and 97th fringes are approached. It is of interest to note, however, that the positions of fringes 96 and 97 are predicted by the simple "quarter wave" approximation within the limits of the usual experimental error.

In addition to these numerical comparisons with previous theory it should be mentioned that for the lowest fringe, $j = 0$, the Airy integral interference condition, equation (26), yields the values 0.95354, 0.78805 and 0.70474 for $e^{-z_j^2} = Y_j/C_t$ when $j_m$ is 100, 10 and 6, respectively.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

# The Pure Quadrupole Spectra of Solid Chloroacetic Acids and Substituted Chloroacetic Acids[1]

BY HARRY C. ALLEN, JR.[2]

RECEIVED JUNE 23, 1952

Using a frequency-modulated super-regenerative spectrometer the pure quadrupole spectrum of $Cl^{35}$ has been measured in the chloroacetic acids and several of their derivatives. In several of these compounds multiple lines are observed, which in the case of small separations (<0.5 mc.) are attributed to crystallographically non-equivalent chlorines. In $CCl_3COCl$ the chemically different chlorines have absorption lines separated by nearly 7 mc. A separation of slightly greater than 1 mc. in $CCl_3CH(OH)_2$ is interpreted as due to intermolecular hydrogen bonding. From the variation of the chlorine frequency in the $CCl_3$ and $CH_2Cl$ groups it is inferred that the electron withdrawal ability of the substituent groups measured increases in the order $COO^-$, $CONH_2$, $COCH_3$, $COCH_2Cl$, $COOC_2H_5$, COOH.

## Introduction

A nuclear electric quadrupole moment arises when the nuclear charge deviates from a spherical distribution. This permanent quadrupole moment can interact with a non-spherical extranuclear charge distribution to produce a variation in the electrostatic energy of the system with nuclear orientation. This type of effect has been observed as hyperfine structure in the rotational spectra of gas molecules and more recently the direct transitions among these energy levels have been observed in crystalline solids in the radio-frequency region of the spectrum.

In this work the pure quadrupole spectrum of chlorine$^{35}$ has been measured in the chloroacetic acids and several of their derivatives. These spectra are very sensitive to small changes in the gradient of the electric field at the chlorine nucleus and hence yield information concerning molecular bonding and solid state effects. It has been found that such resonance lines are influenced by different crystallographic environment[3] and intermolecular bonding in the solid state,[4] and that marked differences in the chemical bonding of a given atom give rise to rather widely separated resonance lines. It is thus possible to obtain considerable information concerning molecular bonding in the solid from a study of these spectra.

## Experimental

The spectra were observed using a frequency-modulated super-regenerative spectrometer similar to that of Dean and Pound.[5] The frequency modulation was a 30 cycles/sec. sine wave; this same frequency was applied to the horizontal plates of the display oscilloscope. A square-wave quench voltage was used, the frequencies giving the greatest sensitivity being in the region of 50–100 kc. Samples were sealed in 2-dram vials which were inserted directly in the coil which formed part of the resonant circuit of the oscillator. When making low temperature runs the sample and coil were immersed directly in the cooling bath.

The frequencies were measured with a war surplus frequency meter set SCR 211 AC. The frequency-meter peaks were superposed on the absorption peaks, a match being ascertained by finding the frequency-meter peak which remained superposed on the absorption peak as the quench frequency was varied. The frequency measurements are accurate to ±5 kc. Temperatures were measured by a pentane thermometer and an iron–constantan thermocouple, both of which had been calibrated at the ice point, Dry Ice Point, and liquid nitrogen temperature. The temperature measurements are believed to be good to ±1°.

Where the absorption was strong enough, the resonance due to $Cl^{37}$ was also measured. In other cases the region was searched where the $Cl^{35}$ resonance would be expected assuming that the observed absorption was due to $Cl^{37}$. The ratio of the quadrupole moments of the two isotopes, $Cl^{35}/Cl^{37}$, found from these measurements agrees within the experimental uncertainty with previously published values.[5,6]

The $CCl_3COOH$ used was Mallinckrodt reagent grade, the $(CH_2ClCHO)_3$ was synthesized in the organic chemistry department, and the rest of the chemicals were obtained from Eastman Kodak Co. In each case the compounds were used without further purification. All samples of solid compounds were crystallized from a melt in order to ensure a maximum number of chlorine nuclei in the absorption coil. It was found necessary to age the chloral hydrate sample prepared in this way for about three months and the $(CH_2ClCHO)_3$ sample for about six weeks before absorption was found.

## Experimental Results

The experimental results are summarized in Table I. It should be noted that in several of the compounds multiple lines were observed. In cases where the splitting is small (<0.5 mc.) this is presumably due to crystallographically non-equivalent chlorines, while the larger separations are presumably due to differences in the chemical bonding of the chlorine atoms. Since the frequencies are temperature dependent, they have been measured from liquid nitrogen temperature up to either the melting point of the compound or room temperature, whichever is lower. The temperature dependence of the frequencies observed in the mono-chloro substituted compounds are plotted in Fig. 1.

Although $CCl_3COOH$ is a solid at room tempera-

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[1] The research reported in this paper was supported in part by the Office of Naval Research under ONR Contract N5ori-76, Task Order V.

[2] Atomic Energy Commission Postdoctoral Fellow.

[3] H. G. Dehmelt, *Z. Physik*, **130**, 356 (1951).

[4] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **20**, 35 (1952).

[5] C. Dean and R. V. Pound, *ibid.*, **20**, 195 (1952).

[6] R. Livingston, *Phys. Rev.*, **82**, 289 (1952).

TABLE I

OBSERVED FREQUENCIES, mc.

| Compound | 295°K. | 196°K. | 77°K. | *eqQ* av. mc. extra-polated |
|---|---|---|---|---|
| $CH_2ClCOOH$ | 34.919 | 35.602 | 36.131 | 73.15 |
| | 35.461 | 35.981 | 36.429 | |
| $CH_2ClCOOC_2H_5$ | | 35.058 | 35.962 | 72.50 |
| $CH_2ClCOCH_2Cl$ | 34.902 | 35.441 | 35.943 | 72.46 |
| $(CH_2ClCHO)_3$ | 34.464 | 34.934 | 35.363 | 71.55 |
| | 34.783 | 35.231 | 35.691 | |
| $CH_2ClCOCH_3$ | | 34.452 | 35.075 | 70.98 |
| | | 34.461 | 35.484 | |
| $CH_2ClCONH_2$ | 34.227 | 34.599 | 34.882 | 70.06 |
| $CH_2ClCOONa$ | 33.943 | 34.417 | 34.794 | 70.00 |
| $CCl_3CH(OH)_2$ | 37.513 | 37.869 | 38.190 | 76.68 |
| | 38.699 | 39.086 | 39.429 | 79.25 |
| | 38.784 | 39.167 | 39.515 | |
| $CCl_3CONH_2$ | | 39.106 | 38.850 | |
| | | 39.229 | 39.478 | |
| | | 39.598 | 39.599 | 79.11[a] |
| | | | 39.665 | |
| | | | 39.817 | |
| | | | 40.007 | |
| $CCl_3COOH$ | | | 39.967 | |
| | | | 40.165 | 80.25[a] |
| | | | 40.240 | |
| $CCl_3COCl$ | | | 33.721 | 67.44[a] |
| | | | 40.132 | |
| | | | 40.473 | |
| | | | 40.613 | 80.81[a] |
| $CHCl_2COOH$ | | 37.436 | 37.979 | |
| | | 38.163 | 38.807 | |

[a] 77°K.

ture no absorption was observed above −158°, and no lines were observed in solid $CCl_3CONH_2$ above −43°. Below this temperature $CCl_3CONH_2$ has three absorption lines down to −158°, but at −196° six lines were observed. These discontinuities in the spectrum are presumably due to phase changes in the solid[5] but no reference to them has been found in previous work.

## Discussion of Results

If the gradient of the electric field at the chlorine nucleus is assumed to be cylindrically symmetric then the measured frequencies are one-half the quadrupole coupling constant,[7] *eqQ*.

On this assumption the coupling constants of $Cl^{35}$ in these compounds have been listed in column 5 of Table I. Where the frequencies could be measured over a sufficient temperature range, they have been extrapolated to 0°K. in order to minimize the effect of lattice vibrations. When multiple lines were observed and the splittings are small, the *eqQ*'s were taken as the average of the extrapolated frequencies. For compounds for which the frequencies could not be measured over a sufficient temperature range to insure a good extrapolation the *eqQ*'s were calculated from the frequencies measured at 77°K.

Many of the compounds investigated exhibited multiple absorption lines. Dehmelt[3] has suggested that in $SnI_4$ such multiple lines arise from crystallographically different iodine atoms. In this series of compounds, only the crystal structure of $CCl_3CH(OH)_2$ is known and this evidence seems to bear out Dehmelt's hypothesis.

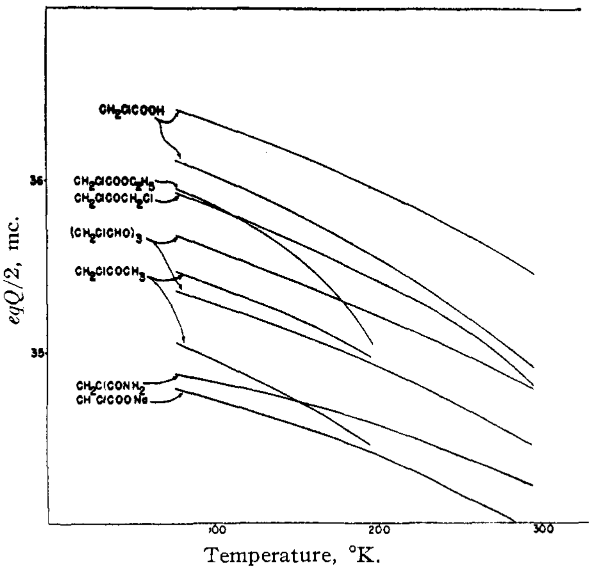

Fig. 1.—Temperature dependence of chloroacetic acid and several of its derivatives.

The crystal structure of chloral hydrate has been investigated by Kondo and Nitta,[8] their results showing three different carbon–chlorine distances, 1.79, 1.78 and 1.72 A. The two chlorines at the longer distances are presumably hydrogen bonded through the hydroxyl groups of adjacent molecules. Such an interpretation is consistent with the quadrupole resonance spectrum. Three resonance lines are found; the highest frequency pair being separated by only 86 kc. at 77°K. This is in line with what might be expected if the splitting is due to small differences in crystallographic environment or if the degree of hydrogen bonding for the two chlorines is slightly different. The third line, however, is 1.239 mc. lower than the nearer of the other two lines. Such a splitting indicates that the bonding of the chlorine giving rise to this line must be quite different. This quadrupole resonance pattern is easily reconciled with the X-ray results if the lowest frequency line is attributed to the non-hydrogen bonded chlorines while the two higher frequency and slightly split lines are attributed to the chlorines involved in hydrogen bonds.

An attempt was made to measure the resonance frequencies in the acid chlorides of acetic acid and the chloroacetic acids. The only acid chloride in which absorption was found is $CCl_3COCl$. In this compound three lines were found in the region of 40 mc. which, although slightly higher in frequency, are analogous to those found in $CCl_3COOH$ (see Table I). These lines obviously arise from the $CCl_3$ group. A fourth line at 33.7 mc. is attributed to the more ionic chlorine attached to the carbonyl group.

The temperature dependence of the frequencies is in qualitative agreement with the theory of Bayer,[9]

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(7) R. V. Pound, *Phys. Rev.*, **79**, 685 (1950).

(8) S. Kondo and I. Nitta, *X Sen*, **6**, 53 (1950).

(9) H. Bayer, *Z. Physik*, **130**, 227 (1951).

although his model is undoubtedly too simple. Pound[10] has found that in order to account for the temperature dependence of the frequencies in solid $I_2$, it is necessary to consider intermolecular bonding as proposed by Townes and Dailey,[4] as well as the effect of the thermal motion of the molecules as proposed by Bayer.

It has been pointed out[11-13] that values of the coupling constant obtained from pure quadrupole spectra of solids may differ by as much as 10% from the values for the same molecule obtained from microwave investigations of the gases. Thus extreme care must be exercised in interpreting these solid state values in terms of molecular bonding. The increase in the absorption frequency observed as acetic acid is successively chlorinated roughly parallels the increases observed in the corresponding chlorinated methanes.[11] If it is assumed that the frequency change from compound to compound is due to the different electron withdrawing power of substituent groups, then by considering the trichloro compounds it is found that the withdrawal effect increases in the order: $-CH(OH)_2$, $-CONH_2$, $-COOH$, $-COCl$. A longer series of substituent electron withdrawal effects can be deduced from the monochloro substituted series of compounds. The observed frequencies in this series indicates that the electron withdrawal ability increases in the order $-COO^-$, $-CONH_2$, $-COCH_3$, $-COCH_2Cl$, $-COOC_2H_5$, $COOH$. These series are both in agreement with those obtained on the basis of chemical evidence alone.

Further evidence for this order comes from the shifts of the carbonyl stretching frequencies in the infrared spectra of these compounds. The carbonyl stretching frequency is presumably related in some way to the charge on the carbon atom of this group. The same residual charge determines the electron withdrawal effect in these series of compounds, hence one might expect a correlation between the observed quadrupole coupling constants and the frequency of the carbonyl stretching frequency in these compounds. Unfortunately these frequencies are not available for all these chlorinated compounds, but if we consider the analogous non-chlorinated compounds[14] it is found that the $C=O$ infrared frequencies increase in the same order as the coupling constants. The carbonyl frequency of chloroacetone could not be found in the literature; however, a measurement shows this frequency to be slightly higher in chloroacetone than in acetone as might have been predicted.

From this evidence it would seem that either the solid state effects are relatively constant in this series or they do not differ enough to invert the order of these series. The correlation of solid-state quadrupole-coupling constants with Hammett's $\sigma$ for a series of substituted benzenes[15] seems to lend additional support to this hypothesis.

**Acknowledgment.**—The author wishes to thank Professor E. Bright Wilson, Jr., for many helpful discussions during the course of this work. He is also indebted to Messrs. L. Hedrick, H. Meal, G. Jones and C. Dean for extensive help on the instrumentation.

[10] R. V. Pound, private communication.

[11] R. Livingston, *J. Chem. Phys.*, **19**, 1434 (1951).

[12] H. G. Dehmelt and H. Kruger, *Z. Physik*, **129**, 401 (1951).

[13] H. G. Dehmelt, *Naturwissenschaften*, **37**, 398 (1950).

[14] Randell, Fowler, Fuson and Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[15] H. C. Meal and E. B. Wilson, Jr., private communication.

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[CONTRIBUTION FROM CALIFORNIA INSTITUTE OF TECHNOLOGY]

# The Infrared Spectra and Structure of the Chloramines and Nitrogen Trichloride[1]

BY GORDON E. MOORE AND RICHARD M. BADGER

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The infrared vibration-rotation spectra of gaseous $NH_2Cl$, $NHDCl$, $NDCl_2$ and $NCl_3$ were investigated from 1.4 to 25$\mu$. Several fundamental vibrations were identified, and the large rotational constants were evaluated for $NH_2Cl$, $NHDCl$ and $NHCl_2$. With the assistance of reasonable assumptions regarding other parameters these were used to calculate an H–N–Cl angle of 102° in $NH_2Cl$, and suggest that $\angle$Cl–N–Cl = 106° and $r_{N-Cl}$ = 1.76 Å. in $NHCl_2$. These parameters are interpreted on the basis of simple electronic considerations.

## Introduction

The chloramines may be regarded as ammonia with one or more of the hydrogen atoms substituted by chlorine. While they have been known for a long time,[2] only the completely substituted compound $NCl_3$ has been investigated extensively. However, as far as we are aware, even its structural parameters have never been determined. Information concerning the properties of dichloramine is particularly lacking. The reason for this lack of experimental data probably lies in the instability of these compounds. Both mono- and dichloramine decompose readily to yield, among other products, the sensitive and powerful explosive nitrogen trichloride.

Since these molecules presumably have a rather simple structure, it was felt that a study of their infrared vibration-rotation spectra should allow one to draw some conclusions regarding their molecular configuration.

## Experimental

Samples were prepared by reaction of aqueous $NH_3$ and NaOCl at 0°. The resulting solution was warmed to 15–25° and connected through a $CaCl_2$ filled drying tower to an evacuated cell. After nearly every preparation it was necessary to cleanse the entire system and replace the desic-

[1] Contribution No. 1696 from the Gates and Crellin Laboratories of Chemistry.

[2] For a good review of their chemistry see J. F. T. Berliner, *J. Am. Water Works Assoc.*, **23**, 1320 (1931).