N-Chloro-chloroformimidoyl chloride: A NQR-Study

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An extension of Bayer's and Tokuhiro's ideas on NQR temperature dependences and molecular librations to the case of polyhalogenated planar molecules results in a method for line assignment, detection of special effects, such as dynamic phenomena, and computation of the absolute values of librational frequencies by using the temperature dependence of different isotopes. This is demonstrated for the case of the title compound.

General Theory

The relationship between the angles of rotation about the inertia tensor principal axes Θ^{I} and the EFG tensor principal axes Θ^{EFG} in a molecule is given by

$$\Theta^{\mathrm{EFG}} = \Theta^{\mathrm{I}} * \alpha\,, \quad \alpha = \sin\eta \tag{1}$$

where η is the angle between the directions of the respective principal axes of the two tensors. This equation was first applied to the interpretation of NQR results in two Japanese papers [1, 2]. It is correct in the frame of Bayer's [3] theory (small angular amplitudes) as can be shown by equating the expression for the EFG, rotated by symmetrized matrix products, with its new components known for geometrical reasons (Figure 1):

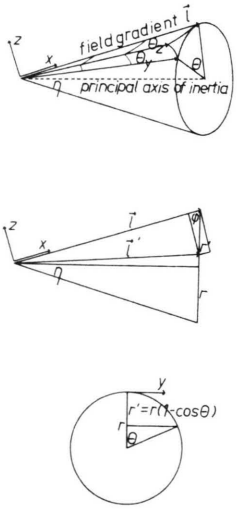

Fig. 1. Rotation of the fieldgradient about a principal axis of inertia. Upper part: Perspective view of the cone of rotation. Middle part: Cross sectional view. Lower part: Front view.

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$$1 * \begin{pmatrix} \cos\Theta_y \cos\Theta_z \\ \tfrac{1}{2}(\sin\Theta_z + \cos\Theta_y \sin\Theta_z) \\ -\tfrac{1}{2}(\sin\Theta_y + \sin\Theta_y \cos\Theta_z) \end{pmatrix} = 1 * \begin{pmatrix} 1 - \tfrac{1}{2}\sin\Theta^2 \sin^2\eta \\ \sin\Theta \sin\eta \\ -\tfrac{1}{2}\sin\Theta^2 \sin\eta\cos\eta \end{pmatrix}. \tag{2}$$

For small amplitudes this gives:

$$\begin{pmatrix} 1 - \tfrac{1}{2}(\Theta_y^2 + \Theta_z^2) \\ \Theta_z \\ -\Theta_y \end{pmatrix} = \begin{pmatrix} 1 - \tfrac{1}{2}\Theta^2 \sin^2\eta \\ \Theta \sin\eta \\ -\tfrac{1}{2}\Theta^2 \sin\eta\cos\eta \end{pmatrix} \tag{3}$$

from which Eq. (1) can be seen to be correct under the specified conditions. Because of its quadratic dependence on Θ the angle of rotation Θ_y does not appear in Equation (1).

The simple linear form of Eq. (1) makes possible its connection with Bayer's theory. For the temperature coefficient of the NQR lines one obtains:

$$\frac{1}{\nu_0}\frac{\mathrm{d}\nu(T)}{\mathrm{d}T} = -\frac{3h^2}{8\pi^2 k T^2} \sum_{\substack{q \\ q=x,y,z}} \frac{\alpha_q^2}{I_q} \frac{\exp\{h\nu_q/kT\}}{[\exp\{h\nu_q/kT\} - 1]^2} \tag{4}$$

ν_0 = NQR-frequency at absolute zero,
α_q = refer to Equation (1),
I_q = moment of inertia,
ν_q = librational frequency.

Planar Molecules

For the determination of the torsional frequencies about the three inertia tensor principal axes one needs the knowledge of the temperature dependences of at least three different NQR-lines to solve the set of linear equations resulting from Eq. (4)

$$\begin{aligned} A &= \alpha_{Ax}^2 f(\nu_x) + \alpha_{Ay}^2 f(\nu_y) + \alpha_{Az}^2 f(\nu_z)\,, \\ B &= \alpha_{Bx}^2 f(\nu_x) + \alpha_{By}^2 f(\nu_y) + \alpha_{Bz}^2 f(\nu_z)\,, \\ C &= \alpha_{Cx}^2 f(\nu_x) + \alpha_{Cy}^2 f(\nu_y) + \alpha_{Cz}^2 f(\nu_z)\,, \end{aligned} \tag{5}$$

A, B, C = temperature coefficients.

With regard to this system of linear equations the important class of planar and "pseudoplanar" (fieldgradients and two principal axes of inertia in one plane) molecules constitutes a special case. As the z-axis of the inertia tensor is vertical to the plane of the molecule, the figures in the last column of the matrix of the coefficients of the above system of equations equal unity. The other coefficients are correlated by the interdependence of the direction sines. So one obtains the vanishing determinant of an unsolvable system of linear equations:

$$\begin{vmatrix} a & 1-a & 1 \\ b & 1-b & 1 \\ c & 1-c & 1 \end{vmatrix} . \qquad (6)$$

This leads to the equation

$$A(b-c)+B(c-a)+C(a-b)=0 . \qquad (7)$$

Thus the knowledge of the temperature dependences of already two NQR-lines instead of three lines in the general case allows one to compute the temperature dependences of all other lines of a molecule. But, following from this result, it is not possible to determine the values of the librational frequencies about the three inertia tensor principal axes.

There seems to be a way to this goal by using the temperature dependences of other isotopes. It is particularly convenient for chlorine and bromine compounds because of the natural abundance of two NQR isotopes in sufficient percentages in these cases. The method is based on the assumption that the inertia tensor principal axes of compounds with varying isotopes at one place are directed nearly equally in the molecular framework. The librational frequencies about the corresponding principal axes of inertia in such molecules are in the reciprocal ratio of the square roots of their moments of inertia. With this in mind, the following equations are easily derived from Equations (5):

$$f(\nu_x) = \frac{B-A}{\alpha_{Bx}^2-\alpha_{Ax}^2}+f(\nu_y) ,$$

$$f(\nu_x)' = \frac{B'-A'}{\alpha_{Bx}^2-\alpha_{Ax}^2}+f(\nu_y)' , \qquad (8)$$

A, B = temperature coefficients for the compound with isotope 1,

A', B' = temperature coefficients for the compound with isotope 2,

$$f(\nu_x) = -\frac{3h^2}{8\pi^2 k T^2}\frac{1}{I_x}\frac{\exp\{h\nu_x/kT\}}{[\exp\{h\nu_x/kT\}-1]^2} ,$$

$$f(\nu_x)' = -\frac{3h^2}{8\pi^2 k T^2}\frac{1}{I_x'}\cdot\frac{\exp\{h\sqrt{I_x/I_x'}\,\nu_x/kT\}}{[\exp\{h\sqrt{I_x/I_x'}\,\nu_x/kT\}-1]^2} ,$$

(analogous equations for y).

The point of intersection of these two relations gives the absolute values of two of the torsional frequencies, from which the value of the third can be computed using any of the Equations (5).

Experimental Results

The foregoing considerations were applied to the case of N-Chloro-chloroformimidoyl chloride (Figure 2), a molecule which was synthesized first in

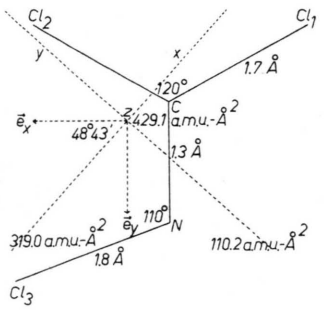

Fig. 2. Geometry and inertia tensor of N-Chloro-chloroformimidoyl chloride. Estimated molecular dimensions were taken from Reference 7. $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$ are unit vectors of the appropriately directed cartesian coordinate system fixed at the center of gravity. Chlorine atoms were numbered arbitrarily.

1969 [4] and whose NQR-spectrum at 77 °K was published in 1973 by Fitzky [5]. Figure 3 shows the results of our measurements. The temperature coefficients at the three points of measurement were corrected for the vibrational influences using Kushida's theory [6] and the results of the IR and Raman work

Table 1. Experimental temperature coefficients $\frac{-1}{\nu}\frac{d\nu}{dT}$ °K^{-1}.

	77 °K	113	147
	$0.988\cdot10^{-4}$	1.86	6.21
$^{35}Cl_a$	0.646	1.37	1.99
	0.951	1.22	1.77
$^{35}Cl_b$	1.79	1.80	1.81
	1.60	1.61	1.62
$^{37}Cl_a$	1.12	1.13	1.13
	1.14	1.14	1.15
$^{37}Cl_b$	2.28	2.30	2.32
	2.00	2.02	2.04

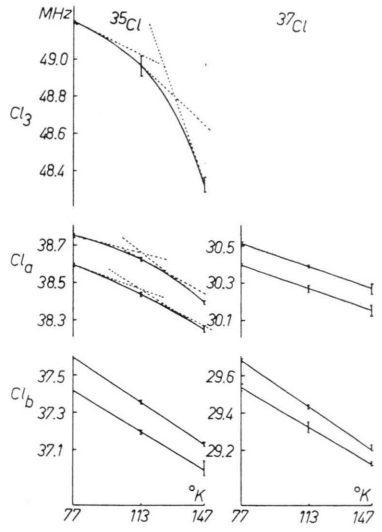

Fig. 3. Temperature dependences of the NQR lines between 77 and 147 °K. Refrigerants: 77 °K liquid N_2, 113 °K melting isopentane, 147 °K melting methylcyclohexane. The melting point of N-Chloro-chloroformimidoyl chloride is not known exactly, but it must lie between −97 °C (melting acetone) and −126 °C (melting methylcyclohexane). Dashed lines represent tangents drawn to get the temperature coefficients (Table 1). The line of the N-bonded ^{37}Cl is hidden under the upper line of Cl_a.

Table 2. Approximate theoretical vibrational influences.

	77 °K	113	147
Cl_1	$0.046 \cdot 10^{-4}$	0.120	0.167
Cl_2	−0.004	0.020	0.039
Cl_3	0.008	0.047	0.034

Table 3. Coefficients α.

	1. α_x 2. α_x^2	1. α_y 2. α_y^2	1. α_z 2. α_z^2
Cl_1	0.321	0.947	1
	0.103	0.897	1
Cl_2	0.981	0.196	1
	0.962	0.038	1
Cl_3	0.481	0.877	1
	0.231	0.769	1

of Burke and Mitchell [7] taking appropriately constructed internal coordinates as approximate normal coordinates. These contributions, however, proved negligible in comparison with the uncertainties of the temperature coefficients. Tables 1, 2 and 3 list the values used in the following interpretation.

Line Assignment

From these values and the rearranged Eq. (7) the curves of Fig. 4 were drawn, assigning the line at 49 MHz with temperature coefficient C to the nitrogen-bonded chlorine because of its chemical shift. The possible two assignments for the remaining two carbon-bonded chlorine atoms, each assignment further multiplied by two because of the two different lattice positions were the starting points for the computation of the eight curves representing one side of the rearranged Eq. (7) equal by theory to C.

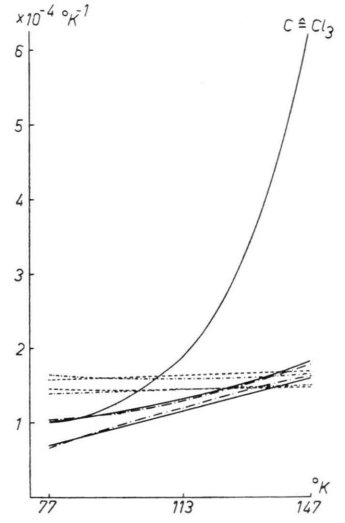

Fig. 4. Possibilities of line assignment. — — — $Cl_a = Cl_2$, upper lines of Cl_a and Cl_b in Fig. 3 belonging to the same lattice position. ····· $Cl_a = Cl_2$, upper line of Cl_a and lower line of Cl_b belonging to the same lattice position. ——— $Cl_b = Cl_2$, upper lines of Cl_a and Cl_b belonging to the same lattice position. — · — · — $Cl_b = Cl_2$, upper lines of Cl_a and Cl_b belonging to different lattice positions.

As can be seen, only the assignment, by which the line near 37 MHz (Cl_b) is identified with the chlorine atom in cis-position to the N-bonded chlorine (Cl_2), represents equation (7) at 77 °K within experimental and theoretical errors. In the worst case (extreme error limits) the C curve does not reach the curves of the alternative assignment. Comparing the trends of all curves, one is forced to assume a still better equality between C and the curves of the above assignment below 77 °K. This assignment seems to be the correct one by comparison with the NQR results for the molecule $Cl_3C-C(Cl)=N-Cl$ [5], whose C-bonded chlorine gives rise to two lines at 36.92 and 37.19 MHz. For

steric reasons the Cl_3C-group will be in trans-position to the N-bonded chlorine atom. So the C-bonded chlorine of the structural element $\overset{R}{C}C=N_{Cl}$ causes a resonance line at approximately 37 MHz. There seems to be still a further proof of this assignment, independent of the value for C, given in the section on the method of isotopes.

The very great deviation of C from the correct curves at higher temperatures must be caused by a special effect because of the principal correctness of our theory. We believe it to be a sign of an enhanced mobility of the N-bonded chlorine atom, although a complete inversion does not take place even near the melting point. From Fig. 3 it can be seen, that the lines of the C-bonded chlorine atoms remain separated, but there is a tendency to converge if one compares the curvatures. The enhanced mobility of the N-bonded chlorine at higher temperatures results also from computations of the method of isotopes.

Method of Isotopes

For the sophisticated problem of computing the values of the principal moments and the directions of the principal axes of inertia for the method of isotopes the use of the natural isotopic composition of the chlorine atoms for the determination of the principal axes' directions and the average of the isotopic configurations of Fig. 5 for the computation of the moments of inertia seems the most logical choice. With these preliminaries one finds points of intersection for the two curves at 77 °K but more and more diverging curves going to higher temperatures which seems to be a further proof for the above described dynamic phenomenon. Regarding the curves for the "false" assignment, here, too, the

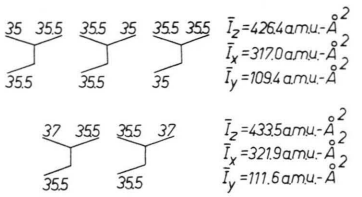

Fig. 5. Isotopic configurations taken into account for the method of isotopes. Average values of the moments of inertia for the ^{35}Cl lines (upper three values) and the ^{37}Cl lines (lower three values) have been computed from the molecules on the left sides.

method of isotopes seems to corroborate the results deduced by the correlations of the temperature dependences for different lines: There are no points of intersection at all.

The absolute values of the librational frequencies at 77 °K are:

$$\nu_x = 13\ \mathrm{cm}^{-1} \quad \nu_y = 26\ \mathrm{cm}^{-1} \quad \nu_z = 22\ \mathrm{cm}^{-1}. \qquad (9)$$

Assuming the frequencies to be in the reciprocal ratio of the square roots of the moments of inertia about the corresponding axes, with equal potential walls for all axes, the theoretical ratios would be:

$$\nu_x : \nu_y : \nu_z = 5.6 : 9.6 : 4.9. \qquad (10)$$

So the ν_x, ν_y values are in good agreement. The potential wall about the z-axis (vertical to the molecular plane) must be two- or three fold as high as the potential walls of rotation about the axes in the molecular plane.

Acknowledgements

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[1] I. Tatsuzaki and Y. Yokozawa, J. Phys. Soc. Japan **12**, 802 [1957].
[2] T. Tokuhiro, Bull. Chem. Soc. Japan **35**, 1293 [1962].
[3] H. Bayer, Z. Physik **130**, 227 [1951].
[4] H. Hagemann, D. Arlt, and I. Ugi, Angew. Chem. **8**, 606 [1969].
[5] H. G. Fitzky, G-I-T Fachz. Lab. **17**, 10 [1973].
[6] T. Kushida, J. Sci. Hiroshima Univ. **A 19 (2)**, 327 [1955].
[7] J. M. Burke and R. W. Mitchell, Spectroch. Acta **28 A**, 1949 [1972].