BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 333—343 (1966)

An Analysis of the Proton Magnetic Resonance Spectra of Acrylic Acid in Solution: A Comparative Discussion of the Methods of the Analysis of ABC Spin Systems

By Takeo YAMAMOTO and Shizuo FUJIWARA

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received June 14, 1965)

In an attempt to examine various existing methods for the analysis of high-resolution NMR spectra, the statistical theory has been applied to the least-squares iteration method presented by Arata, Shimizu and Fujiwara. The standard errors of chemical shifts and spin-spin coupling constants, and the singularity in the normal equation, have been discussed. Two sets of parameters which are placed close together have a possibility of producing a singularity in the normal equation. A way of eliminating the singularity has been presented. The method thus presented has then been applied to an analysis of the vinyl proton spectra of acrylic acid in carbon tetrachloride and in aqueous solutions of various pH values. It has been found that the spin-spin coupling constants do not change beyond the range of experimental errors under the conditions of the present study. The change in chemical shifts has been discussed in terms of the possible conformations of the molecules.

The theory of the analysis of high-resolution NMR spectra seems to be fairly complete. When a set of chemical shifts and coupling constants (molecular constants) is given, ordinary methods[1] of perturbation or exact diagonalization, as well as the direct method of Banwell and Primas,[2] can be used to calculate the spectrum. When a series of measurements is given in an attempt to estimate the most probable molecular constants, the experimental spectrum must first be assigned to the transitions among the energy levels. This is usually done by the trial-and-error method, supplemented by intensity and frequency sum rules.[3,4] Because of the non-uniqueness of the assignments and because of the inevitable experimental errors, however, the procedure is often difficult, and ^{13}C–H satellite line data[5] and double-quantum line data[6] have been used to confirm

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[1] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York (1959).

[2] C. N. Banwell and H. Primas, *J. Mol. Phys.*, **6**, 225 (1963).

[3] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

[4] J. D. Swalen and C. A. Reilly, ibid., **37**, 21 (1962).

[5] R. T. Hobgood, Jr., R. E. Mayo and J. H. Goldstein, ibid., **39**, 2501 (1963).

[6] W. A. Anderson, R. Freeman and C. A. Reilly, ibid., **39**, 1518 (1963).

the assignment.

For an ABC spin system, however, Castellano and Waugh³⁾ have shown that all the possible assignments (energy diagrams) can be obtained from a precise knowledge of all the 15 absorption line positions (the CW method for assignment). When an assignment is obtained, there are two ways to use the observed data for the calculation of the molecular constants. One is to use the data directly for a least-squares adjustment of the molecular constants; the other is to use the absorption line-position data to obtain a set of energy levels, and subsequently to deduce the molecular constants from the energy levels. The former method (the ASF method) was developed by Arata, Shimizu and Fujiwara⁷⁾. Swalen and Reilly⁴⁾ (the SR method) obtained the molecular constants by adjusting the calculated energy levels to the "observed" constants by least-squares iterations. Castellano and Waugh³⁾ (the CW method for calculating molecular constants) used the "observed" energy levels to find, by explicit algebraic calculations, all the sets of molecular constants that regenerate the energy-level diagram.

The ASF method has the advantage over other methods that a suitable choice of the Jacobian matrix enables us to use not only the line positions and intensities, but also the other physical quantities, as input data.⁸⁾ The more fundamental advantage of the method is that it provides direct and unambiguous relations between the variance in the observed values and that in the calculated results. These points, which were not fully examined in the previous paper,⁷⁾ will be discussed later.⁹⁾ The above-mentioned relations are expressed rather indirectly in the SR method, and no such relation has been given for CW method. There are, however, some limitations in the practice of the ASF method, most of which limitations are shared by all least-squares iteration calculations. It will be shown that one of the most serious limitations, i. e., the problem of finding suitable starting constants for all the possible solutions, can be solved by a reduction in the order of the normal equation and by a complementary use of the CW method. Another limitation, the singularity of the normal equation and its eventual omission, will also be discussed.

The analysis was applied to acrylic acid in carbon tetrachloride and in aqueous alkaline media. The chemical shifts and coupling constants obtained will be discussed in connection with possible states of acrylic acid in the above media. The changes in chemical shifts are internal and do not suffer from the large and ambiguous variations caused by macroscopic susceptibility and by other interactions affecting the entire solute molecule.

Method of Analysis

The Calculation of the Spectra.—A spin Hamiltonian for a ABC-type nuclear spin system can be written as follows:

$$\mathscr{H} = -\nu_A I_{AZ} - \nu_B I_{BZ} - \nu_C I_{CZ} + J_{AB}\overrightarrow{I_A}\cdot\overrightarrow{I_B} + J_{BC}\overrightarrow{I_B}\cdot\overrightarrow{I_C} + J_{CA}\overrightarrow{I_C}\cdot\overrightarrow{I_A} \tag{1}$$

Here notations are used in the usual way. In the present work, the vinyl protons cis, geminal and trans to the carboxylic group in an acrylic acid molecule were assigned to A, B and C respectively. When the ν_A, ν_B, ν_C, J_{AB}, J_{BC}, and J_{CA} molecular constants (hereafter called collectively $\{q_i\}$ or $\{q\}$) are known, one can calculate the positions of the absorption lines $\{\omega_j\}$ and the corresponding relative intensities $\{I_j\}$. On the basis of the zeroth order eigenfunctions $\{\varphi_m{}^0\}$ $(m=1,\ldots, 8)$ for a three spin $(I=\frac{1}{2})$ system, the Hamiltonian (1) is represented in a matrix form:

$$(\mathscr{H}_{mn}) = \begin{pmatrix} A & & & & & & & \\ & B & R & Q & & & & \\ & R & C & P & & & 0 & \\ & Q & P & D & & & & \\ & & & & E & R & Q & \\ & 0 & & & R & F & P & \\ & & & & Q & P & G & \\ & & & & & & & H \end{pmatrix} \tag{2}$$

Matrix 2 can be diagonalized by some orthogonal matrices, T, without violating the ordering among the partial matrices in 2:

$$\tilde{T}(\mathscr{H}_{mn})T = \begin{pmatrix} E_1 & & & & & & & \\ & E_2 & & & & & & \\ & & E_3 & & 0 & & & \\ & & & E_4 & & & & \\ & & & & E_5 & & & \\ & & 0 & & & E_6 & & \\ & & & & & & E_7 & \\ & & & & & & & E_8 \end{pmatrix} \tag{3}$$

Since the matrix consists of two 1×1 and two 3×3 matrices, there are $(1!)^2\cdot(3!)^2=36$ T transformations of 2 into Form 4. The eigenfunctions, $\{\varphi_m\}$ $(m=1,\ldots, 8)$, are calculated as:

$$T\begin{pmatrix} \varphi_1{}^\circ \\ \vdots \\ \varphi_8{}^\circ \end{pmatrix} = \begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_8 \end{pmatrix}$$

The positions of the absorption lines $\{\omega_j\}$ and the relative intensities $\{I_j\}$ are obtained as:

$$\omega_j = \omega_{m\leftarrow n} = E_m - E_n$$

$$I_j = I_{m\leftarrow n} = a|\langle\varphi_m|I_x|\varphi_n\rangle|^2$$

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7) Y. Arata, H. Shimizu and S. Fujiwara, ibid., **36**, 1951 (1962).

8) J. Aldous and I. M. Mills, *Spectrochimica Acta*, **18**, 1073 (1962).

9) Recently, Castellano and Bothner-By¹⁰⁾ published their method of analysis based on the Hoffman's method.¹¹⁾ They expressed same interest with us on the general features of the problem of analysis. Our results shown in this paper will present more concrete an example of the problem.

10) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3865 (1963).

11) R. A. Hoffman, ibid., **33**, 1256 (1960).

The normalization coefficient, a, is taken to be $\sum_j I_j = 100$ in the present work.

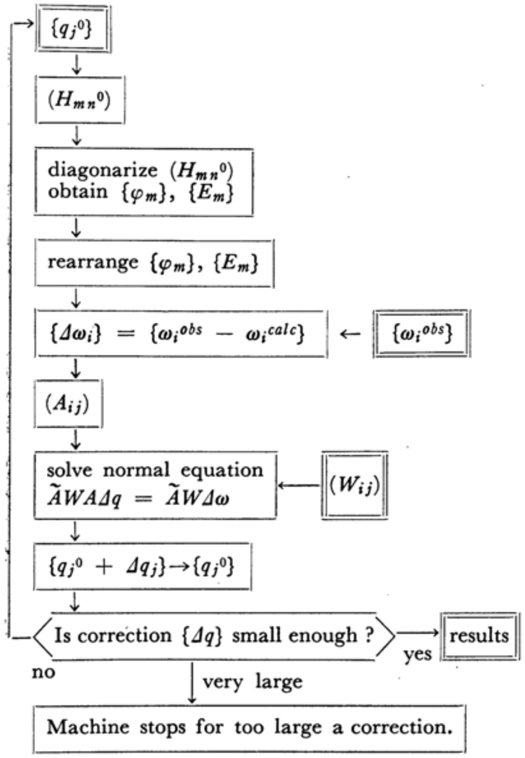

Fig. 1. Flow chart for the ASF method.

Double frames stand for the input and the output data.

The ASF Method.—The flow-chart for the ASF method is reproduced in Fig. 1, where W is the weight matrix for the observed quantities and A is the Jacobian matrix, which contains the differential of the observed quantities with respect to the parameters to be determined. The figure refers to a special case where the weighted squares of the residuals of line positions at a certain resonance frequency are minimized. The method is, however, applicable to any physical quantities expressed as functions of q_i, such as the intensities and the resonant positions at several radiofrequencies.

The estimated variance of the most probable q_i value (the solution of the analysis), $\sigma^2[q_i]$, may be expressed by the variance of an observation of unit weight, σ^2, and by the ii-component of the inverse matrix of the coefficient matrix $\tilde{A}WA$, of the normal equation, $(\tilde{A}WA)^{-1}{}_{ii}$:

$$\sigma^2[q_i] = (\tilde{A}WA)^{-1}{}_{ii}\cdot\sigma^2 \tag{4}$$

The correlation factor between two most probable values of the parameters, q_i and q_j, is given by:

$$\rho[q_i, q_j] = (\tilde{A}WA)^{-1}{}_{ij}\cdot\frac{\sigma^2}{\sigma[q_i]\cdot\sigma[q_j]}$$

$$= \frac{(\tilde{A}WA)^{-1}{}_{ij}}{\{(\tilde{A}WA)^{-1}{}_{ii}\cdot(\tilde{A}WA)^{-1}{}_{jj}\}^{1/2}} \tag{5}$$

The σ^2 quantity in Eq. 4 can be evaluated in two ways.¹²⁾ One way consists of estimating it from the differences (residual vector) between the "observed" and the "calculated" values:

$$\sigma_1^2 = \frac{\Delta\tilde{\omega}W\Delta\omega}{N-M} \tag{6}$$

where N is the number of observed quantities (here, the number of absorption lines) and M is the dimension of the normal equation. It must be noted that the "observed" value is obtained by averaging several measurements. The "calculated" value is obtained from the converged parameters $\{q_i\}$.

The other way consists of estimating σ^2 from the variance of the values in individual observations around their mean values, that is, the "observed values" for the analysis:

$$\sigma_2^2 = \frac{\sum_{j=1}^{n}(x_j - x)^2}{n(n-1)} \tag{7}$$

where x is the average line position of unit weight; x_j is the jth observed value for that position, and n is the number of runs in the observation. The σ_2^2's thus obtained are different for all the lines; their average can be used to estimate σ^2. In each analysis, σ_1 and σ_2 must be normally of the same order of magnitude. When $\sigma_1 \gg \sigma_2$ or $\sigma_1 \ll \sigma_2$, the σ in Eq. 4 must be estimated from the larger value, σ_1 or σ_2.

When the analysis is confined to the line positions obtained at a single frequency, the Jacobian matrix (A_{ij}) can be calculated⁷⁾:

$$\begin{aligned}\tilde{A}_{ij} = A_{ji} &= \left(\frac{\partial E_m}{\partial q_i}\right)_{q^0} - \left(\frac{\partial E_n}{\partial q_i}\right)_{q^0} \\ &\simeq 1/\Delta q_i\{\langle\varphi_m|\mathscr{H}(q_i^0 + \Delta q_i)|\varphi_m\rangle \\ &\quad - \langle\varphi_m|\mathscr{H}(q_i^0)|\varphi_m\rangle - \langle\varphi_n|\mathscr{H}(q_i^0 \\ &\quad + \Delta q_i)|\varphi_n^0\rangle + \langle\varphi_n^0|\mathscr{H}(q_i^0)|\varphi_n\rangle\}\end{aligned} \tag{8}$$

where q_i^0 is the assumed value of the parameter, q_i, and, where Δq_i is the coreection for it.

A Discussion of the ASF Method

The Order in Energy Levels.—In the present work, the Hamiltonian matrix 2 was diagonalized into Form 3 by the Jacobi method. In this method, the choice of the transformation, T, from the 36 possible transformations cannot be controlled, and sometimes a sudden jump in the ordering of the calculated spectrum is observed. The iteration is impossible, in such a case.

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12) Y. Murata and Y. Morino, This Bulletin, **38**, 104 (1965).

In order to avoid this inconvenience, the transformation, T, which gives a definite inequality in energy levels (i. e., $E_2 \geqq E_3 \geqq E_4$ and $E_5 \geqq E_6 \geqq E_7$) was chosen for the subsequent analysis.

This, however, introduces another difficulty, one which will be discussed in the next section.

The Validity of Approximation for the Jacobian Matrix.—Two conditions are required for the first-order approximation (8) for the Jacobian matrix: (1) the non-degeneracy of energy levels (E_2, E_3, E_4) and (E_5, E_6, E_7) and (2) the closeness of the starting constants, $\{q^0\}$, to the final value, $\{q\}$.

Condition 1 is not always warranted; i. e., there can be "cross-over" among the energy levels, in each 3×3 partial matrix in Eq. 3, as the parameters, $\{q\}$, are varied. In the case of cross-over, second-order or higher-order perturbation methods might be applied. However, another difficulty would occur in that case. Figure 2-1 and 2-2 illustrate this kind of situation. In Fig. 2-1, the values of a parameter q_i are plotted against the remaining parameters, $\{q'\}$. A point on the plane represents a point in the multidimensional space, $\{q\}$, that is, a set of values of the parameters. When a set of observed line positions, $\{\omega_j^{obs}\}$, and the weight matrix, W, are given, the weighted sum of residuals for the data, $\Delta\tilde{\omega}W\Delta\omega$, can be calculated for each $\{q\}$ point. The contour lines in the figure build hypersurfaces, on which the values of $\Delta\tilde{\omega}W\Delta\omega$ are invariant. Figure 2-2 shows a sectional diagram of Fig. 2-1 cut along the straight line X–Y. Point O gives a minimum in $\Delta\tilde{\omega}W\Delta\omega$. On the PQR curve (hypersurface), a cross-over occurs in the energy levels. When the $\{q\}$ parameters are varied on XY from O to Q, the displacement in the calculated line positions makes $\Delta\tilde{\omega}W\Delta\omega$ increase. The differential function is discontinuous at Q. Then, $\Delta\tilde{\omega}W\Delta\omega$ decreases as $\{q\}$ values are varied from Q to Y. This phenomenon has nothing to do with the fact that the estimation of the Jacobian matrix was not carried on above the first-order of approximation. At any rate, the least-square calculation cannot converge into the true minimum, O, when the starting set of constants, $\{q^0\}$, is on the right-hand side of the PQR curve in Fig. 2-1. This means that, when the true solution is near the "cross-over region," a spectrum is hard to analyze unless the starting constants are known with a sufficiently good approximation, as is stated in Condition 2.

When the set of starting constants, $\{q^0\}$, is not beyond the cross-over, the violence of Condition 2 may lead to three faults: a halt of the iteration, a falling into a trap on a hillside, and a jumping over the cross-over line. When Condition 2 is violated, the value of the correction, $\{\Delta q\}$, obtained from $\{q^0\}$ may be such that the Jacobian matrix for the next cycle of iteration (A_{ij}^1) is significantly different from the original one (A_{ij}^0). Then (A_{ij}^2) may also differ significantly from (A_{ij}^1), in which case an oscillation or circulation of the iteration sets in. This is shown in Fig. 2-3, where the coordinates and the contour lines have the same meaning as in Fig. 2-1. The iteration procedure gives the P, Q, R, S and T points in turn. If there is a trap on the way, the iteration may converge into the trap. This is shown in Fig. 2-4. Starting from P, a false set of constants R is obtained. Near the "cross-over" line, the large correction, $\{\Delta q\}$, may cause the next set of constant, $\{q\}$, to jump over the line. This is the third case.

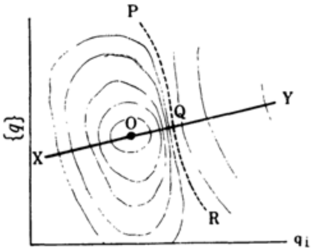

Fig. 2-1. Schematic behavior of $\Delta\tilde{\omega}W\Delta\omega$, the weighted square sum of residuals, as function of $\{q\}$. PQR represents a ridge way where energy levels cross over each other.

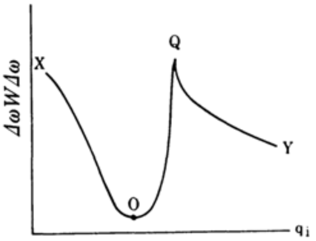

Fig. 2-2. A sectional diagram of Fig. 2-1 cut along the line X–Y.

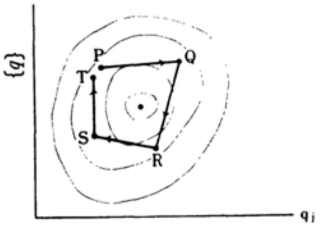

Fig. 2-3. Schematic representation of a halted least-squares iteration.

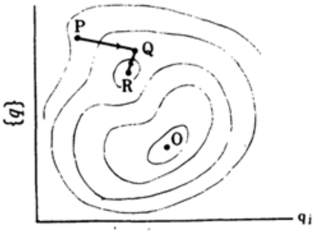

Fig. 2-4. Schematic representation of a case where the iteration settles in a trap.

The Singularity of the Normal Equation.—In the present work, 10 to 14 data of line positions were used to obtain 6 parameters in the least-squares analysis. The symmetry of the molecule is sufficiently low for there to be no identity among the molecular constants. It might be supposed that there would be little possibility for the normal equation to be singular. It was, however, found that the normal equation could sometimes be almost singular.

Table I shows a set of observed line positions and five weight matrices. Table II lists the results obtained for the five weight matrices by the standard ASF least-squares method. These tables show that small changes in input data sometimes result in considerable variations in the converged constants. In Cases I and II, the same line positions and only one change of weight, from 1 to 0, resulted in a difference of 0.3 c.p.s., or of 15%, in the J_{AC} value. When the starting constants or the line positions were varied by small amounts, the least-squares iterations sometimes showed a slow convergence, and in some cases oscillation resulted.

In the above cases, the inverse matrix of the coefficient matrix of the left-hand side of the normal equation $(\tilde{A}WA)^{-1}$ had abnormally large elements. Table III shows the matrix $(\tilde{A}WA)^{-1}$ for the converged value of Case II in Table II. Accordingly, the estimated normal deviations for the resultant values of parameters, $\sigma[q_i]$, were large. This may be seen, for example, in the values in Table III, Column 1, obtained for the 1 data in Table I. In this case, the accuracy for the observed values and that for the result, $\{q\}$, are not, as has often been assumed, of the same order of magnitude.

TABLE I. ABSORPTION LINE POSITION DATA FOR PURE ACRYLIC ACID

The same set of line position data ω_j was used with five sets of weight matrices W_{jj}. Line positions ω_j were obtained by averaging 30 charts, measured at 60 Mc., at room temperature, from an arbitrary zero-point, by c.p.s. Intensities I_j and standard deviations σ_2 were used in the subsequent analysis.

Line No.	ω_j	W_{jj}					σ_2	I_j
		I	II	III	IV	V		
1	36.104	1	0	0	1	1	0.22	0.2
2	31.155	1	1	1	1	1	0.06	2.4
3	26.122	1	1	1	1	1	0.06	3.0
4	16.525	1	1	1	1	1	0.04	8.3
5	11.527	1	1	1	1	1	0.05	14.8
6	8.685	1	1	1	1	1	0.04	9.0
7	6.914	1	1	1	1	1	0.05	5.5
8	−0.897	1	1	1	1	1	0.07	17.6
9	−6.014	1	1	0	1	1	0.07	0.5
10	−10.648	1	1	1	1	1	0.04	13.7
11	−15.604	1	1	1	1	0	0.05	20.4
12		1	1	1	0	0		
13	−20.232	1	1	1	1	1	0.06	4.3
14	−25.250	1	1	1	1	1	0.10	0.5
15	—	0	0	0	0	0	—	0.0

The correlation matrix for the six parameters, $(R_{ij}) = (\rho[q_i, q_j])$, was calculated, as is shown in Table IV, from the inverse matrix in Table III. It has large off-diagonal elements near unity, indicating strong correlations among the parameters.

The above-mentioned features indicate that the normal equation is nearly singular in these cases. The iteration calculations were, therefore, carried out with one parameter fixed. First, the J_{AB}

TABLE II. MOLECULAR CONSTANTS OBTAINED FROM A SET OF LINE POSITION DATA WITH VARIOUS WEIGHT MATRICES

Molecular constants q_i and residuals for line positions (in c.p.s.) were calculated for the five weight matrices I—V in Table I.

Weight matrix data No.	I	II	III	IV	V
q_i					
ν_{AC}	33.456	33.527	33.528	33.371	33.245
ν_{BC}	12.276	12.310	12.308	12.229	12.151
J_{AB}	17.052	16.851	16.841	17.140	17.322
J_{BC}	10.439	10.350	10.359	10.463	10.503
J_{CA}	1.767	2.058	2.059	1.613	1.385
Line No.	Residuals for line positions, $\Delta\omega$				
1	0.18	—	—	0.17	0.15
2	−0.07	−0.02	−0.01	−0.06	−0.07
3	−0.10	−0.05	−0.04	−0.09	−0.07
4	−0.04	0.01	0.01	−0.05	−0.07
5	−0.03	0.02	0.01	−0.05	−0.03
6	−0.02	0.02	0.01	−0.01	0.01
7	0.06	0.03	0.04	0.07	0.09
8	0.00	0.04	0.04	−0.01	−0.02
9	−0.06	−0.02	—	−0.07	−0.05
10	0.01	−0.02	−0.03	0.02	0.04
11	−0.05	−0.01	−0.02	−0.08	—
12	0.06	0.02	0.02	—	—
13	0.03	−0.01	−0.00	0.02	0.01
14	0.01	−0.02	−0.02	0.00	0.02
15	—	—	—	—	—

TABLE III. INVERSE MATRIX FOR THE COEFFICIENTS OF THE NORMAL EQUATION, $(\tilde{A}WA)^{-1}$, FOR A "NEARLY SINGULAR" CASE

Values of molecular constants for this cycle of the iteration are; $\nu_A = 21.217728$ c.p.s., $\nu_B = 0$ c.p.s., $\nu_C = -12.310128$ c.p.s., $J_{AB} = 16.851388$ c.p.s., $J_{BC} = 10.350362$ c.p.s., $J_{CA} = 2.058250$ c.p.s., representing the converged set of molecular constants for weight matrix No. II, Table I. The matrix is symmetric.

j	i					
	ν_A	ν_B	ν_C	J_{BC}	J_{CA}	J_{AB}
ν_A	4.22					
ν_B	1.16	0.84				
ν_C	−5.39	−1.80	7.77			
J_{BC}	−3.52	−1.28	4.84	3.59		
J_{CA}	15.23	4.78	−20.91	−13.36	59.50	
J_{AB}	−11.65	−3.50	15.80	10.16	−44.27	33.78

TABLE IV. A CORRELATION MATRIX (R_{ij}) AMONG THE SIX PARAMETERS FOR A "NEARLY SINGULAR" CASE

Molecular constants used are the same as in Table III. The matrix is symmetric.

j	i					
	ν_A	ν_B	ν_C	J_{BC}	J_{CA}	J_{AB}
ν_A	1					
ν_B	0.61	1				
ν_C	0.94	0.71	1			
J_{BC}	0.90	0.74	0.92	1		
J_{CA}	0.96	0.68	0.97	0.91	1	
J_{AB}	0.98	0.66	0.98	0.92	0.99	1

parameter was fixed. Then, the remaining five parameters, $\{q'\}$, were no more correlated. As may be seen from Table V and Table VI, the inverse matrix has no diagonal element much larger than unity, and the off-diagonal elements in the correlation matrix are much smaller than unity.

The result obtained when J_{AB} is fixed at J_0, $\{q'; J_0\}$, is a point on the $J_{AB}=J_0$ hypersurface, where the square sum of weighted residuals, $\Delta\tilde{\omega}W\Delta\omega$, reaches a minimum. When J_0 is varied by small increments and $\{q'; J_0\}$ is obtained for each J_0 value, the sum, $\Delta\tilde{\omega}W\Delta\omega$, is a function of J_0 and can be minimized at $J_0=J_0^{min}$. Then, the point $\{q'; J_0^{min}\}$ gives a minimum point of the sum in the $\{q\}$ space. Although this procedure gives the same result as that obtained by directly solving the original 6×6 normal equation, it enables us to start from more crude trial constants, $\{q^0\}$. Sometimes, as in the analysis of the pH-5.03 aqueous solution of acrylic acid in Table X, the 6×6 method failed to converge from all the starting constants tried; the 5×5 method was the only means to obtain a solution.

TABLE V. A 5×5 INVERSE MATRIX $(\tilde{A}WA)^{-1}{}_{ij}$ OBTAINED BY FIXING J_{AB}

Molecular constants are the same as in Table III.

j	i				
	ν_A	ν_B	ν_C	J_{BC}	J_{CA}
ν_A	0.20				
ν_B	−0.04	0.48			
ν_C	0.05	−0.17	0.38		
J_{BC}	−0.02	−0.25	0.10	0.55	
J_{CA}	−0.05	0.22	−0.22	−0.08	1.54

TABLE VI. A CORRELATION MATRIX (R_{ij}) AMONG THE REMAINING FIVE PARAMETERS WHEN A PARAMETER J_{AB} IS FIXED

Molecular constants used are the same as in Table III.

j	i				
	ν_A	ν_B	ν_C	J_{BC}	J_{CA}
ν_A	1				
ν_B	0.13	1			
ν_C	0.21	0.39	1		
J_{BC}	0.05	0.49	0.22	1	
J_{CA}	0.08	0.26	0.28	0.09	1

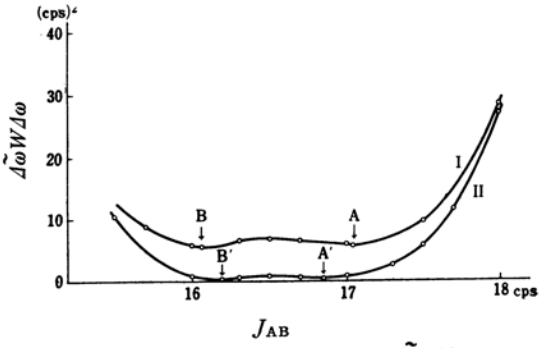

Fig. 3-1. Sectional diagrams of the $\Delta\tilde{\omega}W\Delta\omega$ surface, as obtained by fixing J_{AB}. Curves I and II correspond to data I and II of Table II. Singularity is produced when the saddle point between A and B is low.

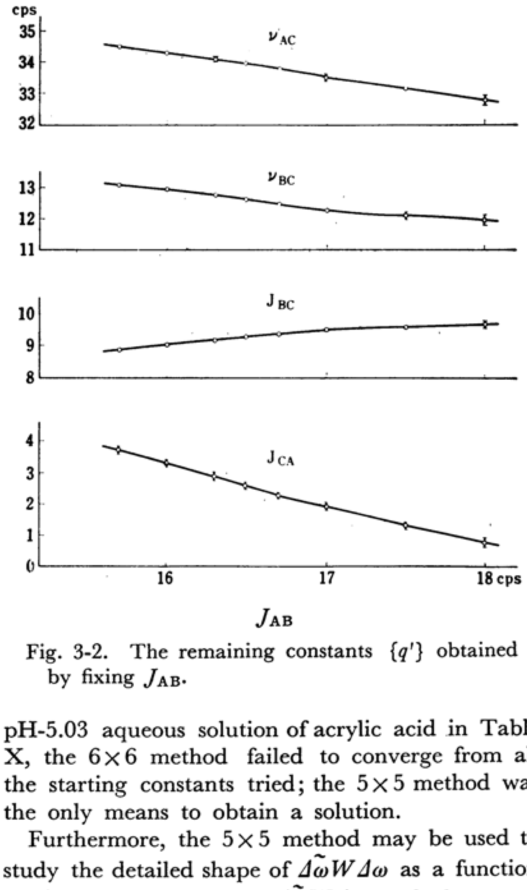

Fig. 3-2. The remaining constants $\{q'\}$ obtained by fixing J_{AB}.

Furthermore, the 5×5 method may be used to study the detailed shape of $\Delta\tilde{\omega}W\Delta\omega$ as a function of $\{q\}$. The values of $\Delta\tilde{\omega}W\Delta\omega$ and the corresponding $\{q'; J_0\}$ are plotted against J_0 in Figs. 3-1 and 3-2. The two curves in Fig. 3-1 are sectional sideviews similar to the curve in Fig. 2-2. The straight line, X–Y, in Fig. 2-2 is now replaced by a curve tracing the bottom of the valley. The abscissa is J_{AB}. Curves I and II correspond to data I and II in Table I respectively.

TABLE VII. CALCULATED SPECTRA CORRESPONDING TO SEVERAL SETS OF MOLECULAR CONSTANTS, $\{q' ; J_0\}$

ν_{AC}		34.506	34.294	33.903	33.499	33.108	32.741
ν_{BC}		13.075	12.918	12.604	12.304	12.076	11.923
$J_0 = J_{AB}$		15.700	16.000	16.500	17.000	17.500	18.000
J_{BC}		9.858	10.010	10.247	10.425	10.531	10.589
J_{CA}		3.647	3.243	2.523	1.836	1.232	0.123
Line positions	1	35.94	35.93	35.92	35.92	35.96	36.01
	2	31.22	31.22	31.21	31.22	31.27	31.36
	3	26.15	26.21	26.25	26.22	26.18	26.13
	4	16.65	16.57	16.54	16.56	16.61	16.68
	5	11.56	11.56	11.57	11.56	11.52	11.45
	6	8.65	8.69	8.72	8.72	8.67	8.64
	7	6.84	6.85	6.87	6.86	6.83	6.80
	8	−0.90	−0.90	−0.91	−0.90	−0.85	−0.75
	9	−5.94	−5.96	−5.96	−5.96	−5.98	−6.04
	10	−10.66	−10.66	−10.66	−10.66	−10.67	−10.67
	11	−15.49	−15.55	−15.59	−15.56	−15.50	−15.44
	12	−15.74	−15.68	−15.62	−15.66	−15.76	−15.92
	13	−20.21	−20.25	−20.29	−20.27	−20.20	−20.09
	14	−25.28	−25.27	−25.26	−25.26	−25.28	−25.32
	15	−42.78	−42.78	−42.78	−42.78	−42.79	−42.81
Intensities	1	0.12	0.16	0.24	0.32	0.40	0.48
	2	2.91	2.84	2.73	2.61	2.49	2.37
	3	3.82	3.73	3.57	3.40	3.22	3.03
	4	9.81	9.57	9.05	8.45	7.85	7.29
	5	14.89	14.84	14.73	14.62	14.55	14.51
	6	7.49	7.62	7.85	8.10	8.38	8.66
	7	1.75	2.16	2.99	3.90	4.79	5.63
	8	18.97	18.96	18.93	18.88	18.82	18.77
	9	0.00	0.00	0.11	0.35	0.65	0.99
	10	14.59	14.53	14.41	14.27	14.12	13.96
	11	8.48	8.73	9.18	9.57	9.85	10.04
	12	11.23	11.17	10.94	10.59	10.16	9.70
	13	4.25	4.21	4.13	4.07	4.05	4.06
	14	1.61	1.41	1.08	0.80	0.59	0.43
	15	0.00	0.00	0.00	0.00	0.00	0.00

In Fig. 3-2, the remaining constants, $\{q'\}$, for the data I are plotted. The short perpendicular bars are the standard deviations estimated from Formulas 4 and 6.

A remarkable feature of the curves in Fig. 3-1 is that each of them has two minima with a low saddle point. The two minima in the curve gave the same line positions and very similar absorption intensities. $\{q'; J_0\}$ points between and near the minima also gave very similar spectra. Table VII shows the calculated spectra for several points, $\{q'; J_0\}$, on Curve I, Fig. 3-1. It may be seen that a large (and correlated) variation in the constants causes little variation in the line positions. For example, the variation in J_{AC} from 3.65 c.p.s. to 0.12 c.p.s. causes line 11 to displace only 0.30 c.p.s, and this is the most prominent of all the line position displacements. The calculated intensities for the two minima for the data are presented in Table VIII. The intensities are not very different.

The above-mentioned results show that, when there are two closely-placed minima in the $\Delta\tilde{\omega}W\Delta\omega$ vs. $\{q\}$ curve, there may be an incomplete singularity in the original least-squares method and a large inaccuracy in the results obtained. Therefore, it is not appropriate to ask whether or not two results of analysis, $\{q^1\}$ and $\{q^2\}$, represent the same solution without considering their normal deviations. A set of data may give $\{q^1\}$, while another set, a little different from the former, or even the same data when processed on another computor, may give $\{q^2\}$, which seems to be substantially different from $\{q^1\}$.

The same situation may be encountered[13] in dealing with the CW method for calculating molecular constants. In the above-mentioned cases of two minima, the solutions from the CW method were also strongly affected by minute changes in the adjusted (observed) line positions and rounding

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[13] J. R. Cavanaugh, *J. Chem. Phys.*, **40**, 248 (1964).

TABLE VIII. ALL THE POSSIBLE SETS OF MOLECULAR CONSTANTS FOR THE LINE POSITION DATA OF PURE ACRYLIC ACID AT 60 Mc.

The four sets were obtained by analyzing the data set I, Table I. All the four sets of molecular constants give the same calculated line positions. Sets I and II are presented with the estimated normal deviations of the constants.

	Set			
q_i	I	II	III	IV
ν_{AC}	33.46±0.26	34.24±0.20	29.63	27.91
ν_{BC}	12.28±0.20	12.87±0.18	9.09	7.45
J_{AB}	17.05±0.39	16.07±0.34	18.11	21.51
J_{BC}	10.44±0.11	10.05±0.20	7.75	8.55
J_{CA}	1.77±0.50	3.14±0.52	12.82	8.62

Line No.	Line positions		Intensities				
	Calcd.	Obs.	Calcd. I	II	III	IV	Obs.
1	35.93	36.10	0.33	0.17	0.05	0.79	0.2
2	31.22	31.16	2.60	2.82	2.23	1.91	2.4
3	26.22	26.12	3.38	3.71	2.77	1.75	3.0
4	16.56	16.53	8.39	9.51	9.06	4.97	8.3
5	11.56	11.53	14.61	14.83	19.10	18.68	14.8
6	8.70	8.69	8.13	7.65	3.78	4.68	9.0
7	6.86	6.91	4.00	2.27	0.15	5.24	5.5
8	−0.90	−0.90	18.87	18.96	24.48	24.18	17.6
9	−5.96	−6.01	0.37	0.01	1.49	2.61	0.5
10	−10.66	−10.65	14.26	14.52	18.98	18.39	13.7
11	−15.56	−15.60	9.60	8.80	3.60	6.26	20.4
12	−15.66		10.55	11.14	9.00	7.60	
13	−20.26	−20.23	4.07	4.19	2.88	2.80	4.3
14	−25.26	−25.25	0.77	1.36	2.29	0.04	0.5
15	−42.78	—	0.00	0.00	0.06	0.02	0.0

errors in the calculations.

In conclusion, two closely-placed minima cause a poor convergence in the calculation and large estimated normal deviations in the result. The convergence may be improved by the reduction of the parameter, but the only way to eliminate uncertainty in the result is to introduce independent information, such as a change in the medium, data at another radiofrequency, or the parameters of related compounds.

The Starting Constants.—In an analysis of an unknown ABC spin system with the ASF method, the first one or two sets of solutions are usually easy to obtain. A few trial-and-error assumptions of starting constants based on a first-order analysis, chemical or structural considerations or explicit analysis can give the desired result. When the iteration does not converge, it may be improved by reducing a parameter.14)

However, it is sometimes difficult to obtain all the possible solutions by the trial-and-error method.15) The CW method for calculating molecular constants is suitable for this purpose. The calculated spectrum of the first solution can be used for the "adjusted absorption frequencies data." When the biquadratic equation described in Ref. 3 yields complex solutions with small imaginary components, the real part may be used to obtain an approximate set of molecular constants. The refinement by the ASF method then removes the uncertainty about the line-adjustment13) and the reliability of the result.

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14) In order to reduce the parameters, the choice of the new set of parameters is important. In principle, it may be selected by solving a secular equation for the $\{q\} \sim \widetilde{\Delta\omega} W \Delta\omega$ solid. A set of linear combinations of the original parameters is obtained. The most efficient way to eliminate the singularity is to fix one of the linear combinations and to take the others for the new set of parameters. In the present work, in order to simplify matters, the new set chosen was similar to the original one except for the fixed parameter. The parameter, J_{AB}, was fixed because the correlation matrix had comparatively large elements in the corresponding column. The choice proved to be effective, as has been discussed in the text. We also tried to fix all the parameters in turn and to make the calculation self-consistent; that is, one parameter was fixed in a cycle and the solution was used for the input data of the next cycle, where another parameter was fixed. This method failed to improve the convergence, however.

15) Swalen and Reilly4) say that there is no problem of uniqueness about their iteration method. However, energy levels are not uniquely determined from a set of observed line positions. Even when the levels are determined from double quantum lines or by other techniques, other sets of solutions are still possible. Their "transformation vector," which diagonalizes the approximate Hamiltonian, is not a constant vector when the correction, $\{\Delta q\}$, is large. It follows that if they start from different sets of approximate constants, different solutions will be obtained. The situation is the same between the SR method and the ASF method as far as the uniqueness is concerned.

TABLE IX. TWO SETS OF MOLECULAR CONSTANTS FOR THE LINE POSITION DATA OF 11% BY WEIGHT ACRYLIC ACID IN CCl_4

q_i	Set I	Set II
ν_{AC}	34.08±0.15	35.61±0.11
ν_{BC}	10.88±0.13	12.19±0.11
J_{AB}	17.36±0.22	15.29±0.20
J_{BC}	10.42±0.06	9.76±0.12
J_{CA}	1.42±0.25	4.14±0.29

Line No.	Line positions Calcd.	Line positions Obs.	Intensities Calcd. I	Intensities Calcd. II	Intensities Obs.
1	36.22	36.17	0.52	0.13	0.5
2	31.93	31.95	2.88	3.28	3.1
3	26.59	26.55	3.45	4.20	3.7
4	17.67	17.71	7.52	9.70	8.0
5	12.34	12.35	14.21	14.60	13.1
6	8.05	—	4.79	1.46	
7	7.91	7.94	7.72	6.80	14.6
8	−1.70	−1.67	18.74	18.90	15.4
9	−6.35	−6.39	0.70	0.03	0.7
10	−10.64	−10.66	14.39	14.91	12.5
11	−15.96	−15.94	10.43	8.92	23.9
12	−15.97		10.50	11.58	
13	−20.25	−20.29	3.80	4.02	4.1
14	−25.58	−25.58	0.35	1.47	0.2
15	−44.26	—	0.00	0.00	0.0

TABLE X. TWO SETS OF MOLECULAR CONSTANTS OBTAINED FOR ALKALINE SOLUTIONS OF ACRYLIC ACID

	q_i	Aq. soln.	pH 3.70	pH 3.96	pH 4.37	pH 5.03	pH 5.40	pH 13
Set I	ν_{AC}	24.86±0.10	24.21±0.10	23.88±0.11	23.09±0.18	22.4±10.5	22.30±0.65	22.01±0.10
	ν_{BC}	10.38±0.10	15.31±0.14	17.10±0.12	21.85±0.20	26.2±13.3	27.37±0.83	28.60±0.12
	J_{AB}	17.29±0.10	17.42±0.10	17.29±0.07	17.36±0.06	17.3± 5.0	17.52±0.41	17.52±0.08
	J_{BC}	10.56±0.09	10.60±0.12	10.36±0.08	10.47±0.10	10.6± 6.3	10.54±0.55	10.45±0.10
	J_{CA}	1.27±0.10	1.14±0.16	1.28±0.12	1.42±0.16	1.4±11.2	1.36±0.76	1.54±0.12
Set II	ν_{AC}	27.98	26.94	23.88	23.09	22.84	23.32	23.72
	ν_{BC}	12.37	16.05	17.39	25.98	25.16	24.90	24.20
	J_{AB}	13.41	15.10	15.47	16.33	17.62	18.33	19.05
	J_{BC}	8.39	7.55	6.92	8.63	10.99	11.43	11.90
	J_{CA}	7.32	6.50	6.55	4.27	0.70	−0.34	−1.44

Experimental

The acrylic acid and carbon tetrachloride were purified by distillation from commercial products. The pH measurements were made to a precision of ±0.1 pH units with glass electrodes calibrated with standard buffer solutions. The concentrations were determined by weight.

The NMR measurements were made with a standard 60 Mc. apparatus without NMR control, at room temperature. The sideband frequencies were calibrated by a frequency counter to a precision of ±0.1 c.p.s. The absorption line positions were measured from a line in the spectrum which served as a zero point. One sample was measured for 5—40 sweeps. These charts were then averaged to obtain one set of observed data.

A digital computor, PC-2, was used for the statistical processing of the charts, the CW method for calculating molecular constants, and the ASF least-squares calculations. The ASF method with or without the J_{AB} parameter fixed, and the CW method were used for analyses.

In the ASF method, the weight matrices were taken to be diagonal.[16] Except for the data listed in Table I, the diagonal elements were taken to be 1 or 0, depending on whether or not the corresponding line was observed. The lines which were not observed clearly because of weakness or line overlapping were given weights of 0.5 or 0.

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[16] In the above case, the line-position data from a chart sheet are not mutually-independent measurements, and the weight matrix may have some off-diagonal elements.[12] This point was, however, not studied in the present work. When the diagonal elements were varied, there were no significant changes in the results provided the normal deviation was taken into account.

Results and Discussion

Acrylic Acid in Carbon Tetrachloride.—Four sets of molecular constants, $\{q\}$, were obtained as the results of the analysis of pure acrylic acid. They are shown in Table IX. In view of the intensity data, Sets III and IV are obviously not suitable, whereas Sets I and II almost equally fit to the observed spectrum. Though the intensities of Lines No. 9 and No. 14 seem to be favorable to Set I, the choice is not clear. The estimated standard deviations are large in both cases.

In order to determine which of the two sets is the more suitable, the spectrum of a carbon tetrachloride solution of acrylic acid, 11% by weight, was analyzed. Two sets of molecular constants were obtained near Sets I and II of the pure substance, as is shown in Table IX. One of them, Set I, has very similar coupling constants to those of Set I in the pure substance. Though the observed spectra of the two systems are rather similar, the other sets of molecular constants, the II sets, were considerably different. The saddle-point between the two minima was found to increase in height, and the calculated absorption intensity for the two sets I and II was also appreciably different, in the 11% solution. In this case, therefore, there was little ambiguity in choosing Set I as the better set.

The spectra in 63% and 2% solutions were also analyzed. Again there was a series of sets of constants with small variations in coupling constants and with good agreement in intensities. From those facts we have concluded that the sets corresponding to the Set I in pure substance are the correct sets of the molecular constants of the systems. These results are shown in Fig. 4, together with other results.

Acrylic Acid in Aqueous Alkaline Media.—The variation in $\{q\}$ was studied for a 10%-in-wt. aqueous solution of acrylic acid at various pH values. The pH was adjusted by the addition of sodium hydroxide. In these systems, the fact that we again obtained the Set II of molecular constants caused some difficulty. The variation in these two sets of solutions with the pH of the system is shown in Table X. This table shows that, in Set I, J_{AB} and J_{AC} are not changed by more than ±0.2 c.p.s. by the cange in pH, while in Set II they vary over a wide range. The pH dependence of the shifts is smooth in Set I, while in Set II it is irregular. These facts suggest that Set I is the more suitable solution. Moreover, a comparison of the intensities shows that in the two extreme cases, i. e., in the aqueous solution and in the pH-13 solution, Set I gives the correct intensity while Set II does not. Hence, Set I may be said to represent the true molecular constants over the entire pH range.

In the intermediate range of pH, where the two sets approach and cross each other, the estimated normal deviations of $\{q\}$ became broad and convergence was difficult to obtain, as has been discussed in the previous section. At pH 5.03, the least-squares analysis was made by the 5×5 method because convergence was not reached by the 6×6 method. The corresponding reliability range, shown in Table XIII, is very large. When, however, the calculation is made by assuming the J_{AB} constant to be in the same reliability range as it is at the other pH's, i. e., at 17.4 ± 0.2 c.p.s, the corresponding range of the other parameters becomes much narrower, as is shown by the perpendicular bars in Fig. 4.

Figure 4 also shows that the coupling constants do not vary appreciably with the pH. The following assumptions were made to explain the pH dependence of the chemical shifts:

(a) The only solute species in a 10% aqueous solution and in a pH ~13 alkaline solution are an acid monomer molecule, HA, and a monoanion, A^-, respectively.

(b) In a solution with an intermediate pH

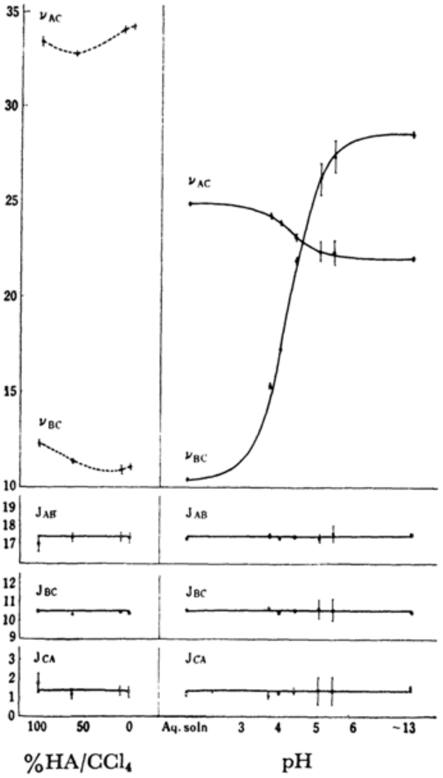

Fig. 4. Variation of the molecular constants. The left half of the figure shows the molecular constants of acrylic acid in CCl_4, and the right one those in 10% aqueous solutions of various pH. Perpendicular bars are the estimated normal deviations (see text). Solid curves for ν_{AC} and ν_{BC} represent theoretical lines for a pK_a of 4.20.

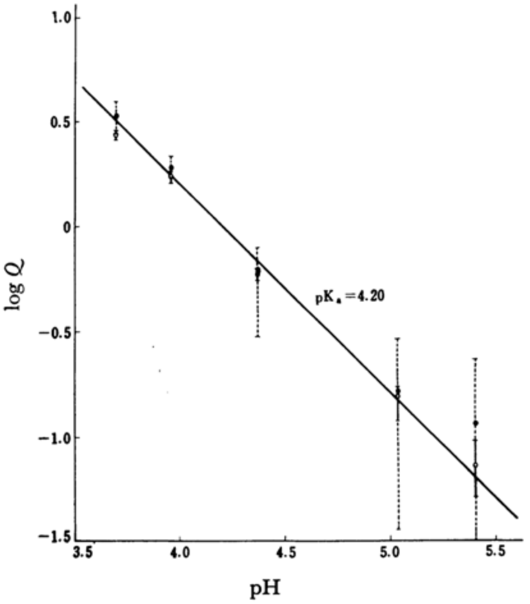

Fig. 5. The relation between log Q and pH. White circles refer to log Q's obtained by ν_{AC} and black circles to those by ν_{BC}. Solid or broken bars attached to each circle represents the variation in each value.

value, HA and A^- exist in a chemical equilibrium:

$$[H^+]\cdot[A^-] = [HA]\cdot 10^{-pK_a} \tag{9}$$

and the exchange between them is sufficiently fast. The activity expressed in Eq. 9 by a square bracket can be approximated by the analytical concentration.

Therefore,

$$pK_a - pH = \log Q$$

where

$$Q = \frac{q_A - q_{HA}}{q - q_{HA}} - 1$$

Figure 5 shows the log Q vs. pH plot for $q=\nu_{AC}$ and for $q=\nu_{BC}$. The perpendicular bars are estimated widths, corresponding to the standard deviations of q, q_{A^-} and q_{HA}. The points agree with the solid straight line with a gradient of −1. From the intercept of the straight line with the line for log $Q=1$, $pK_a=4.20\pm0.10$ was deduced. This value agrees fairly well with the value of 4.25 reported in the literature, which was determined potentiometrically.

The results given above suggest that the molecular constants for a 10% aqueous solution and a pH ∼13 aqueous solution of acrylic acid represent those of a monomer acid molecule and a monoanion respectively. The chemical shifts can be explained in terms of bond-anisotropy. It was assumed that an acid monomer molecule has a *s-cis* structure; that the C=O bond susceptibility tensor is axially symmetric with an anisotropy of $\Delta\chi$ and with the axis perpendicular to the molecular plane, and that the induced dipole is at the center of the bond. The monoanion COO^- group was assumed to have a similar group anisotropy, $\Delta\chi'$, and the induced dipole was assumed to be at the center of gravity of two C–O bonds. The reported values of anisotropy in C=O[17,18] and $CO_3{}^{2-}$ [19] groups leads to $\Delta\chi$ and $\Delta\chi'$ values of -5–-10×10^{-6} e.m.u. If we take $\Delta\chi=\Delta\chi'=-8\times10^{-6}$ e.m.u., $\nu_{AC}=22.6$ c.p.s. and $\nu_{BC}=13.9$ c.p.s. in an acid monomer, and $\nu_{AC}=12.1$ c.p.s. and $\nu_{BC}=22.3$ c.p.s. in a monoanion. These values are in fairly good agreeement, in order of magnitude and in sense of variation, with the observed values. The difference of about 10 c.p.s. in ν_{AC} value between the 10% aqueous solution and carbon tetrachloride solutions seems to reflect the change from the acid monomer structure interacting with the solvent water molecules to the acid dimer or polymer structure interacting with the other solute molecules. A simple explanation in terms of bond-anisotropy was not sufficient for a more quantitative discussion. Solutions in carbon tetrachloride showed only a small change in chemical shifts with the concentration, suggesting that dilution with the nonpolar solvent carbon tetrachloride down to 2 wt.% or 5 mol.% affects the solute-solute interactions little.

According to the concept of electronegativity, a –COOH group must be considerably different from a $-COO^-$ group, and the relationship between coupling constants and electronegativity in vinyl compounds predicts corresponding changes in coupling constants. Such changes were not observed, however. The coupling constants and, particularly, their sums are quite invariable in spite of the great change in molecular states and in chemical shifts.

The authors wish to thank Drs. Yuzuru Fujiwara, Masaharu Toyama and Yoji Arata for valuable discussions. We are also much indebted to Dr. Osamu Yamamoto of the Government Chemical Research Institute, Tokyo, and Dr. Ichiro Yamaguchi of Japan Atomic Energy Research Institute for their aid in NMR measurements.

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19) J. A. Pople, ibid., **38**, 1276 (1963).