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Abstract

Nuclear magnetic resonance of oriented molecules provides a convenient and precise technique for determination of molecular geometry. The precision is often high enough for the effect of the vibrational motions to be felt. In this paper the vibrational corrections are discussed in detail, and a novel formulation is presented which, apart from its simplicity, provides distinct advantages in numerical calculations. Although this formulation has not been published so far, a computer program based on it has been used extensively and with excellent results by the authors and their collaborators for several years.

Keywords: NMR spectra, Oriented molecules, Liquid crystal, Nematic, Vibrational correction, Normal coordinates

Vibrational Corrections in NMR Spectra of Oriented Molecules

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Nuclear magnetic resonance of oriented molecules provides a convenient and precise technique for determination of molecular geometry. The precision is often high enough for the effect of the vibrational motions to be felt. In this paper the vibrational corrections are discussed in detail, and a novel formulation is presented which, apart from its simplicity, provides distinct advantages in numerical calculations. Although this formulation has not been published so far, a computer program based on it has been used extensively and with excellent results by the authors and their collaborators for several years.

INTRODUCTION

Nuclear magnetic resonance spectra of molecules oriented in anisotropic solvents (1) often yield extremely precise data on the molecular geometry of the dissolved species. Since its origins, the method has developed into a standard tool for molecules whose internal motions are limited to harmonic vibrations around an equilibrium structure. We will call such molecules rigid. It was suggested very early in the development of the technique that the *apparent* geometry of rigid molecules, calculated from the NMR spectra of their nematic solutions, should be corrected for the effects due to vibrational motions (2). These effects lead to *internally inconsistent* apparent structures. A typical example is the so-called shrinkage effect (3, 4): in a linear molecule of type ABC, for example, the apparent distance r_{AC} between atoms A and C is always smaller than $r_{AB} + r_{BC}$. Moreover, the vibrational motions are weighted differently in different techniques used for determining the geometrical structure of molecules. This hinders direct comparisons between NMR results and data obtained by X-ray diffraction, infrared and microwave spectroscopy, electron or neutron scattering, etc. The results obtained by different techniques can be

compared among themselves only after they have been *separately* corrected for the vibrational effects.

Ideally, the corrections should provide the equilibrium structure (or r_e structure). This is the hypothetical molecular structure which minimizes the electronic potential within the Born–Oppenheimer approximation. Obviously, the r_e structure is both consistent and independent of the experimental technique used. The corrections are calculated by expanding the relevant observable quantities (such as the direct-coupling constants in NMR) in terms of deviations of the nuclear coordinates from the r_e structure. Within the harmonic approximation, the linear terms average out and the quadratic terms give rise to the so-called harmonic correction, which can be calculated rather easily. This correction may be quite large (5) and often exceeds considerably the experimental errors involved. The molecular geometry calculated from the experimental data corrected for the harmonic effects is referred to as r_α structure (6), where r_α is defined as the distance between the average nuclear positions at thermal equilibrium.

The difference between the r_e structure and the r_α structure is due to the anharmonicity of the vibrational potential and, for directly bonded nuclei, is often larger than the experimental errors (7). The r_α structure, however, is internally consistent and should be comparable with structures obtained by other techniques.

For the sake of completeness, we should also note two other limitations of the r_α structures due to the approximations involved, even though their effects are negligible for all practical purposes. The first approximation consists in neglecting the third- and higher-order terms in the expansion of the observable quantities in terms of deviations from the r_e structure. Second, the averaging over vibrational motions requires a complete solution of the vibrational problem in terms of vibrational frequencies and normal coordinates. This is done by approximating the molecular potential by a quadratic function of the deviations from the r_e structure. Apart from eliminating all the odd (anharmonic) and the higher-order even terms, this approximation is also sensitive to the choice of coordinates (8). In non-Cartesian coordinates even the kinetic energy part of the Hamiltonian must be approximated. Somewhat different results are therefore expected for different coordinate sets employed.

In this paper we present a résumé of the theory of the harmonic vibrational corrections in NMR of molecules dissolved in axially oriented solvents. The problem has never been presented in a comprehensive form. It coinvolves three very distinct disciplines: the vibrational normal-coordinate theory (classical), the vibrational mean-amplitude and covariance theory (quantum), and the NMR theory of strongly coupled high-resolution spectra. The main original contribution of our treatment as compared with preceding treatments (8) consists in the fact that the vibrational calculation is done only once for any particular molecule. Its results are conveniently tabulated in a set of tensors which are then used to calculate the corrections to the observed direct-coupling constants for any set of orientation tensor components. This sort of factorization between the vibrational and NMR aspects of the problem greatly reduces the computer time and allows a better understanding of the observed phenomena.

THEORETICAL

The spin Hamiltonian of a rigid molecule must be averaged both with respect to the molecular tumbling and with respect to the vibrational motions. Given the difference of the frequencies characteristic for these two types of motion, it is reasonable to assume that there is no correlation between them. In this case the two averages can be considered as independent, commutative operations. We will use the symbol $\langle \dots \rangle_m$ for the average over molecular tumbling and $\langle \dots \rangle_v$ for the average over vibrational motions.

Consider an interaction of the type $\mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S}$, where \mathbf{I} and \mathbf{S} are spin operators of two nuclei and \mathbf{T} is a traceless second-rank tensor. Its contribution to the Hamiltonian is

$$H_T = \langle \mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S} \rangle_{m,v} = \langle \langle \mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S} \rangle_m \rangle_v. \quad [1]$$

Expanding $\mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S}$ into its components, considering that the molecular-tumbling averages must respect the symmetry of the surrounding medium which is assumed to be axial, and taking into account the tracelessness of \mathbf{T} , we obtain (9)

$$\langle \mathbf{I} \cdot \mathbf{T} \cdot \mathbf{S} \rangle_m = \frac{1}{2} \langle T_{zz} \rangle_m (3I^z S^z - \mathbf{I} \cdot \mathbf{S}). \quad [2]$$

Hence

$$H_T = D (3I^z S^z - \mathbf{I} \cdot \mathbf{S}), \quad [3]$$

where

$$D = \frac{1}{2} \langle \langle T_{zz} \rangle_m \rangle_v \quad [4]$$

is the direct-coupling constant.

In practice the most important mechanisms contributing to D are the dipolar interaction and the indirect-coupling anisotropy. The dominant term is generally due to the dipolar interaction. To our knowledge, the effect of molecular vibrations on the indirect-coupling anisotropy has never been considered.

The tensor \mathbf{T}^{ij} describing the dipolar interaction between nuclei i and j is given by

$$T^{ij} = -(k_{ij}/r_{ij}^3)(3\mathbf{r}^{ij}\mathbf{r}^{ij}/r_{ij}^2 - 1), \quad [5]$$

where \mathbf{r}^{ij} is the internuclear vector, r_{ij} is its length, and $k_{ij} = \hbar^2 \gamma_i \gamma_j$; γ_i and γ_j are the gyromagnetic ratios and \hbar is the Planck constant.

Denoting by θ_{ij} the angle between \mathbf{r}^{ij} and \mathbf{H}_0 , we get

$$\frac{1}{2} \langle T_{zz}^{ij} \rangle_m = -(k_{ij}/r_{ij}^3) \langle P_2(\cos \theta_{ij}) \rangle_m, \quad [6]$$

where $P_2(x) = (3x^2 - 1)/2$ is the Legendre function.

Let us now choose a system of coordinates X , Y , and Z fixed with respect to the (average) molecular structure. Let Θ_X , Θ_Y , and Θ_Z be the angles between the respective axes of this system and \mathbf{H}_0 . Then the tensor defined as

$$S_{\alpha\beta} = \frac{1}{2} \langle 3 \cos \Theta_\alpha \cos \Theta_\beta - \delta_{\alpha\beta} \rangle_m, \quad [7]$$

where $\alpha, \beta = X, Y, Z$, is called the *orientation tensor*. Also expressing the coordinates of \mathbf{r}^{ij} with respect to the laboratory system and using the theorem on composition of

spherical functions, we may show (9) that

$$\frac{1}{2}\langle T_{zz} \rangle_m = -k_{ij} \text{Tr}(\mathbf{S}\boldsymbol{\varphi}^{ij}), \quad [8]$$

where Tr stands for trace and the tensor $\boldsymbol{\varphi}^{ij}$ is defined by

$$\varphi_{\alpha\beta}^{ij} = r_{\alpha}^{ij} r_{\beta}^{ij} / r_{ij}^5; \quad \alpha, \beta = X, Y, Z. \quad [9]$$

Returning to Eq. [4] we therefore get

$$D_{ij} = -k_{ij} \text{Tr}(\mathbf{S}\boldsymbol{\Phi}^{ij}), \quad [10]$$

where

$$\boldsymbol{\Phi}_{\alpha\beta}^{ij} = \langle r_{\alpha}^{ij} r_{\beta}^{ij} / r_{ij}^5 \rangle_v. \quad [11]$$

In the following we will deal only with quantities pertinent to the same generic pair of nuclei i and j . For the sake of brevity we may therefore temporarily drop the indices i and j . Let us write

$$\mathbf{r} = \mathbf{R} + \boldsymbol{\Delta}, \quad [12]$$

where \mathbf{R} is the equilibrium value of \mathbf{r} and $\boldsymbol{\Delta}$ is the instantaneous excursion of \mathbf{r} from \mathbf{R} . The tensor $\boldsymbol{\Phi}$ can be expanded in powers of the components of $\boldsymbol{\Delta}$. The result of the straightforward but cumbersome calculation is

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}^e + \boldsymbol{\Phi}^a + \boldsymbol{\Phi}^h + \text{third- and higher-order terms}, \quad [13]$$

where

$$\boldsymbol{\Phi}_{\alpha\beta}^e = R_{\alpha} R_{\beta} / R^5 = \zeta_{\alpha} \zeta_{\beta} / R^3, \quad [14]$$

$$\boldsymbol{\Phi}_{\alpha\beta}^a = - \left[\sum_{\gamma} (5\zeta_{\alpha} \zeta_{\beta} \zeta_{\gamma} - \delta_{\alpha\gamma} \zeta_{\beta} - \delta_{\beta\gamma} \zeta_{\alpha}) \langle \Delta_{\gamma} \rangle_v \right] / R^4, \quad [15]$$

$$\boldsymbol{\Phi}_{\alpha\beta}^h = \left[C_{\alpha\beta} - 5 \sum_{\gamma} \zeta_{\gamma} (C_{\alpha\gamma} \zeta_{\beta} + C_{\beta\gamma} \zeta_{\alpha}) + \frac{5}{2} \zeta_{\alpha} \zeta_{\beta} \sum_{\gamma\delta} C_{\gamma\delta} (7\zeta_{\gamma} \zeta_{\delta} - \delta_{\gamma\delta}) \right] / R^5, \quad [16]$$

and $\zeta_{\alpha} = \cos \varphi_{\alpha}$; φ_{α} is the angle between \mathbf{R} and the α axis of the molecular coordinate system. As before, $\alpha, \beta, \gamma, \delta = X, Y, Z$. The quantities $C_{\alpha\beta}$, called covariance matrices, are defined as

$$C_{\alpha\beta} = \langle \Delta_{\alpha} \Delta_{\beta} \rangle_v. \quad [17]$$

With the third- and higher-order terms neglected, Eq. [10] now gives

$$D = D^e + d^a + d^h, \quad [18]$$

where

$$D^e = -k(\mathbf{R} \cdot \mathbf{S} \cdot \mathbf{R}) / R^5 \quad [19]$$

corresponds to the e structure,

$$d^a = -k \text{Tr}(\mathbf{S}\boldsymbol{\Phi}^a) \quad [20]$$

corresponds to the anharmonic term, and

$$d^h = -k \text{Tr}(\mathbf{S}\boldsymbol{\Phi}^h) \quad [21]$$

is the harmonic correction term.

The corrected D values, given by

$$D^\alpha = D - d^h = D^e + d^a, \quad [22]$$

correspond to the r_α structure discussed in the Introduction.

In order to determine d^h for any desired pair of nuclei, it is necessary to know the corresponding tensor Φ^h which, according to Eq. [16], depends only on the geometry and on the vibrational properties of the molecule. Since the geometry is approximately known a priori, Φ^h need be calculated only once; the refinements of the structure deduced from NMR data have no appreciable effect on its numerical values.

In order to evaluate Φ^h one must determine the covariance matrices $C_{\alpha\beta}$. Reintroducing the nuclear indices i and j , one may write Δ^{ij} as

$$\Delta_\alpha^{ij} = \sum_{\nu=1}^{3N} (u_{i\alpha}^{(\nu)} - u_{j\alpha}^{(\nu)}) Z_\nu, \quad \alpha = X, Y, Z, \quad [23]$$

where Z_ν is the amplitude of the normal coordinate of the ν th vibrational state, and $u_{i\alpha}^{(\nu)}$ stands for the mass-weighted Cartesian components of the normal-coordinate vector of the ν th vibrational state;

i.e.,

$$u_{i\alpha}^{(\nu)} = U_{i\alpha}^{(\nu)} / M_i^{1/2}, \quad [24]$$

where M_i is the mass of the i th atom. The components $\{U_{i\alpha}^{(\nu)}\}_{i\alpha}$ represent the ν th eigenvector of the matrix

$$\mathbf{W} = \mathbf{G}^{-1/2} \mathbf{F} \mathbf{G}^{-1/2}, \quad [25]$$

where \mathbf{G} is the diagonal $3N \times 3N$ matrix with elements

$$G_{i\alpha, j\beta} = M_i \delta_{\alpha\beta} \delta_{ij}, \quad [26]$$

and \mathbf{F} is the force-field matrix which approximates the molecular potential energy V through the formula

$$V = \frac{1}{2} \sum_{i\alpha, j\beta} F_{i\alpha, j\beta} \Delta_{i\alpha} \Delta_{j\beta}. \quad [27]$$

The ν th eigenvalue of \mathbf{W} will be denoted as ω_ν^2 , where ω_ν is the ν th vibrational frequency.

Using the well-known formulas (3, pp. 74–78) for the meansquare amplitudes of the normal coordinates, and the orthogonality of the latter, we obtain from Eqs. [17] and [23]

$$C_{\alpha\beta}^{ij} = \sum_{\nu=1}^{3N} (u_{i\alpha}^{(\nu)} - u_{j\alpha}^{(\nu)})(u_{i\beta}^{(\nu)} - u_{j\beta}^{(\nu)}) f(\omega_\nu, T), \quad [28]$$

where the function $f(\omega_\nu, T)$ is defined by

$$f(\omega_\nu, T) = \langle Z_\nu^2 \rangle_\nu = (A/\omega_\nu) \coth(B\omega_\nu/T), \quad [29]$$

where T is absolute temperature, $A = h/8\pi^2c$, and $B = ch/2k$; c and k are the velocity of light and the Boltzmann constant, respectively. When ω_ν is expressed in

inverse centimeters, T in degrees Kelvin, and f in square angstroms · atomic mass unit, then $A = 16.858$ and $B = 0.71942$.

In practice, therefore, the calculation reduces to (i) finding an appropriate field and expressing it in terms of Cartesian displacements in accordance with Eq. [27], (ii) finding the eigenvalues and eigenvectors of matrix \mathbf{W} defined by Eq. [25], (iii) calculating the covariance matrices $C_{\alpha\beta}^{ij}$ for all nuclear pairs of interest using Eq. [28], (iv) determining the tensors $\Phi^{h,ij}$ for each of the nuclear pairs using Eq. [16], and finally (v) evaluating the correction terms d^h from Eq. [21].

The last step involves the \mathbf{S} -tensor values. These are normally estimated together with the molecular geometry on the basis of the experimental D values. Special fitting programs have been developed for this purpose (10). The normal procedure is to start with uncorrected D values in order to obtain approximate geometry (r_d structure) and an approximate \mathbf{S} tensor. The d^h values are then calculated as described and the D values are corrected in accordance with Eq. [22]. These corrected values are used for a new fit of the structure and the \mathbf{S} tensor. The process is repeated until self-consistency is achieved (usually, one iteration is sufficient). As has been pointed out before, the successive refinements of the structure have a negligible effect on the numerical values of the Φ^h tensors so that only step (v) of the above algorithm need be repeated in each cycle. It should be pointed out that R in Eq. [16] is the equilibrium nuclear distance which in actual calculations is approximated by its r_α value because the anharmonic corrections are usually unknown. This introduces an error in the harmonic correction itself which can reach 4% for directly bonded $^{13}\text{C-H}$ pairs.

A package of subroutines called VIBR for the individual steps of the algorithm described above has been written in the FORTRAN language and is available on request. The routines include calculation of atomic coordinates from a versatile structural code, conversion of valence- and central-force constants into Cartesian coordinates, calculation of normal coordinates and vibrational frequencies, evaluation of the covariance matrices for specified pairs of nuclei, evaluation of the corresponding Φ^h tensors, and calculation of the corresponding d^h values. Molecular symmetry is not taken into account in the calculations: the molecules to which the NMR technique can be applied are generally not too large, and encoding their symmetry would be more costly than the straightforward solution of the unfactorized eigenvalue problem. A comment should be also made on the use of Cartesian coordinates in the vibrational part of the calculation. It is generally true that the molecular potential energy is better approximated in valence-bond coordinate systems. On the other hand, use of such nonlinear coordinate sets implies that the kinetic energy matrix must also be approximated and that a further approximation is needed in order to expand the Cartesian displacements in terms of normal coordinates (Eq. [23]). Altogether we feel not only that the use of Cartesian coordinates from the beginning simplifies the formulas, but that it is hardly inferior even in terms of precision.

REMARKS AND SPECIAL CASES

From Eq. [16] it is apparent that d^h decreases with the internuclear distance as R^{-5} . Since D^e decreases with R^{-3} , the relative value of the harmonic correction

correlates with R^{-2} . The biggest relative corrections can therefore be expected for pairs of directly bonded nuclei. Note that the same reasoning leads to the R^{-1} dependence for the *relative* value of the anharmonic term. These tendencies can best be demonstrated by a simple example. Suppose the molecule has an at least three-fold symmetry axis and identify the latter with the Z axis of the molecular coordinate system. Then the \mathbf{S} tensor is diagonal and $S_{XX} = S_{YY} = -\frac{1}{2}S$, $S_{ZZ} = S$. Consider a pair of nuclei coincident with the axis. For symmetry reasons the covariance matrix \mathbf{C} for this pair is also diagonal and $C_{XX} = C_{YY} = C^\perp$ and $C_{ZZ} = C^\parallel$. Equations [16] and [19] then give

$$d^h = -6kS(C^\parallel - C^\perp)/R^5 = 6(C^\parallel - C^\perp)D^e/R^2. \quad [30]$$

Also for symmetry reasons, $\langle \Delta_X \rangle_v = \langle \Delta_Y \rangle_v = 0$, so that Eqs. [15] and [20] give

$$d^a = +3kS\langle \Delta_Z \rangle_v/R^4 = -3\langle \Delta_Z \rangle_v D^e/R. \quad [31]$$

Another general tendency is due to the fact that the mean amplitudes of vibrational motions decrease with the masses of the atoms involved. The corrections for pairs of heavy nuclei will therefore generally be much smaller than the corrections for pairs involving at least one light nucleus such as a proton.

The relative correction may become very large if the corresponding D^e value happens to be small due to an opportune orientation of the nuclear pair under consideration. This can occur quite often. Due to the tracelessness of the \mathbf{S} tensor there is always a conical set of directions (in general the set forms an elliptical cone) such that D^e is zero for any pair of nuclei whose interconnecting vector is parallel to one of these "null" directions. The harmonic correction d^h , however, may be nonzero even for such nuclear pairs. In order to give an example, consider a molecule with two mutually perpendicular planes of symmetry δ_v and δ_h . Identify the Z axis with the intersection of δ_v and δ_h and let the X and Y axes lie in the δ_h and δ_v planes, respectively. Consider a pair of nuclei lying on the Z axis. For symmetry reasons, both the \mathbf{S} and \mathbf{C} tensors must be diagonal. Writing C_α and S_α instead of $C_{\alpha\alpha}$ and $S_{\alpha\alpha}$, respectively, we obtain for Eqs. [16] and [19]

$$\begin{aligned} d^h &= -(k/R^5)[(C_Y - C_X)S_Y + \frac{1}{2}(12C_Z - 7C_X - 5C_Y)S_Z] \\ &= (D^e/R^2)[\frac{1}{2}(12C_Z - 7C_X - 5C_Y) + (C_Y - C_X)(S_Y/S_Z)]. \end{aligned} \quad [32]$$

Since $C_X \neq C_Y$, the relative correction can become very large whenever S_Z is nearly zero. Only if the Y axis coincides with an at least three-fold symmetry axis of the molecule, the relative correction remains nonsingular since then $S_Y = S$ and $S_X = S_Z = -\frac{1}{2}S$ and therefore

$$d^h = \frac{1}{2}(D^e/R^2)(12C_Z - 3C_X - 9C_Y). \quad [33]$$

As an example, in benzene (11) the harmonic correction for the directly bonded $^{13}\text{C-H}$ nuclei is of the order of 8%; for all the nonbonded nuclear pairs it is less than 2%. It turns out that, if the structure determination is based exclusively on proton couplings and the required relative precision is less than 0.5%, the harmonic correction is not really necessary.

A case with two independent S values, illustrating the behavior of the harmonic correction as given by Eq. [32] for a small S_Z value, has been encountered in

m-dichlorobenzene dissolved in Merck Phase IV (unpublished results). The degree of order for the C_2 symmetry axis of this molecule is $S_Z = 0.002$ while the S_Y value is about -0.13 . The vibrational corrections for the two $^{13}\text{C-H}$ pairs coincident with the symmetry axis are about $+25$ Hz, which is about five times the corrected D value!

CONCLUSION

In a certain sense, this paper is a summary of the theory of the harmonic vibrational corrections in NMR spectra of rigid molecules dissolved in nematic solvents. The approximations involved have also been discussed in detail.

The importance of the harmonic corrections in structure determinations has been demonstrated in several papers (5, 11, 12). Since for sets of noncorrected D values it is in general impossible to find an internally consistent structure, the effect of the correction can be demonstrated by the decrease of the rms deviation δ between the experimental D values and the corresponding values obtained by fitting the structure (10). For example, in *o*-diiodobenzene (5) δ drops from 0.376 to 0.101 upon correction. The main change in geometry is a decrease of C-H bond lengths by about 0.04 \AA . This illustrates the general fact that vibrational correction is absolutely essential for directly bonded pairs of nuclei involving one light atom.

As we have already pointed out, further refinement of the vibrational correction procedure is still possible, especially if data become available on the anharmonicity-dominated quantities $\langle \Delta_\alpha \rangle_v$ (see Eq. [15]). The final goal would then be to determine the currently inaccessible equilibrium structure.

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