] The *n*-propyl and *n*-butyl cases are also complicated by their lack of sharp Q branches. The sharpness of a Q branch is dependent on molecular size, shape, and symmetry. As symmetry and structure change in the progression from methyl chloride to *n*-butyl chloride, the Q branch diminishes in height, while the R branch is enhanced. Since the bands also decrease in sharpness, the Q branch appears to merge with the R branch, and eventually becomes indistinguishable. This effect is not serious for ethyl chloride but becomes so for *n*-propyl chloride. In order to compare peaks of the same type, the position of the Q branch in *n*-butyl chloride has been estimated from the observed trend in splitting between the Q and R branches for the first three chlorides, and from a measurement of the R branch absorption for the *n*-butyl chloride. Even with this correction, Table I shows that both *n*-butyl frequencies are 1 to 1.5 cm^{-1} higher than the corresponding *n*-propyl frequencies. Other workers have reported this feature;[6,7,14] studies on higher normal chlorides show that the C–Cl stretching frequency approaches an equilibrium around the *n*-butyl value, but may vary slightly in either direction.

Table I. Measured Carbon–Chlorine Stretching Frequencies

Compd	$^{12}C-^{35}Cl$ stretch, cm^{-1} [a,b]	^{37}Cl isotopic shift, cm^{-1} [c]	Q–R splitting, cm^{-1}
CH_3Cl[d]	732.2	5.90 ± 0.1	15
EtCl[d]	676.4	4.65 ± 0.1	9
n-PrCl(P_H)[d–f]	663.7	4.2 ± 0.15	7
n-BuCl(P_H)[d–g]	665.1	4.0 ± 0.25	6[g]
n-PrCl(P_C)[d–f]	746.6	3.9 ± 0.2	5
n-BuCl(P_C)[d–f,h]	747.6	3.5 ± 0.3	4[h]
i-PrCl[d]	632.1	3.99 ± 0.1	9
t-BuCl[d]	585.0	2.63 ± 0.1	7

[a] Measured for Q line. [b] Estimated uncertainty for expanded abscissa scan ≤0.3 cm^{-1}. [c] Uncertainties estimated from spectral slit widths and peak sharpness. [d] From 99.32% ^{35}Cl compound. [e] From 96.05% ^{37}Cl compound. [f] Notation of Mizushima, *et al.*; see text. [g] Estimated; tallest peak maximum (presumed R branch) measured at 671.1 cm^{-1}. [h] Estimated; tallest peak maximum (presumed R branch) measured at 751.6 cm^{-1}.

Normal Coordinate Analysis. Normal coordinate analysis on a *tert*-butyl chloride model was performed, using a set of computer programs originally written by Rouda,[20] and modified extensively by these authors. The programs utilize Wilson's FG method,[21] and permit iterative improvements of force constants, if a sufficient number of measured frequencies are available. The model chosen was an isotopically invariant methyl chloride skeleton with point methyl groups of mass 14.40 amu. Angles and bond lengths used are those of Lide,[22] while the mass used for methyl was that calculated from methyl chloride shift data.[10] The use of a slightly different geometry or methyl mass would not materially affect the results presented here. Of the nine normal modes of this model, three exhibit A_1 symmetry, and three exhibit twofold degenerate E symmetry. The most consistent choice of symmetry coordinates is given in Table II. This set contains a redundant coordinate of symmetry A_1. Because equations deleting the redundant coordinate are applicable only to nearly tetrahedral molecules, the redundant coordinate was explicitly retained in the symmetry coordinates, but all force constants associated with it were taken to be zero. This is equivalent to eliminating the coordinate in this particular model. The symmetry-factored E matrix thus contains only twelve nonzero force constants, as opposed to 16 in the general valence force

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Table II. Symmetry Coordinates of the *tert*-Butyl Chloride Model[a]

A_1	$S_1 = 3^{-1/2}(r_1 + r_2 + r_3)$
	$S_2 = s$
	$S_3 = 6^{-1/2}(\alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3)$
	$S_r = 6^{-1/2}(\alpha_1 + \alpha_2 + \alpha_3 + \beta_1 + \beta_2 + \beta_3) = 0$
E	$S_{4a} = 6^{-1/2}(2r_1 - r_2 - r_3)$
	$S_{5a} = 6^{-1/2}(2\alpha_1 - \alpha_2 - \alpha_3)$
	$S_{6a} = 6^{-1/2}(2\beta_1 - \beta_2 - \beta_3)$
	$S_{4b} = 2^{-1/2}(r_2 - r_3)$
	$S_{5b} = 2^{-1/2}(\alpha_2 - \alpha_3)$
	$S_{6b} = 2^{-1/2}(\beta_2 - \beta_3)$

[a] s = C–Cl; r_i = C–$(CH_3)_i$; $\alpha_i = \angle(CH_3)_j$–C–$(CH_3)_k$, $i \neq j \neq k$; $\beta_i = \angle$Cl–C–$(CH_3)_i$.

Table III. Observed and Calculated Frequencies, Isotopic, Shifts, and Eigenvectors of the *tert*-Butyl Chloride Gas-Phase Model

	Observed		Calculated			*t*-Bu^{35}Cl eigenvectors (normalized)					
	t-Bu^{35}Cl, cm^{-1} [a]	$\Delta\nu$, cm^{-1} [b]	*t*-Bu^{35}Cl, cm^{-1}	% error[c]	$\Delta\nu$, cm^{-1}	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	818	0.5 ± 0.3[d]	818.09	0.011	0.72	1.000	0.718	−0.839	0	0	0
ν_2	585	2.63 ± 0.1	585.04	0.007	2.71	0.202	0.815	1.000	0	0	0
ν_3	372	3.77 ± 0.5	372.19	0.051	4.16	−0.165	−0.127	−0.000	0	0	0
ν_4	1210[e]	≤0.2[f]	1210.10	0.008	0.20	0	0	0	1.000	0.790	−0.414
ν_5	408		408.05	0.012	0.10	0	0	0	−0.479	1.000	0.247
ν_6	301	≤1.5[g]	300.99	0.003	1.48	0	0	0	−0.169	−0.391	1.000

[a] Estimated uncertainty ±1, except for ν_2, which is ±0.3. [b] Uncertainties estimated from spectral slit widths and peak sharpness. [c] (|^{35}calculated − ^{35}observed|^{35}observed) × 100%. [d] 0.6 used in iterative calculation. [e] Estimated, see text. [f] 0.0 used in iterative calculation. [g] 1.5 used in iterative calculation.

field (GVFF). Because the symmetry-factored force constants also have the desirable feature that changes in the force constants of one symmetry type do not affect normal modes of a different symmetry, it was decided to use them (without correcting for anharmonicity), subject to the constraint that GVFF constants calculated from them compare reasonably with values for similar molecules.[13,14,16,23] The relative contribution of each symmetry mode to a calculated mode could then be determined directly from the eigenvectors of the normal mode calculation, and the individual valence bond contributions could be calculated using the appropriate desymmetrizing transformations, if desired.

Vapor Phase. Five of the skeletal modes used for this model are directly observable, and may be considered to be free of appreciable interaction with modes involving hydrogen, although they may interact among themselves. These were used directly as observed. One mode, that of the asymmetric CC_3 stretch, has been reported as strongly interacting with CH_3 rocking modes and perhaps others.[15,16] The 1241-cm^{-1} band has been analyzed as being principally CC_3 stretch coupled with some CH_3 rocking contribution, while a band at 927 cm^{-1} seems to consist of these same modes in reversed proportions.[15] Since this model does not explicitly include hydrogen interaction, the "pure" value for this mode was chosen to be 1210 cm^{-1}, and this value was weighted less for iterative calculations; slight changes in the assigned value do not change the conclusions of this paper materially. Initially, iterative force-constant improvement was tried using the six skeletal frequencies, and the isotope shift for ν_2, varying four force constants in the A block, and 3 in the E block, and weighting ν_2 somewhat more than other modes. Regardless of the force field chosen, a large isotope shift was calculated for ν_3, and the eigenvectors showed a strong interaction between ν_2 and ν_3. The spectrum of the 585-cm^{-1} band also indicated complications, both in the presence of a strong shoulder 2.30 cm^{-1} below the Cl peak (which did not disappear on ^{35}Cl labeling), and the unreasonably low isotopic shift. Subsequent high-resolution studies confirmed the calculated prediction that ν_3 exhibits a shift greater than ν_2, and that ν_1 and ν_6 also show slight isotopic shifts. The first two columns of Table III show the observed frequencies and isotopic shifts. Using these additional shifts, iterative improvement was again attempted. It was possible simultaneously to vary five of the A_1 and three of the E symmetry force constants. The small isotopic shift of ν_1, and the small weighting used for ν_4 prevented varying an additional force constant of each symmetry type. For the A_1 symmetry force constants, F_{11} was fixed and varied manually between runs; for the E symmetry block, the technique was to fix all diagonal constants for one run and vary the off-diagonal values, then to reverse the procedure on the following run, using the final results of the previous run as input. The alternative possibility to independently calculate all force constants through the use of perdeuterio data as additional input was considered and discarded. One of the assumptions implicit in this model is that the high frequency hydrogen vibrations are separable and do not mix with lower frequency skeletal vibrations.[21,24] This approximation is considerably poorer for lower frequency deuterium vibrations: not only does ν_1 mix with CH_3 rocking modes, but relative contribution of the two modes in ν_4 may change.[15] Moreover, *tert*-butyl chloride exhibits strong secondary deuterium isotope effects[25,26] which are difficult to describe explicitly without describing all the deuterium modes. The situation is further complicated by the observation that the geometry is also slightly altered upon deuterium substitution.[27]

Results achieved using only the hydrogen isotopes were very good. All reasonable choices of force constants eventualy converted to the same final set. Divergence occurred only when initial values were so poorly chosen that algebraic sequence of modes as reversed (*i.e.*, $\nu_3 > \nu_2$, etc.), causing corrections to the

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Table IV. Calculated Force Constants for the *tert*-Butyl Chloride Gas-Phase Model

Symmetry factored force constants, mdyn/Å[a]			
F_{11}	4.350	F_{12}	−0.060
F_{22}	2.861	F_{13}	0.677
F_{33}	0.918	F_{23}	−0.745
F_{44}	4.245	F_{45}	0.918
F_{55}	1.420	F_{46}	1.382
F_{66}	1.193	F_{56}	0.686

[a] All force constants associated with S_r assumed zero.

Table V. Observed *tert*-Butyl Chloride Vibrations in Methanol/Methanol-d_1

	Volume % *tert*-BuCl[a]					
	100	75	50	25	12.5	6.25
ν_1	805	809/808	807/810[b]	806/808[b]	806/809[b]	803/809[b]
ν_2	566	565/564	562/562	561/561	562/561	563/560[b]
ν_3	372	370/370	370/371	371/370	370/370	370/369
ν_4	1238	1240/1240	1240/1239	1239/1240	1241/1239	1240/1234[c]
ν_5	408	407/407	404/403	405/403		
ν_6	301	295/296	297/296	294/300[b]		

[a] Estimated uncertainty ±2 for 100%, ±3 for 75 and 50%, ±5 for 12.5 and 6.25%. [b] Apparent difference caused by contributions of large broad solvent peaks. [c] Methanol-d_1 has a weak band at 1231 cm^{-1}, which is interfering.

Table VI. "Observed" and Calculated Frequencies, Isotopic Shifts and Eigenvectors of *tert*-Butyl Chloride Solution Model

	Observed		Calculated			*t*-Bu^{35}Cl eigenvectors (normalized)					
	t-Bu^{35}Cl, cm^{-1} [a]	$\Delta\nu$, cm^{-1} [b]	*t*-Bu^{35}Cl, cm^{-1}	% error[c]	$\Delta\nu$, cm^{-1}	S_1	S_2	S_3	S_4	S_5	S_6
ν_1	806	0.60	806.09	0.010	0.77	1.000	−0.649	−0.695	0	0	0
ν_2	560	2.52	560.04	0.007	2.60	0.113	0.802	1.000	0	0	0
ν_3	370	3.75	370.18	0.049	4.12	−0.222	−0.106	1.000	0	0	0
ν_4	1210	0	1210.10	0.008	0.20	0	0	0	1.000	0.786	−0.413
ν_5	404	0	404.05	0.012	0.10	0	0	0	−0.476	1.000	0.267
ν_6	296	1.48	295.98	0.007	1.44	0	0	0	−0.164	−0.411	1.000

[a] Estimated 0.05 *M* *t*-BuCl in MeOH; see text. [b] $\Delta\nu_1 = (\nu_1/\nu_v)\Delta\nu_v$; see text. [c] (100%) (|^{35}calculated − ^{35}observed|/^{35}observed).

wrong force constants. Occasionally such a reversal might result in a stable solution, but this was clearly evident from the eigenvectors, and was discarded. Some of the less reliable measured isotope shifts were varied manually, to determine their effect on iteratively improved force constants. Small changes in these caused appreciable change in the off-diagonal constants, and in the calculated magnitudes of individual isotopic shifts, but not in the sums of calculated isotope shifts. For the same set of C_3C–^{35}Cl frequencies, the sum of isotopic shifts is essentially constant, apparently fixed by the geometry of the model. Final calculations were performed, requiring a worst case deviation of less than 0.065% for convergence. The calculated frequencies, force constants, eigenvectors, and per cent error are presented in Tables III and IV.

Solution Phase. In order to calculate kinetic isotope effects of *tert*-butyl chloride in solution, it is necessary to know the vibrational frequencies and isotope shifts corresponding to a 0.05 *M* solution of *tert*-butyl chloride in methanol. To do this, the six skeletal frequencies were measured in neat solution, and in increasingly dilute solutions of methanol or methanol-d_1. Data were then extrapolated to 0.05 *M*. Due to methanol band interferences, not all frequencies could be observed in both methanol and methanol-d_1. Frequencies which were observable in both cases were compared and found to be identical, after consideration of the overlapping methanol band interference. Observed data are shown in Table V, while the extrapolated 0.05 *M* result appears in the first column of Table VI. To determine the isotope shift, high-resolution spectra of saturated solutions of $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ in methanol-d_1 were made. (The combination of solution phase and overlapping peak interferences preclude high-resolution examination of the ν_2 *tert*-butyl chloride peaks in either methanol or methanol-d_1.) The C–^{35}Cl mode was observed at 713.15 ± 0.5 cm^{-1}, and the C–^{37}Cl mode was 5.75 ± 0.3 cm^{-1} lower. Within experimental limits, these data are consistent with either of two propositions: that the isotopic shift is independent of frequency, or that the isotopic shift changes in proportion to the change in frequency. The former case does not seem reasonable, and the latter is indicated by the fact that the liquid frequency and isotopic shift are 97.4 and 97.5% of their gas-phase values, respectively. This conclusion is also supported by the normal coordinate analysis data. All of the isotopic shifts used for gas phase were therefore decreased proportionately to their frequency decrease in solution. Iterative force constant and frequency calculations were then performed, as for the gas phase, using the same convergence criterion. Results are shown in Tables VI and VII.

Discussion

Several trends are apparent in Table I. The dependence of the C–Cl stretching frequency on size and type of alkyl group is in good agreement with liquid- and solid-phase studies[6,7,11,12,14] and is only summarized here for comparison with the shift data: frequency decreases with increasing complexity (primary, secondary, tertiary) of the chloride, and with increasing chain length of attached alkyl groups; the latter effect is of decreasing importance as more methylene groups are added to the chain, and is of minimal importance beyond *n*-propyl. The isotopic shifts appear to follow this same pattern with certain exceptions. Although the isotope shift appears to approach an equilibrium value

Table VII. Calculated Force Constants for *tert*-Butyl Chloride Solution Model

Symmetry factored force constants, mdyn/Å[a]			
F_{11}	4.35	F_{12}	−0.244
F_{22}	2.740	F_{13}	0.851
F_{33}	0.965	F_{23}	−0.827
F_{44}	4.271	F_{45}	0.918
F_{55}	1.384	F_{46}	1.382
F_{66}	1.177	F_{56}	0.686

[a] All force constants associated with S_r assumed zero.

of 3.9–4.0 cm^{-1} for the low frequency (P_H) vibration of normal chlorides, the P_C band shift is less than the P_H band shift in cases of conformational splitting, even though the P_C band occurs at a higher frequency. Moreover, it is not clear whether the P_C shift is strongly or weakly dependent on alkyl chain size beyond *n*-butyl; there does still seem to be an appreciable effect between *n*-propyl and *n*-butyl. Thus, for kinetic isotope effect calculations involving longer chains, the P_H shift may be assumed to be near 4.0 cm^{-1} but further data may be necessary to establish a trend for the P_C shift. These isotopic labeling studies have thus led to a more complete correspondence between the relevant infrared vibrations and their molecular motions.

The model proposed adequately describes ground-state *tert*-butyl chloride molecules in gas phase and in methanol solutions, where only isotopic substitution on the chlorine is allowed. Diagonal force constants are reasonable when compared with literature values.[14,16,23] F_{22} is somewhat low, but this can be explained by the somewhat greater carbon–chlorine bond length.[22] Some off-diagonal constants are unusually large, but are justified by the strong mixing of modes, as shown both by the eigenvector calculations and the observed isotopic splittings of other modes. (The method of elimination of the redundant coordinate is also a factor and makes comparison of off-diagonal elements qualitative at best.) Perhaps the most interesting conclusion is that there is *no* vibration which is *principally* C–Cl stretch and that the vibration which has the largest carbon–chlorine contribution does not show the largest isotopic shift. Although this may be an artifact of the C_{3v} symmetry involved here, it does serve to emphasize that the common practice of labeling absorption bands with normal mode descriptions is at best approximate, and may be erroneous in some cases. Specifically, the common assumption that the nominal carbon–chlorine stretching frequency and isotopic shift alone are sufficient for simplified KIE calculations must fail for *tert*-butyl chloride, and may not be valid for other chlorocarbons. The model presented here successfully predicted all major frequency shifts and should, therefore, be directly applicable to the calculation of chlorine kinetic isotope effects in solution. In later papers[5,28] we shall discuss the results of simplified KIE calculations involving several ground-state vibrations and compare them with detailed computer-model transition state calculations.

Acknowledgment. This research was supported by the Wisconsin Alumni Research Foundation and the National Science Foundation through Grants GP-8369 and GP-23762. We wish to express our appreciation to Professor Robert West for the use of his Perkin-Elmer Model 457 spectrophotometer.

(28) R. C. Williams and J. W. Taylor, to be submitted.

Dynamic Nuclear Polarization in Phosphonitrilic Fluorides

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Abstract: Dynamic nuclear polarization has been observed in solutions of a series of phosphonitrilic fluorides $(PNF_2)_{n=3-7}$ with three free radicals. Generally, much weaker scalar coupling between the free radicals and the ^{31}P nuclei is found in the fluorides than in the corresponding chlorides. The alternating series trend and strong scalar couplings found for ^{31}P enhancements with the chlorides is not evident in ^{19}F enhancements with the free radicals bis(diphenylene)phenylallyl and galvinoxyl; in contrast, diphenylpicrylhydrazyl shows a strong scalar coupling to the ^{19}F nuclei which decreases monotonically with increasing ring size. Viewed by DNP, fluorine appears essentially unconjugated with the ring π-orbital system and behaves as on aliphatic hydrocarbons. The DNP results are correlated with other details of receptor molecular orbitals and radical-receptor collision attitudes.

Various properties of phosphonitrilic ring compounds of the type $(PNX_2)_n$ have been studied[2–5] to determine the nature of the bonding orbitals. In these molecules, a basic σ molecular framework is supplemented by a dual π system comprised of combinations of phosphorus 3d orbitals with the nitrogen valence shell orbitals. Dynamic nuclear polarization (DNP) with a variety of free radicals as probes responds to the receptor molecule electronic structure *via* stereospecific hyperfine interactions and thereby illuminates the

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