Chlorine Quadrupole Coupling in Methyl Chloride. Variation of Quadrupole Coupling Strength with Isotopic Substitution

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Abstract: High-resolution measurements of hyperfine structure on the $J = 1 \rightarrow 0$ transitions in $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ were made using a molecular beam maser spectrometer. The measured ^{35}Cl quadrupole coupling strength is $eqQ = 74{,}753 \pm 2$ kHz and spin-rotation constant $C(^{35}Cl) = 2.4 \pm 0.6$ kHz. The measured ^{37}Cl quadrupole coupling strength is $eqQ = 58{,}910 \pm 2$ kHz and spin-rotation constant $C(^{37}Cl) = 1.4 \pm 0.6$ kHz. These results are compared with ^{35}Cl quadrupole coupling strengths obtained for CH_2DCl and CD_3Cl and a systematic decrease in ^{35}Cl quadrupole coupling is related to changes in the structure and properties of the methyl group on deuterium substitution.

The resonance line width of the molecular beam maser spectrometer is 5 kHz (F. W. H. M.) at 26 GHz so highly accurate values of molecular interaction strengths may be obtained. Precise values for quadrupole coupling strengths provide information on changes of electric field gradients associated with rather small changes in the structure of molecules. These changes in field gradient may also be related to chemical properties of substituent groups.

Some effects of deuterium substitution on molecular structure have been observed previously. Laurie and Hershbach[1] observed that CH bonds are 0.003 to 0.005 Å longer than corresponding CD bonds. Miller, *et al.*,[2] first reported this effect in methyl chloride although the magnitude given by them may be too large. A study of isotopic effects on bond length in ethane and diborane was reported by Kuchitsu.[3] There is also evidence from steric effects that the deuterated methyl group is smaller. Mislow, *et al.*,[4] observed an increase in racemization rate constants when methyl groups were deuterated in a system with a crowded transition state. Halevi[5] has related the shorter C–D bond to a higher charge density and therefore a greater electron-donating effect relative to C–H bonds.

Nuclear quadrupole coupling strength is dependent on electric field gradients which can be related to the charge distribution in a molecule so we would also expect changes in quadrupole coupling strength on deuterium substitution. A qualitative difference in ^{35}Cl quadrupole coupling on deuterium substitution was observed by Simmons and Goldstein[6] but their reported difference was off by a factor of 5. The high resolution of the maser spectrometer ($\sim 3 \times 10^{-7}$) makes it possible to measure this effect to an accuracy better than 1%. The ^{35}Cl quadrupole coupling strengths for CH_2DCl and CD_3Cl were obtained previously[7] using the same high-resolution spectrometer.

Experimental Section

The molecular-beam maser spectrometer has been described previously.[8] A cylindrical TM_{010} mode silver cavity 10 cm long was used. A single-hole nozzle-type beam source with a 0.1-mm diameter hole was operated at 30 mm of pressure. The $J = 1$ rotational state was focused into the cavity using an electric quadrupole lens 20 cm long. Methyl chloride was taken directly from a cylinder with stated purity of 99.5%. The stimulating signal was obtained as the third harmonic of an X-13 klystron near 9 GHz. The microwave power level in the cavity was measured with a superhet receiver. The local oscillator signal was the second harmonic of an X-12 klystron near 23 GHz. Both klystrons were phase locked to a harmonic of a reference signal near 100 MHz. Frequency modulation and phase-sensitive detection at 1 kHz were used to record derivative spectra. A recorder trace of the $F = {}^1/_2$ component of the transition is shown in Figure 1 as an example of line width obtained. Other transitions were somewhat weaker due to smaller Stark effects.

Results

The frequencies of the three components for the $J = 1 \rightarrow 0$ transitions are listed in Tables I and II. The components for $F = {}^3/_2$ and ${}^5/_2$ ($\bar{F} = \bar{I}_{Cl} + \bar{J}$)

Table I. Frequencies of Observed $J = 1 \rightarrow 0$ Transitions in $CH_3{}^{35}Cl$ and ^{35}Cl Quadrupole Coupling and Spin-Rotation Strengths[a]

Parameter	Frequency, kHz
$F = \frac{3}{2} \rightarrow \frac{3}{2}$ transition	26,570,728.8 ± 1.0
$F = \frac{5}{2} \rightarrow \frac{3}{2}$ transition	26,589,421.5 ± 1.0
$F = \frac{1}{2} \rightarrow \frac{3}{2}$ transition	26,604,365.1 ± 0.5
$eq_{zz}Q(^{35}Cl)$	74,753.3 ± 2.0
$C(^{35}Cl)$	2.4 ± 0.5
$J = 1 \rightarrow 0$ (rotational level separation)	26,585,688 ± 2.0

[a] The $J = 1 \rightarrow 0$ level separation, if no hyperfine structure was present, is also listed.

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(2) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes, and J. Kraichman, *ibid.*, 20, 1112 (1952).

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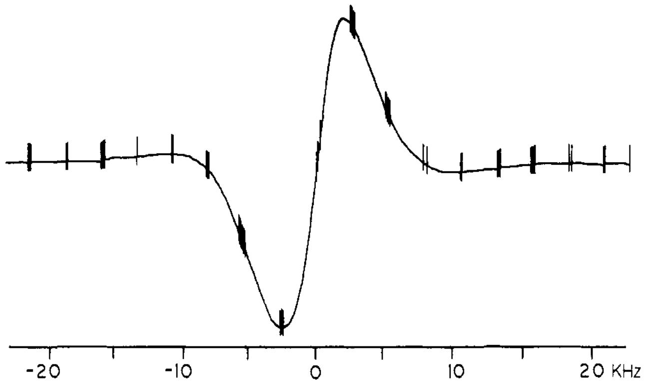

Figure 1. Recorder trace of the $F = {}^1/_2$ component of the $J = 1 \rightarrow 0$ transition in $CH_3{}^{35}Cl$. Frequencies in kHz relative to 26,604,365.0 kHz.

Table II. Frequencies of Observed $J = 1 \rightarrow 0$ Transitions in $CH_3{}^{37}Cl$ and ^{37}Cl Quadrupole Coupling, Spin-Rotation Strength, and $J = 1 \rightarrow 0$ Rotational Level Separation

Parameter	Frequency, kHz
$F = \frac{3}{2} \rightarrow \frac{3}{2}$ transition	26,164,490 ± 2
$F = \frac{5}{2} \rightarrow \frac{3}{2}$ transition	26,179,220 ± 2
$F = \frac{1}{2} \rightarrow \frac{3}{2}$ transition	26,190,998 ± 1
$eq_{zz}Q(^{37}Cl)$	58,910.2 ± 1.5
$C(^{37}Cl)$	1.4 ± 0.6
$J = 1 \rightarrow 0$ level separation	26,176,271 ± 3

were further split by the hydrogen spin–spin interaction and the line shape was calculated using a spin–spin interaction strength calculated using the H–H bond length obtained from Costain's data.[9] We note that although accurate variations in the structure with deuterium substitution are not readily obtained from Costain's analysis, the average structure is probably the best available. The calculated line shapes were in reasonable agreement with observed spectra, indicating that the hydrogen spin-rotation interaction strength is less than 3 kHz. The quadrupole coupling strength, spin-rotation interaction strength, and rotational transition frequency (if no hyperfine structure were present) are listed in Tables I and II. These interactions were discussed previously[7] for CH_3Cl. Corrections have been included in the data analysis for quadrupole coupling terms off diagonal in rotational states as discussed by Townes and Schawlow.[10]

The ^{35}Cl quadrupole coupling strengths along the molecular symmetry axis (C–Cl bond direction) for $CH_3{}^{35}Cl$, $CH_2D^{35}Cl$, $CD_3{}^{35}Cl$, and $CH_3{}^{37}Cl$ are listed in Table III. This quantity is plotted in Figure 2 as a function of the number of deuterium substitutions for these three species and we clearly see a linear relation.

Discussion

The strength of the ^{35}Cl quadrupole coupling is observed to decrease by 180 kHz when the methyl group is fully deuterated. This represents a decrease in the electric field gradient at the chlorine nucleus of 0.2%. We will consider the two mechanisms which contribute to this effect and the relative contribution from each.

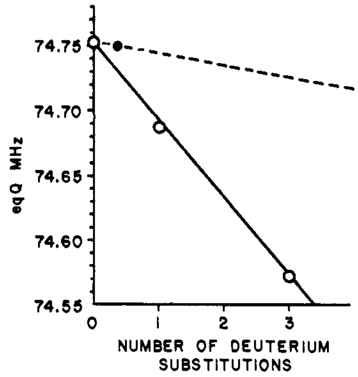

Figure 2. ^{35}Cl quadrupole coupling in MHz as a function of the number of deuterium atoms substituted for hydrogen on the methyl group (open circles). Solid dot and dotted line indicate change in eqQ^* (^{37}Cl) for change in reduced mass which is 12% of the change in reduced mass for deuterium substitution.

Table III. Cl Quadrupole Coupling Strength $eq_{zz}Q$ and Rotational Constant B_0 for Four Isotopic Species of Methyl Chloride[a]

Molecule	$eq_{zz}Q$	B_0
$CH_3{}^{35}Cl$	74,753	13,292,844
$CH_2D^{35}Cl$	74,687	12,328,130
$CD_3{}^{35}Cl$	74,573	10,841,888
$CH_3{}^{37}Cl$	58,910	13,088,136

[a] Frequencies in kHz to an accuracy of ±2 kHz or better.

First there is a direct effect due to the increased mass of the methyl group. The anharmonic contribution to the potential energy associated with changes in the carbon–chlorine bond length will cause the r_0 (mean bond length in lowest vibrational state) bond distance to change when the reduced mass of the system is changed. The $CH_3{}^{37}Cl$ measurements were made to determine the relative importance of this effect. Although the nuclear quadrupole moment is different for ^{37}Cl, the ratio $Q(^{35}Cl)/Q(^{37}Cl)$ is known to extremely high accuracy. The ratio obtained by Holloway,[11] *et al.*, using atomic beam magnetic resonance was $Q(^{35}Cl)/Q(^{37}Cl) = 1.268877 \pm 0.000002$. Using this ratio we can calculate $eqQ^* = eqQ(^{37}Cl) \cdot Q(^{35}Cl)/Q(^{37}Cl)$, a quadrupole coupling strength which we can compare with the ^{35}Cl results. This value is 74,750 ± 2 kHz. This is only a decrease of 3 ± 3 kHz from the $CH_3{}^{35}Cl$ value. If we only consider the above mechanism we would expect a shift of 22 ± 22 kHz when the methyl group is fully deuterated. The observed shift is 180 ± 3 kHz.

The solid dot in Figure 2 indicates the frequency shift of $eqQ^*(^{37}Cl)$ and reduced mass change compared with that for full deuteration. The slope of the dotted line which we interpret as the direct change associated with the change in reduced mass is clearly different from the solid line representing the effects of deuterium substitution on the methyl group.

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The second and apparently most important mechanism is an indirect effect involving changes in the chemical properties of the methyl group with deuterium substitution. It appears that the shortening of the C–D bond tends to reduce the electron-withdrawing effect of the carbon–hydrogen bond and make the methyl group less electronegative. Miller, *et al.*,[2] observed that the C–D bond length was 0.009 Å shorter and the D–C–D bond angle 12 min greater in the fully deuterated methyl group than in the ^1H species. The presence of this effect in other molecules was confirmed by Laurie and Hershbach.[1] The inductive effect involving a change in electronegativity of the methyl group is discussed by Halevi[5] and Van Hook.[12] Decreasing the electronegativity of the methyl group will increase the electronegativity difference across the C–Cl bond and therefore increase the ionic character of this bond. According to the Townes–Dailey theory,[10] the increase in ionic character will decrease the quadrupole coupling strength. Following this model our measurments indicate an increase in ionic character by 0.17% for the deuterated form. We should note that there will be further contributions to variation in quadrupole coupling on deuteration due to changes in hydrogen positions. The C–Cl bond length was observed to decrease by 0.0008 Å when the methyl group was fully deuterated.[13] This change in bond length may also be related to changes in electronegativity and this effect is in qualitative agreement with the above results from quadrupole coupling.

The quadrupole coupling strengths in methyl bromide are considerably larger so previous microwave results[14] may be analyzed to obtain quadrupole coupling variations with deuterium substitution for this molecule. In this case full deuteration of the methyl group leads to a decrease of 0.27% in quadrupole coupling. This is very similar to the decrease of 0.24% we observed in methyl chloride.

Our measurements of quadrupole coupling in $CH_3{}^{35}Cl$ strength indicate a systematic decrease in electric field gradient at Cl on deuterium substitution. Further measurements on $CH_3{}^{37}Cl$ show that the decreased field gradient is not a direct result of the increased mass of the methyl group. Therefore, it appears that the chemical properties of the methyl group are modified by deuterium substitution.

Acknowledgment. This research was supported by the National Science Foundation.[15] The authors would like to thank George Whitesides and Tom Cromartie for helpful comments on this paper.

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[15] NSF Grant No. GP-21110—Structural Chemistry.

Laser-Excited Fluorescence Emission from Cis and Trans Isomers of 2,3- and 2,4-Dimethylcyclobutanone. Ultra-Short-Lived Excited Molecules[1]

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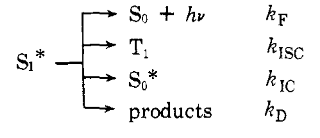
Received September 18, 1972

Abstract: The singlet lifetimes (τ_s) of the dimethylcyclobutanone (DMCB) isomers are estimated by using the relationship $\tau_s = \tau_0\Phi_F$ where τ_0 is the radiative lifetime and Φ_F is the measured quantum yield of fluorescence. τ_s for the DMCB isomers (S_1*) produced by uv-laser excitation at 325.0 nm is estimated as 0.3 nsec for *cis*-2,3-DMCB, 0.1 nsec for *trans*-2,3- and *cis*-2,4-DMCB, and 0.01 nsec for *trans*-2,4-DMCB. Facile α cleavage of the cyclobutanone ring "predissociation," facilitated effectively by α-methyl substitution, is held responsible for the observed short lifetimes in these "isolated" molecules in the gas phase, and some explanations are given for their variation. This α-substitution effect in the cyclobutanones is *opposite* to the α-substitution effect observed in the cyclopentanones and the cyclohexanones, since the singlet lifetimes of these C_5 and C_6 cyclic ketones are mainly determined by the $S_1 \rightsquigarrow T_1$ intersystem crossing rate ($\sim 10^9$ sec^{-1}). Practical limitation of measuring the weak luminescence signal and general validity of estimating the ultrafast transformation rates of the electronically excited molecules are briefly discussed.

Fluorescence emission, if measurable, provides valuable kinetic information about primary unimolecular processes which largely govern the fate of the photoexcited carbonyl compounds. The fluorescence emission process competes with singlet–triplet intersystem crossing, internal conversion, and chemical decomposition (and/or isomerization) on the first excited singlet manifold as shown in Scheme I. If these unimolecular processes are either comparable to or relatively slow compared with the collision frequency of

Scheme I



[1] This research has been supported by National Science Foundation Grant GP-28010X.