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Carbon-13 Dipolar Spectroscopy of Small Organic Molecules in Argon Matrices

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Abstract: A study of the $^{13}C-^{13}C$ dipolar interaction in $^{13}C_2H_2$, $^{13}C_2H_4$, and $^{13}CH_3{}^{13}CHO$ in argon matrices has been made. The $^{13}C-^{19}F$ coupling in $^{13}CH_3F$ has also been studied. It is shown that both bond lengths and chemical shift tensor orientations can be derived from the resulting spectra. This method provides an approach for determining bond distances for molecules isolated in noble-gas matrices. Application of a simple correction to account for librational motions allows bond distances to be determined with an accuracy of ±0.02 Å. A derivation of the powder spectrum for two spin $^1/_2$ nuclei including fully anisotropic chemical shift and indirect dipolar coupling is presented for the general case in which the tensors in question do not have the same principal frames. The full orientation of the shift tensor is obtained if the direction of one tensor element can be ascertained through symmetry. Previously the orientation of ^{13}C shift tensors have been obtained only from rotation patterns of single crystals or in powders in which an abundant heteronucleus was coupled to the ^{13}C. The method detailed here has the advantages of (1) being less sensitive to intermolecular contributions to the shielding, (2) not requiring a single crystal, and (3) not requiring that a large number of spectra be acquired.

Matrix isolation has become an increasingly popular technique in the synthesis and characterization of reactive species. In addition to quenching chemical reactions, the low temperatures (ca. 15 K) at which noble-gas matrices are formed freeze out molecular reorientation and allow the measurement of static molecular properties such as dipolar couplings or chemical shift tensors with little or no motional averaging.[1,2] At 15 K even barriers below 1 kcal will prevent molecular reorientation on the NMR time scale, making it possible to study many molecules locked in either their lowest energy or other metastable conformations.[3] If the sample can be quenched before it equilibrates at the cryogenic temperature, enhanced populations of metastable forms can be made to persist almost indefinitely.[4]

Traditionally matrix-trapped species have been investigated with optical spectroscopies, but recently it has been shown that matrix environments, especially argon, are uniquely well suited for NMR studies.[1,2] The Boltzmann distribution of nuclear spins at 15 K results in a magnetization which is a factor of 20 times greater than that at room temperature. When signal averaging techniques are used, time savings of up to 400-fold may be realized. This gain in sensitivity means that a matrix with a typical concentration of 0.5 mol % can be observed in the same time the experiment could be done on a 10 mol % sample at room temperature, all other factors being equal.

Direct structural determination of molecules which do not form single crystals in the condensed state but exist only as amorphous polycrystalline phases such as in these noble-gas matrices is not possible with the usual diffractional techniques. A number of NMR techniques have been developed, however, which deal with such situations. All of them depend upon the dipolar interaction between two nuclei, which is a sensitive measure of the interspin distance r. This dipolar term is directly proportional to $\langle P_2(\cos\theta)/r^3\rangle$, where θ is the angle between H_0 and the dipole–dipole vector. In order to successfully use this interaction in a structure determination, the dipolar couplings between adjacent molecules must be suppressed. Otherwise, the dipolar spectrum is a featureless band from which little if any structural information can be derived. In the liquid-crystal or electric-field techniques,[6] this is accomplished by the relatively rapid translational molecular motion which averages the intermolecular couplings to zero. Preferential orientation of the molecules does however preserve the intramolecular couplings. These experiments require that the molecule of interest be stable in a solution environment and in the past have been plagued with a history of being susceptible to large solvent[7] and temperature effects.[8] Several clever multipulse[9] and two-dimensional[10] dipolar oscillation methods have also been

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developed to suppress intermolecular couplings. While avoiding some of the complications encountered in liquid crystals, considerable computations and often much more sophisticated hardware are required.

Another method which is more easily used with typical NMR equipment and computer software is to simply dilute the molecules in a spinless lattice and thereby use the sensitive $1/r^3$ dependence to suppress the intermolecular interactions. Pake[11] utilized this technique early in the development of NMR and was the first to observe what is now termed a "Pake doublet" for the H_2O molecules dispersed in gypsum. The ^1H powder spectrum reveals a characteristic structure that is solely determined by $\langle 1/r_{H-H}{}^3 \rangle$. Dilution of spin pairs in an argon matrix will also eliminate intermolecular interactions as argon has no magnetic isotopes. Kohl et al.[2] have reported a well-resolved Pake doublet for the hydrogen-bonded dimer of HCl in argon and thus determined the H–H distance for this species. For nuclei other than protons such as ^{13}C the spectra are not determined only by the interspin distance but are modified by the anisotropic chemical shift tensors. Further complications are encountered when second-order effects appear. Techniques are developed in this work which resolve these difficulties and are applicable to measuring the carbon structural parameters in molecules in argon matrices.

Besides geometric information obtained from intramolecular dipolar interactions, one can learn much about the electronic structure of a molecule from the anisotropy of its chemical shift tensors which are primarily governed by the molecular structure. In neat solids the crystalline environment may also be anisotropic in a number of ways, and this will give rise to intermolecular contributions to the shielding that may lead to changes in both the orientation and magnitude of the tensor elements.[12] These effects should be greatly reduced for molecules diluted in the more isotropic argon matrix.

In addition to the shift tensor magnitude, one also would like to measure the orientation of the tensor with respect to the molecular frame. As the molecular orientations in a matrix are random such as found in powders, the usual single-crystal studies[13] using a goniometer are not possible. However, the dipolar tensor and chemical shift tensor have a fixed geometric relationship, and the spectrum depends intimately on the mutual orientation of these two tensorial quantities. As the dipolar tensor is directly related to the molecular frame, the relation of the chemical shift tensor to the molecular frame is also known, at least in part, within an arbitrary rotation about the dipole–dipole axis. This relationship has been verified from splitting patterns produced by dilute pairs of nuclei in single crystals under different orientations.[14] The powder pattern produced by such pairs of nuclei with axially symmetric chemical shift anisotropy is a modified Pake doublet. Theoretical calculations[15,16] of such spectra along with a few experimental results for two dipolar coupled nuclei with axially symmetric shift tensors[17–19] have been reported. These same principles apply for a pair of spins in a matrix-isolated molecule.

In this work the technique is applied for the first time to systems which are not axially symmetric and which do not have one of the shielding axes along the dipolar vector. The presence of symmetry elements such as a reflection plane in the molecule can also aid in establishing the direction of one or more tensor elements. Using both dipolar and symmetry information, one may have sufficient data to determine completely the absolute orientation of the shielding tensor. Therefore, not only can the distance between two magnetic nuclei in a matrix-isolated molecule be determined but information on the spatial electronic structure is also obtained.

The powder spectrum has been derived here for two spin $^1/_2$ nuclei involving direct dipolar and anisotropic indirect dipolar coupling in the presence of chemical shift anisotropy. The calculation is similar to that[16] for an ESR spectrum in which one has both an anisotropic **g** and hyperfine interaction tensors. A number of special cases have been derived previously under certain simplifying assumptions.[15] In this paper, the completely general case is treated. If the difference in resonance frequencies of the two nuclei, $\Delta\omega$, is either 0 or much greater than the dipolar coupling, the equations for the line shapes can be solved exactly even though the tensors of both spins have different orientations with respect to the internuclear vector. When $\Delta\omega$ is comparable to the direct and/or indirect dipolar coupling, second-order mixing terms arise which perturb the spectral response of the coupled spins and must be taken into account to explain the solid NMR powder patterns obtained. Although the appropriate equations can be written, they are not tractable, and one must resort to numerical techniques to calculate the spectra.[16] Comparing the computed patterns with the experimental results allows one to extract the parameters of interest.

So that usefulness of the above described technique could be demonstrated, ^{13}C dipolar spectra have been obtained for $H_3{}^{13}C^{19}F$, $H^{13}C{\equiv}^{13}CH$, $H_2{}^{13}C{=}^{13}CH_2$, and $H_3{}^{13}C{-}^{13}CHO$, all isolated at 1% in argon at 15 K. The spin pairs represented here run the gamut of all two spin cases including $AX(CH_3F)$, $AB(CH_3CHO)$, and $A_2(C_2H_2$ and $C_2H_4)$ type systems. The four molecules also can be grouped into those with axially symmetric (CH_3F and C_2H_2) and fully anisotropic (C_2H_4 and CH_3CHO) shielding tensors. In the case of acetaldehyde, the dipole–dipole vector does not lie along any of the principal shielding axes as in the other three molecules. As all spectra were taken under high-power proton decoupling, the ensuing treatment therefore assumes subspectral analysis to be valid. The respective bond lengths and shift tensor orientations have been determined. The significance of anisotropy in the indirect dipolar coupling is also investigated.

Theory

In this treatment only the nuclear Zeeman and direct and indirect spin–spin coupling interactions are considered in the Hamiltonian. Furthermore, the nonsecular terms of the dipolar and chemical shift Hamiltonians are neglected. Also, only the symmetric parts of the chemical shift and indirect dipolar tensors are kept as the asymmetric parts contribute in second order alone and have no measurable effect upon the spectra. Under these constraints for two spin $^1/_2$ nuclei the Hamiltonian written in Hz is

$$\mathcal{H} = -\nu_1 I_{z_1} - \nu_2 I_{z_2} + A I_{z_1} I_{z_2} + B[I_{+1} I_{-2} + \mathrm{L}_1 \mathrm{I}_{+2}] \qquad (1)$$

The spin labels refer to nuclei 1 and 2. The ν_i are given by the tensorial expressions

$$\nu_i = \mathbf{r}'_i{}^{\mathrm{T}} \cdot \boldsymbol{\nu}_i \cdot \mathrm{r}'_i \qquad \boldsymbol{\nu}_i = \gamma_i \mathrm{H}_0 (1 - \boldsymbol{\sigma}_i) \qquad (2)$$

where σ_i is the chemical shift tensor of nucleus i $\mathbf{r}'_i$ is the unit vector giving the direction of H_0 in the ith shift tensor's principal frame, and $\mathbf{r}'_i{}^{\mathrm{T}}$ is the transpose of $\mathbf{r}'_i$. A is the sum of the geometric parts of the direct and indirect dipolar interactions and is

$$A = \mathrm{r}''^{\mathrm{T}} \cdot \mathbf{D} \cdot \mathrm{r}'' + \mathrm{r}'''^{\mathrm{T}} \cdot \mathbf{J} \cdot \mathrm{r}''' \qquad (3)$$

D and **J** are the direct and indirect dipolar tensors, $\mathbf{r}''$ and $\mathbf{r}'''$ are again unit vectors along H_0 in the principal frames of the two tensors, respectively, and B is defined as

$$B = {}^3\!/_4[J - (A/3)] \qquad J = ({}^1\!/_3)\ \mathrm{Tr}\ \mathbf{J} \qquad (4)$$

In the spin product basis for two spins this Hamiltonian gives us one 2 × 2 and two 1 × 1 secular equations. The solution of these equations for the four energy levels parallels that for the

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spectrum of a general two spin system in solution.[21] At any one orientation (θ,ϕ) the four resulting transitions and concomitant transition probabilities are

$$\nu_{a\pm}(\theta,\phi) = \frac{\nu_1 + \nu_2}{2} - \frac{A}{2} \pm C \qquad P_{a\pm}(\theta,\phi) = 1 \pm B/C \tag{5}$$

$$\nu_{b\pm}(\theta,\phi) = \frac{\nu_1 + \nu_2}{2} + \frac{A}{2} \pm C \qquad P_{b\pm}(\theta,\phi) = 1 \mp B/C \tag{6}$$

where

$$C = \left(\frac{\Delta\nu}{2} + B\right)\left[1 - \frac{4B\Delta\nu}{(\Delta\nu + 2B)^2}\right]^{1/2} \tag{7}$$

$$\Delta\nu = \nu_1 - \nu_2 \tag{8}$$

The results of eq 5–8 may in principal be used to derive a powder pattern for each of the four transitions. Formally the resultant spectra[22] are

$$I(\nu) = \int_{-\pi}^{\pi} P(\theta,\phi)\left(\frac{\delta\nu(\theta,\phi)}{\delta\phi}\right)^{-1} \sin\theta \, d\theta \tag{9}$$

where the ϕ dependence must be eliminated so that the integrand is expressed only in terms of θ and ν. This requires that eq 5 and 6 must be solved for $\sin\phi$. In general, an analytic solution cannot be found unless ν_1, ν_2, **J**, and **D** can be made simultaneously diagonal. In this instance, the problem reduces to solving a quadratic in $\sin^2\phi$. However the resulting solution is still very cumbersome and numerical solutions with the use of computers are usually more convenient.

Fortunately, two limiting cases, which are frequently encountered experimentally, are tractable. The first is the AX spin system where $\Delta\nu \gg A$ at all orientations. The second case, where $\Delta\nu = 0$ to give an A_2 system, is also very common. In both cases $\nu(\theta,\phi)$ is of the form

$$\nu_\pm(\theta,\phi) = \nu \pm \gamma(A - \beta) \qquad P_\pm(\theta,\phi) = \text{constant} \tag{10}$$

where the subscripts referring to the nuclei have been dropped. For the two cases, ν, γ, and β are

$$\begin{array}{ll} A_2 & AX \\ \nu = \nu_A & \nu = \nu_A \text{ or } \nu = \nu_X \\ \gamma = {}^3/_4 & \gamma = {}^1/_2 \\ \beta = J & \beta = 0 \end{array} \tag{11}$$

In the A_2 case the spectrum consists of one doublet of powder patterns while in the AX case there is a doublet of powder patterns for each nucleus. So that the spectrum can be calculated from eq 10, all of the shift and coupling tensors must be expressed in the same reference frame.

With the use the rotation matrices defined by

$$\mathbf{R}''\cdot\mathrm{r}'' = \mathrm{r}' \qquad \mathbf{R}'''\cdot\mathrm{r}''' = \mathrm{r}' \tag{12}$$

eq 10 can be rewritten as

$$\nu_\pm(\theta,\phi) = \mathrm{r}'^{\mathrm{T}}\cdot[\nu_\pm(\mathbf{R}''\cdot\gamma\mathbf{D}\cdot\mathrm{R}''^{\mathrm{T}} + \mathrm{R}'''\cdot\gamma(\mathbf{J} - \beta\cdot\mathbf{E})\cdot\mathrm{R}'''^{\mathrm{T}})]\cdot\mathrm{r}' = \mathrm{r}'^{\mathrm{T}}\cdot\mathbf{S}^\pm\cdot\mathrm{r}' \tag{13}$$

where **E** is the unit tensor and $\mathbf{S}^\pm$ is defined as the bracketed term in the previous line.

As $\mathbf{S}^\pm$ is a symmetric matrix, it is guaranteed that it may be diagonalized with a unitary transform to give

$$\nu(\theta,\phi) = \mathrm{r}^T\cdot\mathrm{T}^\pm\cdot\mathrm{r} \tag{14}$$

where $\mathrm{T}^\pm$ is the result of diagonalizing $\mathrm{S}^\pm$ and r is now defined as the unit vector along H_0 in the principal frame of $\mathrm{T}^\pm$. Thus

$$\nu_\pm(\theta,\phi) = T_1^\pm \sin^2\theta \sin^2\phi + T_2^\pm \sin^2\theta \cos^2\phi + T_3^\pm \cos^2\theta \tag{15}$$

θ and ϕ being the polar angles in the $\mathrm{T}^\pm$ or r frame.

The powder spectrum given this particular $\nu(\theta,\phi)$ is easily calculated from eq 9. It is identical in form with that of a chemical shift powder pattern by substituting $T_1^\pm$, $T_2^\pm$, and $T_3^\pm$, which have the units of frequency for ν_1, ν_2, and ν_3. Dropping the $\pm$ superscripts for covenience and taking $T_3 > T_2 > \mathrm{T}_1$ allows the spectrum[22] for $T_3 > \nu > T_2$ to be given as

$$I(\nu) = [(\nu - T_1)(T_3 - T_2)]^{-1/2}K(k) \qquad k = \frac{(T_2 - T_1)(T_3 - \nu)}{(\nu - T_1)(T_3 - T_2)} \tag{16}$$

and for $T_2 > \nu > T_1$

$$I(\nu) = [(T_3 - \nu)(T_2 - T_1)]^{-1/2}K(k) \qquad k = \frac{(T_3 - T_2)(\nu - T_1)}{(T_3 - \nu)(T_2 - T_1)} \tag{17}$$

where $K(k)$ is the complete elliptic integral of the first kind.

Thus the spectrum consists of an asymmetric doublet of powder patterns, one given by T^+ and the other by T^-. The six characteristic frequencies, three for T^+ and three for T^-, can be identified in the spectrum as done for the components of ν in a simple single-spin powder pattern. The components of $\mathrm{T}^\pm$ for the A_2 doublet, or for either the A or X doublet in the AX case, depend on the three shielding tensor components of the nucleus, the three components of **J**, the distance between the two nuclei, and the five angles needed to relate the dipole–dipole vector and the axes of the ν and **J** tensors. Clearly the six $T_i^\pm$ frequencies do not uniquely determine the 12 parameters upon which they depend. However, the three shielding components for the nucleus are usually easily determined from a spectrum in which the other nucleus is decoupled or substituted by a nonmagnetic isotope. If the elements of **J** are also small compared to those of **D** and σ they can be set to the isotropic J without introducing any significant error in the calculated spectrum. When this approximation holds and σ is known, only the interspin distance and the polar angles of the dipole–dipole vector in the shift tensor frame are left to be determined. These three can easily be calculated from the $T_i^\pm$ elements determined experimentally. Thus, from spectra on a singly and on a doubly spin labeled molecule, the bond length and the orientation of the spin–spin vector relative to the principal axes of the shift tensor can be determined.

In general, this still leaves a degree of arbitrariness as the dipole–dipole tensor is cylindrical and does not fully determine a molecular frame. Thus, the orientation of the shift tensor is known only within an arbitrary rotation about the dipole–dipole vector. However, if the molecule contains symmetry elements (e.g., a reflection plane, etc.) which specify at least one tensor axis other than along the dipole–dipole vector, then at least in principle the shift tensor orientation can be fully determined.

To illustrate these points, let us consider a few specific examples. Consider an AX or A_2 case where the principal frame of **J** and σ are coincident. $\mathrm{S}^\pm$ is then as shown in eq 18, where $D = (\gamma_1\gamma_2\hbar)/r^3$ in Hz and r is the distance between spins 1 and 2. The polar angles θ and ϕ relate the direction of the dipolar vector to the axes of the chemical shift tensor with σ_{33} along the z axis. The elements of $\mathrm{T}^\pm$ are now just the eigenvalues of this $\mathrm{S}^\pm$. If the shielding tensor elements are independently measured, the six $T_i^\pm$ uniquely determine the six remaining parameters: θ, ϕ, D, and the elements of **J**.

$$\mathrm{S}^\pm = \begin{array}{ccc} \begin{array}{l}\nu_{11} \pm \gamma(J_{11} - \beta) \\ \quad \pm D\gamma(1 - 3\sin^2\theta\cos^2\phi)\end{array} & \mp 3D\gamma \sin^2\theta \sin\phi\cos\phi & \mp 3D\gamma \sin\theta\cos\theta\cos\phi \\ \mp 3D\gamma \sin^2\theta \sin\phi\cos\phi & \begin{array}{l}\nu_{22} \pm \gamma(J_{22} - \beta) \\ \quad \pm D\gamma(1 - 3\sin^2\theta\sin\phi)\end{array} & \mp 3D\gamma \sin\theta\cos\theta\sin\phi \\ \mp 3D\gamma \sin\theta\cos\theta\cos\phi & \mp 3D\gamma \sin\theta\cos\theta\sin\phi & \begin{array}{l}\nu_{33} \pm \gamma(J_{33} - \beta) \\ \quad \pm D\gamma(1 - 3\cos^2\theta)\end{array} \end{array} \tag{18}$$

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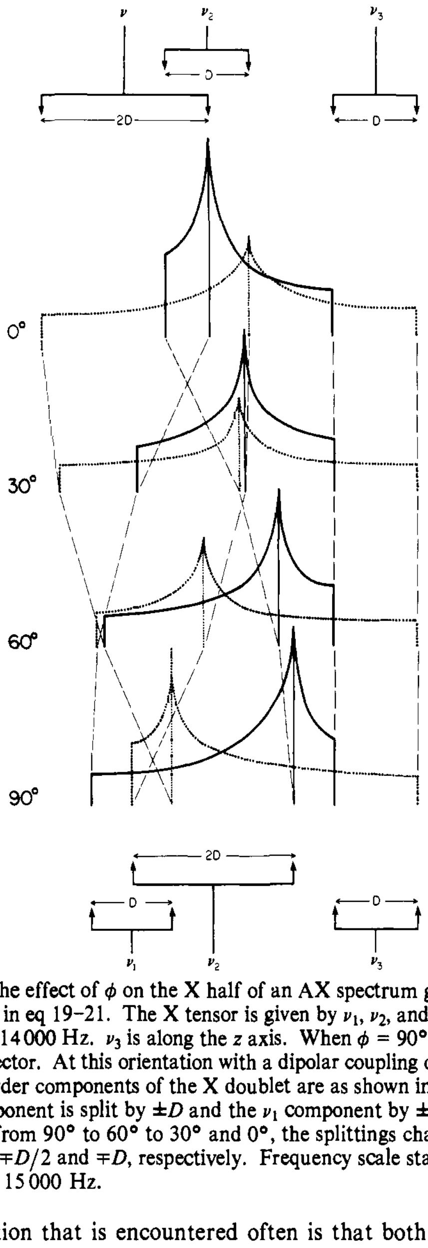

Figure 1. The effect of ϕ on the X half of an AX spectrum given by $T^{\pm}$ components in eq 19–21. The X tensor is given by ν_1, ν_2, and ν_3 at 8000, 10 000, and 14 000 Hz. ν_3 is along the z axis. When $\phi = 90°$, ν_2 is along the dipole vector. At this orientation with a dipolar coupling of 2000 Hz, the two powder components of the X doublet are as shown in the figure. The ν_2 component is split by $\pm D$ and the ν_1 component by $\pm D/2$. As ϕ is changed from 90° to 60° to 30° and 0°, the splittings change monotonically to $\mp D/2$ and $\mp D$, respectively. Frequency scale starts at 7000 and goes to 15 000 Hz.

A situation that is encountered often is that both magnetic nuclei are contained in a reflection plane. Such will be the case in many small molecules containing an sp^2-hybridized ^{13}C atom bonded to another spin. The reflection plane of the sp^2 carbon requires that one of the components of ν be perpendicular to the plane. Since the dipolar vector is contained in this plane, it then is also perpendicular to this component of ν. If ν_{33} is chosen as the perpendicular component, θ can be set equal to 90° in eq 18. The resulting $T^{\pm}$ components become

$$T_3^{\pm} = \nu_{33}^{\pm} \pm \gamma D$$

$$T_1^{\pm} = \frac{\nu_{11}^{\pm} + \nu_{22}^{\pm} \mp \gamma D}{2} + (1/2)\alpha^{\pm}$$

$$T_2^{\pm} = \frac{\nu_{11}^{\pm} + \nu_{22}^{\pm} \mp \gamma D}{2} - (1/2)\alpha^{\pm} \qquad (19)$$

where $\nu^{\pm}_{ii}$ are defined by

$$\nu^{\pm}_{ii} = \nu_{ii} \pm \gamma(J_{ii} - \beta) \qquad (20)$$

$$\alpha^{\pm} = [(\nu_{11}^{\pm} + \nu_{22}^{\pm} \mp \gamma D)^2 - 4(\nu_{11}^{\pm}\nu_{22}^{\pm} - 2\gamma^2 D^2 \pm \nu_{11}^{\pm}\gamma D(1 - 3\sin^2\phi) \pm \nu_{22}^{\pm}\gamma D(1 - 3\cos^2\phi))]^{1/2} \qquad (21)$$

Figure 1 shows the effect of different ϕ on the spectrum. It is seen that the spectra are quite sensitive to variation of this angle. Again, if ν had been obtained from the spectrum for a single spin, the $T_i^{\pm}$ would uniquely determine **J**, D, and ϕ.

As stated earlier, if the spin system is second order, numerical techniques must be used to simulate the spectra. The frequencies given by eq 5 and 6 are calculated for a set of points, prescribed by θ and ϕ, that are uniformly distributed on a finely divided θ,ϕ grid. These are assigned intensities of $P(\theta,\phi)\sin\theta$. The possible spectral range is then divided into a number of increments. When a frequency falls within a given increment, its intensity is added to a sum assigned to that increment. The simulated spectrum obtained from this computation is then a plot of the intensity within each increment vs. the average frequencies of the increments. Figure 2 is the result of such a calculation for a set of hypothetical cases. The shift tensors are assumed to differ only in their traces and have σ_{33} along the dipolar vector. With the value of D fixed, the traces of the shielding tensors are moved closer together so that the spin system progresses from AX to AB to A$_2$ situations. In Figure 2a the two tensors are shown with no dipolar coupling. When a dipolar coupling of 2000 Hz is turned on, the spectrum in Figure 2b is obtained, essentially an AX case. As the spin system becomes more and more strongly coupled, the two inner powder pattern components decrease in intensity as the outer ones increase (Figure 2c). When the shift tensors begin to overlap, the separation into components as in eq 5 is not readily apparent (Figure 2d) as $\Delta\nu$ can now be positive or negative and as such mixes up the levels as they have been grouped here. As with other second-order problems of this type, the difficulty arises from the sign of term C (see eq 7) which contains a square root. Depending on which sign is used, the multiplet is arbitrarily divided into different components. In any event the sum of the components is identical regardless of the convention adopted, and this ambiguity need not create any confusion in the ultimate analysis of experimental data. When the two tensors overlap completely, the resultant is an A$_2$ spectrum (Figure 2e).

Motional Averaging Corrections

So that bond length from the value of $\langle (P_2\cos\theta)/r^3 \rangle$ measured in a dipolar spectrum could be derived, the effect of vibration, rotation, and libration of the molecule in the matrix should be taken into account. The neglect of vibrational corrections to r values measured with the liquid-crystal technique was at one time postulated to be the source of the rather large discrepancies between these r values and those obtained by microwave or electron diffraction. Several authors[23,24] have shown that a full vibrational analysis of a molecule such as CH$_3$F yields corrections which are 2 orders of magnitude smaller than the typical experimental error. At 15 K, rotation of molecules as large as the ones studied here should be effectively quenched in the argon lattice. Methyl fluoride for instance has been found to be static on the IR time scale[25] in an argon matrix. However librational motion of an isolated molecule is to be expected,[26] if from nothing else than the zero point motion of the crystal lattice of argon atoms.

To get an estimate of the magnitude of the effect of such motion on the measured value of $\langle P_2\cos\theta/r^3\rangle$ one must consider an AX spin system in which σ and **J** are both axially symmetric with their unique axis along the dipole–dipole vector. The $T^{\pm}$ components follow directly from comparison of eq 10 and 12 for this case. They are

$$T_1^{\pm} = T_2^{\pm} + T_{\perp} = \nu_{\perp} \pm (1/2)[D' + J]$$

$$T_3^{\pm} = T_{\parallel}^{\pm} = \nu_{\parallel} \pm (1/2)[-2D' + J] \qquad (22)$$

The spectrum is determined by $\nu_{\perp} - \nu_{\parallel}$, J, and D', where D' is defined as $D' = D + (J_{\perp} - J_{\parallel})/3$. For a given set of these three parameters the spectrum is shown in Figure 3.

In extracting the value of D' from the spectrum, the best features to use are the two break points associated with the molecule

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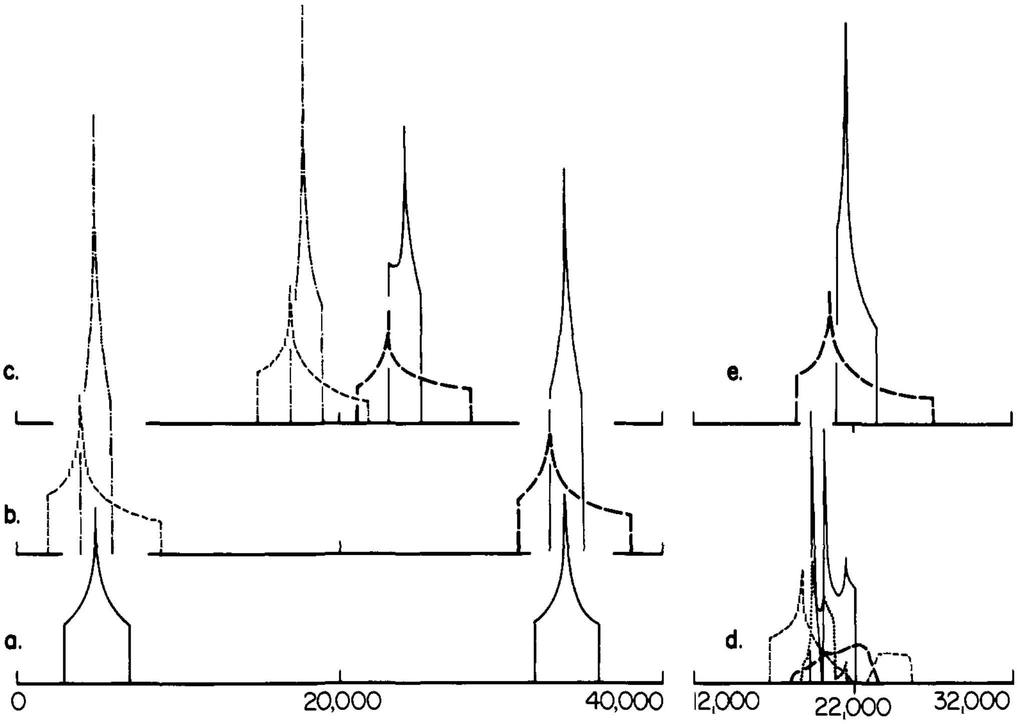

Figure 2. Progress of AX spectrum to AB and A_2 spectrum as two shift tensors are moved closer and closer together as discussed in text: (a) Two nuclei with ν tensors given by 3000, 5000, 7000, and 32000, 34000, and 36000 Hz and no dipolar coupling, (the difference in the isotropic value of the two shifts is 29000 Hz); (b) same tensors with a dipolar coupling of 2000 Hz; (c)–e) dipolar coupling of 2000 Hz, difference in the trace of the tensors progresses from (c) 6000 Hz to (d) 1000 Hz to (e) 0 Hz.

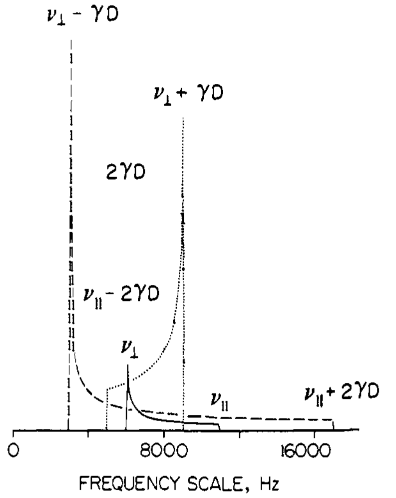

Figure 3. A representative AX or A_2 dipolar spectrum with an axially symmetric shift tensor. The solid line is the unperturbed shift tensor. For deriving D', the most easily measured spectral parameter is the difference between the $\nu_\perp - \gamma D'$ and $\nu_\perp + \gamma D'$ components. The difference between these is $2\gamma D'$. The parameters used here are appropriate for $^{13}C_2H_2$: $D' = 4100$ Hz and $\nu_\parallel - \nu_\perp = 4900$ Hz.

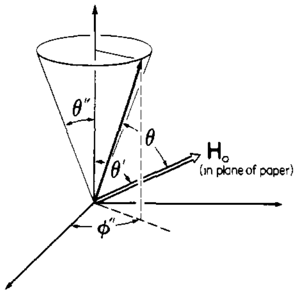

Figure 4. Coordinate system for description of the libration of a molecule by an angle θ'' about an axis at an angle of θ' from the magnetic field.

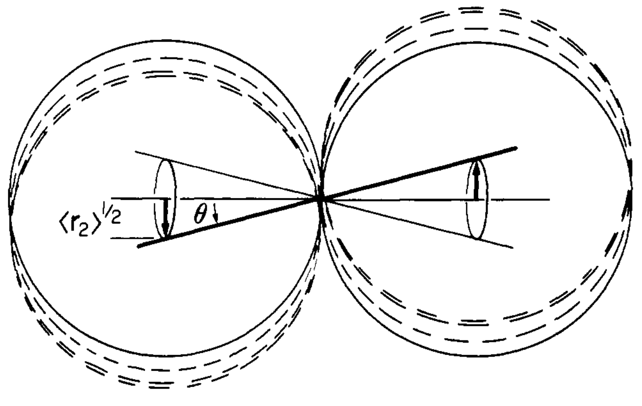

Figure 5. Scheme demonstrating the angular motion of the internuclear vector of two argon atoms due to their average displacement from zero-point motion.

oriented at 90° relative to the magnetic field. The difference in these two frequencies is $\langle D'P_2(\cos\theta)\rangle|_{\langle\theta\rangle=90°}$. If the molecule is librating about the 90° position, the value of $\langle P_2 \cos\theta\rangle$ will be somewhat less, giving an apparently longer r value. One way to estimate the correction is to assume that the principal axis of the molecule librates in a cone by some mean angle θ''. With the use of the coordinates in Figure 4, it can be shown that

$$\langle 3\cos^2\theta - 1\rangle|_{\langle\theta\rangle=90°} = 3\langle \sin^2\theta''\rangle - 1 \simeq 3\sin^2\langle\theta''\rangle - 1 \tag{23}$$

if the motion is then averaged over ϕ'' and θ' is set to 90°.

A reasonable motional model to obtain an estimate of θ'' is based on the pseudorotating cage model given recently by Manz.[26] The molecules under consideration here (CH_3F, C_2H_2, CH_3CHO, C_2H_4) have volumes between that of one and two argon atoms, and for the purpose of the estimate, the cage may be approximated as a double vacancy in the lattice. The maximum inertial mass is taken as the mass of two argon atoms as this exceeds that of any of the molecules. Under these assumptions the angular movement of the long axis (i.e., the dipole–dipole axis) of these four molecules is approximated by the angular motion of the internuclear vector of two argon atoms in the argon lattice. As a further simplification, only motion due to zero-point energy will be taken into account. From Figure 5, $\tan \theta''$ is then given by the root mean square of the average displacement at zero-point energy divided by the radius of an argon atom.

$$\tan \theta'' = \frac{\langle r^2 \rangle^{1/2}{}_{\text{zero point}}}{R_{\text{argon atoms}}} \qquad (24)$$

The root-mean-square displacement can be calculated from the Debye model of a solid. As given by Reissland[27]

$$\langle r^2 \rangle^{1/2}{}_{\text{zpe}} = \left[\frac{9}{4} \frac{\hbar^2}{m K_B \Theta_D} \right]^{1/2} \qquad (25)$$

where K_B is the Boltzmann constant, Θ_D is the Debye temperature, and zpe is zero-point energy. For argon this gives $\langle r_2 \rangle^{1/2}{}_{\text{zpe}} = 0.179$ Å.

Using equations 23–25 this results in $\langle 3 \cos^2 \theta - 1 \rangle|_{\langle \theta \rangle = 90^\circ} \simeq -0.97$ as opposed to −1 for no motion. Thus the measured D' is at least 3% lower than the actual value. For a ^{13}C–^{13}C coupling on the order of 2075 Hz, corresponding to a bond length of 1.54 Å, a 3% decrease in D results in an apparent bond length of 1.557 Å, or an error of −0.0165 Å. The typical estimated experimental error of ±100 Hz in these experiments is of the same size as this correction and as such might be ignored for bonds longer than 1.54 Å. However for large dipolar couplings in shorter C–C bonds a correction based on a fixed percentage will be outside the experimental errors. When this is the case the motional correction must be applied if the difference between the measured D' and a D calculated from a known bond length is to be attributed to anisotropic indirect dipolar coupling. Such motion will also partially average the measured chemical shift tensors. In this study it is found that these corrections are comparable with the experimental errors and should be taken into account when making comparisons with theory.[18]

Experimental Section

Samples of $H^{13}C{\equiv}^{13}CH$, $H_2{}^{13}C{=}^{13}CH_2$, $H_3{}^{13}C{-}^{13}CHO$, and $H_3{}^{13}CF$ 90% enriched ^{13}C were purchased from Merck Isotopes, Ltd., for use in these experiments. All were subjected to several freeze–pump–thaw cycles to remove N_2 and O_2. One to 0.5% v/v mixtures of each in Ar were made on a vacuum line and 200 mL at STP deposited on a sapphire rod held at 15 K by an Air Products Displex 202B closed-cycle helium refirgerator. The procedure and apparatus have already been described elsewhere.[28] ^{13}C spectra were recorded at 20.12 MHz under ^1H decoupling with $({}^{1}H_{\gamma}H_{1})/2\pi = 50$ kHz. The ^{13}C magnetization was prepared by either a single $\pi/2$ pulse or a single shot cross polarization sequence. For the CP experiments, a mixing time of 3 ms was typically used. The experiments were repeated every 3–6 s, and it was found that about 200 transients provided sufficient signal to noise ratios. Digitization followed immediately after the pulse. In the cross polarization experiments, removal of artifacts due to the observe pulse was facilitated through a phase alternated pulse sequence in conjunction with inversion of the ^1H spin temperature.

Results and Discussion

Methyl Fluoride. $H_3{}^{13}CF$ is an example of an AX system in which σ and **J** are both axially symmetric with their unique axis along the C–F bond. The spectrum is given by the $T^{\pm}$ components in eq 22. It is evident that the anisotropy in **J** is inseparable from the value of D in this case. The spectrum then is determined only by $\nu_\perp - \nu_\parallel$, D', and J as stated earlier.

Figure 6 compares the experimental CP spectrum with one calculated for $D' = 9900$ Hz, $\nu_\perp - \nu_\parallel = -1800$ Hz, and $J_{CF} = -158$ Hz. This was convolved with both Lorentzian and Gaussian broadening functions with half-width at half-height of 400 and 200 Hz, respectively. The Lorentzian and Gaussian widths were chosen to best mimic the width of the two peaks at the perpendicular orientation and the wings. It was not possible to get the base of the calculated spectrum as broad as the experimental one without excessively broadening the central features of the spectrum. It should also be noted that the small peak in the center of the spectrum was suppressed by the choice of an appropriate mixing time. Both features may be indicative of incomplete isolation in the matrix. The broadening in the base may be due to aggregates of CH_3F molecules, and as such these ^{19}F–^{13}C couplings would broaden their spectrum into a structureless Gaussian. The peak in the middle may be due to smaller aggregates such as dimers and trimers with resolvable dipolar spectra. For dilution factors as low as the 150:1 used in this sample, it has been shown by IR that a measurable portion of the CH_3F in an argon matrix[25] exists as dimers. These have been postulated to be linear hydrogen-bonded species. The dipolar spectrum for four such spin $^1/_2$ particles in a straight line has been calculated by Nicol,[29] who points out the spectral similarity between the 2 and 4 spin cases and that such central features may be the only way to differentiate between the two.

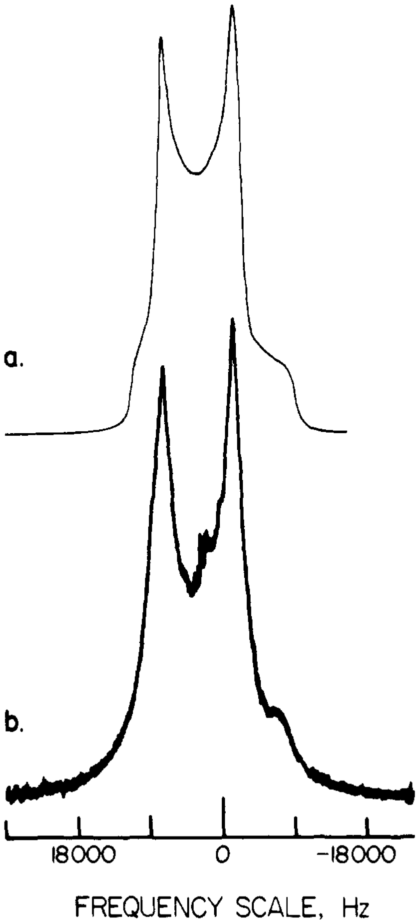

Figure 6. Comparison of the (a) calculated and (b) experimental dipolar spectrum of $^{13}CH_3F$ by using the parameters given in Table I.

The comparison between the major features of the experimental and theoretical lineshapes is quite good. Correcting the apparent D' of 9900 Hz for libration results in $D' = D + (J_\perp - J_\parallel)/3 = 10200$ Hz. The errors in D' are estimated at ±400 Hz. If $J_\perp - J_\parallel = 0$, the calculated $r = 1.40_5 \pm 0.02$ Å, which is within experimental error of the microwave and electron diffraction[30] values of 1.3885 ± 0.0003 Å. Conversely if this number for the bond length is used to calculate D, the value is 10570 Hz. Subtracting this from D' gives an apparent anisotropy in **J** of $J_\perp - J_\parallel = -1200 \pm 1200$ Hz. Thus, within the estimated error limits it is unfortunately not possible to arrive at a value of the magnitude of the anisotropy in the C–F **J** coupling which has been a subject of some interest in the literature. Reported values from liquid-crystal[31] studies, however, are not inconsistent with these results.

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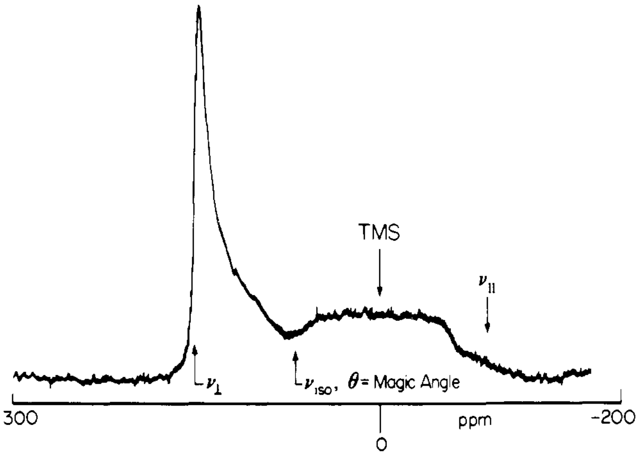

Figure 7. CP powder spectrum of natural abundance acetylene: $\nu_{\perp} = 150 \pm 5$ ppm and $\nu_{\parallel} = -90 \pm 5$ ppm from Me_4Si.

With the use of $^1/_3$ Tr $\sigma = 75$ ppm from Me_4Si, the components of the ^{13}C shift tensor for CH_3F are found to be $\sigma_{\perp} = 105 \pm 10$ ppm and $\sigma_{\parallel} = 15 \pm 10$ ppm from Me_4Si, respectively.

Acetylene. Acetylene is an A_2 spin system which, like methyl fluoride, has axially symmetric σ and **J** tensors with the unique axis along the bond. The $T^{\pm}$ components for this geometry follow from eq 11 and 14 as

$$T_1^{\pm} = T_2^{\pm} = T_{\perp}^{\pm} = \nu_{\perp} \pm {}^3\!/_4\left(D + \frac{J_{\perp} - J_{\parallel}}{3}\right)$$

$$T_3^{\pm} = T_{\parallel}^{\pm} = \nu_{\parallel} \pm {}^3\!/_2\left(D + \frac{J_{\perp} - J_{\parallel}}{3}\right) \tag{26}$$

Due to the axial symmetry of **J** and its coincidence with **D**, the effects of the two coupling tensors on the spectrum are not separable and the spectrum is determined by $\nu_{\perp} - \nu_{\parallel}$ and D'. When eq 22 for the AX case and eq 26 for the A_2 case are compared, it is noted that only the AX case depends on the trace of **J**. The A_2 case has a stronger dependence on D', its coefficient being $^3/_4$ compared to $^1/_2$. Consequently the separation between the two perpendicular components as observed in Figure 3 is $^3/_2D'$ for the A_2 spectrum. Thus the relative error in the determination of D' in the A_2 case would be $^2/_3$ of that in the AX case for the same value of D' and the same uncertainty in frequency measurements.

Due to the linear structure of acetylene, all dipolar couplings between the spins vanish when it is aligned at the magic angle. At this orientation cross polarization does not occur between the ^{13}C and ^1H in the same molecule.[32] Magnetization can be transferred only from intermolecular protons. In neat natural abundance acetylene, the transfer of magnetization between molecules is so inefficient that very little intensity is present at the isotropic shift (corresponding to θ = magic angle, Figure 7) even for mixing times as long as 20 ms. Dilution in an argon matrix further decouples the intermolecular dipolar interactions and makes the magnetization transfer even less efficient.

In order to record a representative spectrum, we used standard FT methods. We collected 600 FID's following a $\pi/2$ pulse. A recycle time of 60 s was used to avoid problems with anisotropic relaxation. The calculated and experimental spectra are shown in Figure 8. The peak in the center is due to the single labeled material in the matrix. The best agreement between a calculated and an experimental spectrum was for $D' = 4100$ Hz, using the value of $\sigma_{\perp} - \sigma_{\parallel} = 240$ ppm measured for the natural abundance material. A Lorentzian of 200 Hz combined with a Gaussian of 100 Hz half-width at half-height were used to broaden the calculated spectrum. The best value of D' was determined by comparing a series of spectra calculated with different values of D' to the experimental result. When D' and $\nu_{\perp} - \nu_{\parallel}$ are of comparable magnitude, the spectral form is very sensitive to the value of D'. In this case the parallel component with a negative coupling ($T_{\parallel}^-$) provides a good spectral feature from which the spectral parameter can be determined. As shown in Figure 3, the difference between the T^- components is

$$T_{\perp}^- - T_{\parallel}^- = (\nu_{\perp} - \nu_{\parallel}) - {}^3\!/_4D' \tag{27}$$

Figure 8. Comparison of (a) calculated and (b) experimental dipolar spectra of $^{13}C_2H_2$ with the use of the parameters given in Table I and II.

It is interesting to note that at some value of H_0, $T_{\perp}^-$ will equal $T_{\parallel}^-$ and the T^- half of the doublet will be a single line.

After correcting for libration, $D' = 4220 \pm 150$ Hz. This gives a C≡C bond length of $1.21_5 \pm 0.02_0$ Å if **J** is assumed to be isotropic. As in methyl fluoride, this is slightly above the 1.20 ± 0.02 Å reported by X-ray, but the two values agree within experimental error. If the differences in the two bond distances were ascribed solely to anisotropy in **J**, a value of $J_{\perp} - J_{\parallel} = 3(D'_{\text{measd}} - D_{\text{calcd}}) = -528 \pm 450$ Hz would be obtained. This is 1 order of magnitude larger than the currently available theoretical estimate[34] of −51 Hz. Unfortunately the magnitude of the estimated errors make it impossible to address the very interesting question of the magnitude of the anisotropy in the J coupling constant. The small difference between the X-ray and dipolar bond distances also could be due to additional motional effects other than the zero-point motional corrections which have been estimated herein.

Ethylene. The ethylene spectrum also belongs to the A_2 spin system, and the molecules possess D_{2h} symmetry. The three mirror planes of the molecule require that the principal axes of both σ[20] and **J** be coincident with the frame defined by the C=C bond and the perpendiculars to the two mirror planes containing the C=C bond. From eq 11 and 14, the $T^{\pm}$ components are

$$T_1^{\pm} = \nu_{11} \pm {}^3\!/_4(D + J_{11} - J)$$

$$T_2^{\pm} = \nu_{22} \pm {}^3\!/_4(-2D + J_{22} - J)$$

$$T_3^{\pm} = \nu_{33} \pm {}^3\!/_4(D + J_{33} - J) \tag{28}$$

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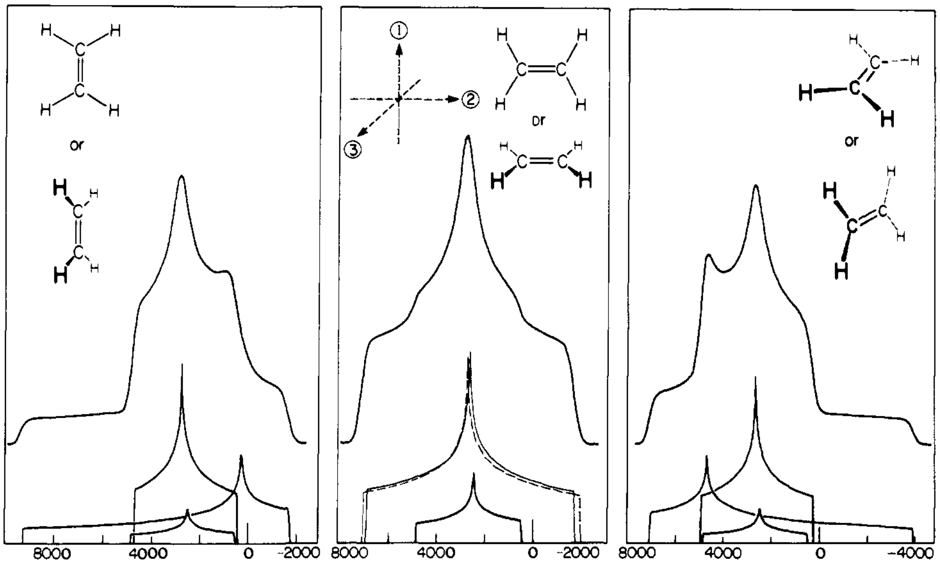

Figure 9. With use of the parameters in Table I, the dipolar spectra for $^{13}C_2H_4$ for the three possible orientations of the dipolar vector relative to the ν tensor's principal frame are shown. The second choice is clearly the one found experimentally (see Figure 10).

where ν_{22} is taken to be along the bond. In this case it can be seen that if **J** is anisotropic it will manifest itself in the spectrum independently from D and thus in principle the anisotropy of **J** will be directly observable. Unfortunately the sign of **J** is unavailable as the measurables are the deviations of the individual tensor elements from J.

The shift tensor of ethylene in argon has previously been measured.[1] Within the restrictions imposed by the molecular symmetry, there are three possible assignments of this tensor relative to the dipole–dipole vector. The three possibilities each involve having one of the three elements lie along the C=C bond.

Using the literature value of 1.335 Å for the C=C distance and neglecting the much smaller **J** for the moment, we calculated the spectra for the three possible orientations of σ. Comparison of these three spectra (see Figure 9) with the experimental spectrum in Figure 10 clearly shows that the intermediate shielding component (σ_{22}) lies along the double bond. The assignment of the other two components relative to the molecular plane is not determined as the dipolar tensor D is cylindrically symmetric and rotation of σ_{11} and σ_{33} about the bond will not change the spectrum. Although they must lie along the normals of the two mirror planes containing the bond, either of the two possible orientations indicated in Figure 9 are consistent. However, there are experimental and theoretical precedents for assigning σ_{33} to be perpendicular to the plane of the molecule. In one other olefin, dihydromuconic acid,[36] it has been shown that σ_{33} is within 11° of the perpendicular to the sp^2 plane. In other sp^2 carbons, aromatic,[13] carboxylic,[14] or carbonyl,[37] it is also generally found that σ_{33} is perpendicular to the sp^2 plane. Theoretically[38] this is qualitatively understood in rather simple terms. To a first approximation the value of a chemical shielding tensor component results from circulation of the electrons in the plane perpendicular to the shielding axis and containing the nucleus. As the sp^2 plane is a node in the π-electron system, the shielding perpendicular to it depends primarily on the σ electrons. The resulting σ_{33} shift for ethylene at 29 ppm falls in the middle of the typical aliphatic range where only sigma electrons are relevant to shielding. This assignment then provides a consistent picture of the shielding.

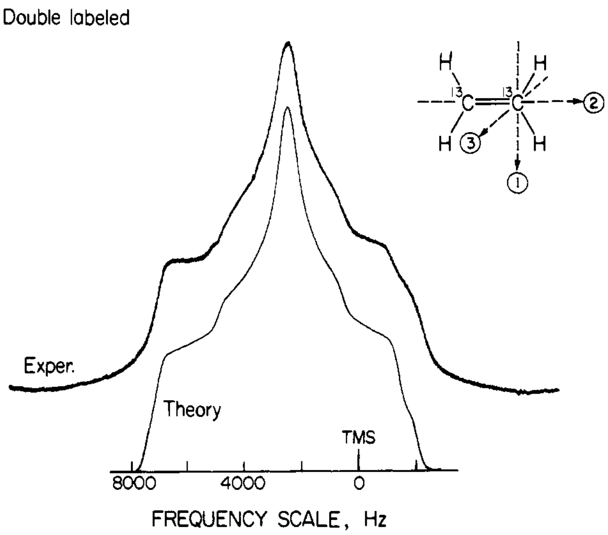

Figure 10. Comparison of experimental and calculated dipolar spectra of $^{13}C_2H_4$ by using the parameters in Table I. The shift tensor's orientation is determined to be as in the inset.

Upon closer inspection of the experimental spectrum, it is found that no value of D can be found that satisfactorily fits all of the break points in the spectrum simultaneously without inclusion of some anisotropy in **J**. In particular, the separation between the two upfield break points cannot be reproduced without a large distortion of the rest of the calculated spectrum. If **J** is allowed to be anisotropic, the best comparison is obtained with

$$D = 3100 \pm 100 \text{ Hz}$$

$$J_{11} - J = 400 \pm 100 \text{ Hz} \qquad J_{11} = 467 \pm 100$$

$$J_{22} - J = 200 \pm 100 \text{ Hz} \qquad J_{22} = 267 \pm 100$$

$$J_{33} - J = -600 \pm 100 \text{ Hz} \qquad J_{33} = -533 \pm 100$$

The isotropic value of $J = +67$ Hz was used to calculate the individual components which are also labeled the same as those for σ. It is likely that the remaining differences between the experimental and calculated line shapes are due to small anisotropic motional or relaxation effects.

For the C=C indirect coupling, the anisotropy parameter defined as $J_{22} - {}^1/_2(J_{11} + J_{33})$, with J_{22} along the bond, is measured here as 300 ± 150 Hz. As in acetylene this is 1 order of magnitude larger than theoretical prediction (22 Hz),[34] and it is about 3 times

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Table I. Dipolar Couplings, Derived Bond Lengths, and Apaprent Anisotropies in J

compd	r, Å (lit.^{a})	D', Hz predicted	D', Hz measd	D', Hz libration corr	r_D, Å (from D')	$J_{xx} = \frac{1}{2}(J_{yy} - J_{zz})$ apparent	$J_{xx} = \frac{1}{2}(J_{yy} - J_{zz})$ theory^b	J
CH_3F	1.3852 ± 0.005	10580 ± 20	9900 ± 400	10200 ± 400	$1.40_5 \pm 0.02_0$	−1209 ± 1200	−262 (−700 ± 200)^c	−158
C_2H_2	1.20 ± 0.02	4390 ± 200	4100 ± 150	4230 ± 150	$1.21_5 \pm 0.01_5$	−480 ± 450	−51	171.5^e
C_2H_4	1.335 ± 0.003	3190 ± 20	3100 ± 100	3195 ± 100	$1.34 \pm 0.01_5$	300 ± 100	22 (90)^d	67.6^e
CH_3CHO	1.512 ± 0.004	2195 ± 20	2000 ± 75	2062 ± 75	$1.54 \pm 0.01_5$			59.6

^{a} References 30, 33, 35, and 43. ^{b} Reference 34b. ^{c} Experimental value.[31] ^{d} Experimental value.[39] ^{e} Reference 45.

larger than that determined by a liquid-crystal study (90 Hz).[39] If one cannot escape the conclusion that the anisotropy in J is required in order to get agreement with the calculated result, then the anisotropy must be 1 order of magnitude larger than present theoretical results. However this conclusion must await the resolution of the question of what effect anisotropic motional corrections would have on the spectrum through variation in the components of **D**.

Regardless of the uncertainty as to the role of anisotropy in either J or the effects in averaging **D** upon the spectrum, good agreement with electron diffraction is obtained for the bond length. With correction of D for molecular libration, a value of 3195 ± 100 Hz is obtained. This yields an r of 1.34 ± 0.015 Å (1.335 ± 0.003 by electron diffraction). While the electron diffraction and dipolar results are in good agreement with each other, a recent[39] low-temperature X-ray study has yielded a smaller value of r = 1.31 Å.

Acetaldehyde. In the double-labeled $^{13}C_3{}^{13}CHO$, $\Delta\omega \simeq A$ at most orientations. As discussed earlier, this leads to second-order AB behavior in the spectrum. For this molecule the most preferred conformation is the one in which a methyl proton eclipses the C=O.[40] This conformer has a mirror plane which specifies the direction of one shielding tensor component for each nucleus. The angle of rotation about this component is then all that is needed to determine the orientation of the shift tensor with respect to the dipolar vector.

With use of σ values obtained from a 10:1 mixture of argon and natural abundance acetaldehyde, spectra were calculated for a number of orientations of the two shift tensors relative to the C–C bond for the doubly-enriched material. The anisotropy in J is expected to be quite small for a C–C bond[34] compared to those of C–F, C=C, or C≡C bonds. As the anisotropy for these have been found to be of the same size as the experimental errors here, it has been neglected for the present calculations. By comparison of theoretical with experimental spectra, it was found that σ_{33} for the aldehyde carbon had to lie along the perpendicular to the sp^2 plane. For the methyl carbon σ_{22} was determined to be in the same direction. Further calculations determined that the angle between the dipole–dipole vector and σ_{11} of the aldehyde was 55° ± 5. For the methyl, σ_{33} and the dipolar vector make an angle of 35^a ± 5. By analogy with previous studies on carbonyls[41] and the results presented on ethylene here, it is concluded that the σ_{22} component for the CHO moiety is most likely to lie along the C=O direction. This orientation which gives the best theoretical fit of the data is given in Figure 11 for both carbons. For the methyl carbon there are two possible assignments. Both place σ_{33} at 35° ± 5 from the dipole and differ only in whether the angle is a plus or minus 35°. If σ_{33} is at −35°, it is then approximately perpendicular to the plane defined by the methyl carbon and the two hydrogens not contained in the molecule's reflection plane. Circulation of electrons in this plane involve C–H σ electrons much more so than the other two axes and as such is expected to give a more methane like or upfield shift as observed.[42] Although the other possible assignment (+35°) cannot be totally ruled out, it does not allow one to explain the relative shifts of the tensor components in as simple and consistent a fashion. These assignments of the orientations for both carbons are further supported by their very close agreement to those calculated by Ando, Nishioka, and Kondo.[43]

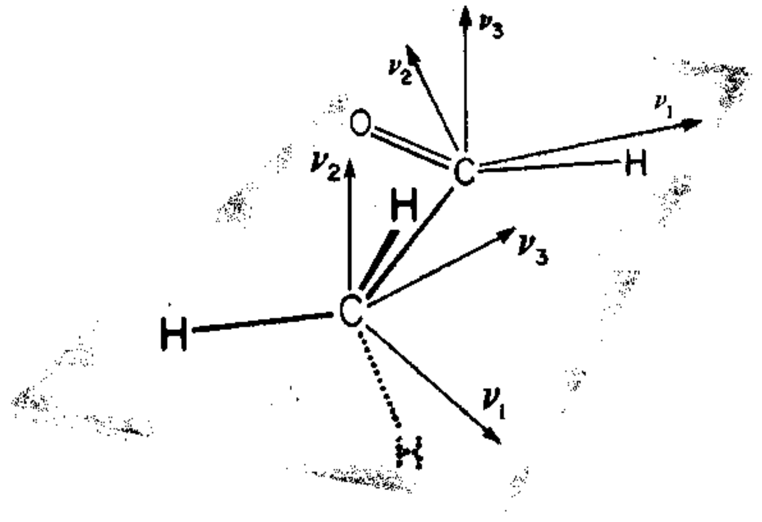

Figure 11. Orientation of the two shift tensors in $^{13}CH_3{}^{13}CHO$ as determined by dipolar spectroscopy. The angle between ν_1 for the CHO group and the C–C axis is 55°. The angle between ν_3 of the CH_3 group and the C–C axis is 35°.

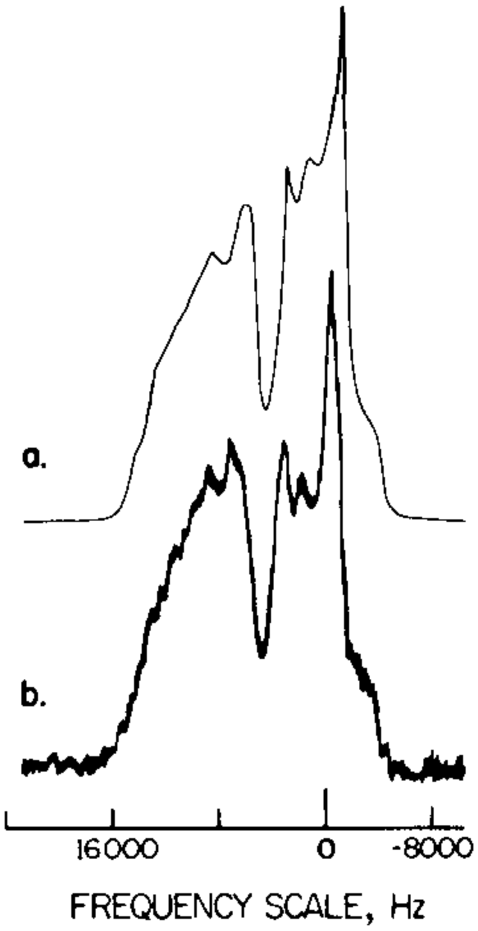

Figure 12. Comparison of (a) calculated and (b) experimental dipolar spectra for $^{13}C_3{}^{13}CHO$ by using the parameters in Tables I and II.

The experimental spectrum and the calculated spectrum using the preceding tensor orientations are compared in Figure 12. The best value of D was determined as 2000 ± 75 Hz. Correcting for libration gives D = 2062 ± 75 Hz, which is almost within experimental error of the value of 2195 ± 20 Hz calculated for the literature[44] value of 1.512 ± 0.004 Å. The bond length derived

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Table II. Chemical Shift Tensors and Their Orientations

compd	σ_{11}	σ_{22}	σ_{33}	orientation determination	
				d by dipole	by comparison
CH_3F[b]	105 ± 10	105 ± 10	15 ± 10	σ_{33} along C–F bond	
C_2H_2[c]	150 ± 2.5	150 ± 2.5	−90 ± 5	σ_{33} along C–C bond	
C_2H_4	239 ± 2.5	129 ± 2.5	29 ± 2.5	σ_{22} along C–C bond	σ_{33} ⊥ to sp^2 plane
$CH_3CHO(C_1)$	285 ± 2.5	231 ± 2.5	84 ± 2.5	σ_{33} ⊥ to sp^2 plane, σ_{11} 55° from dipole axis	σ_{22} closest to C=O direction
(C_2)	53 ± 2.5	40 ± 2.5	−1 ± 2.5	σ_{22} ⊥ to mirror plane, σ_{33} 35° from dipole axis	σ_{11} approximately bisects HCH angle

[a] Chemical shifts in ppm from external Me_4Si. [b] To be compared with $\sigma_{11} - \sigma_{33}$ of 68 ± 15 ppm from a liquid-crystal study (Bhattacharyya, P. K.; Dailey, B. P. *J. Magn. Res.* 1974, *13*, 317) and a theoretical result of 81 ppm (Ditchfield, R. Conference on Critical Evaluation of Chemical and Physical Structural Information, Dartmouth College, June 1973). [c] To be compared with $\sigma_{11} - \sigma_{33}$ fo 245 ± 15 from a liquid-crystal study (Mohanty, S. *Chem. Phys. Lett.* 1973, *18*, 581) and a theoretical value of 237 ppm (Hayamiza et al., *J. Magn. Reson.* 1980, *39*, 343).

from the corrected experimental D is $1.54_0 \pm 0.015$ Å. A Lorentzian of 100 Hz full-width at half-height was used to convolve the calculated spectrum. As can be seen the agreement is excellent between the two plots.

Conclusion

The dipolar couplings and the derived bond lengths along with the apparent anisotropies in **J** are collected together and placed in Table I. The measured D' is in nearly all cases at least 3–5% lower than that predicted by using equilibrium bond lengths derived from microwave, electron diffraction, or X-ray results. If only the reorientation of the molecule due to the zero point motion of the argon lattice is taken into account in the simple manner employed here, the new D' values are all very close to being within experimental error of those predicted. More sophisticated motional models may produce better results. Bond lengths derived from the corrected D' values are always on the long side of other determinations but usually within ±0.02 Å. As such the method should provide a reasonably accurate and rapid means for determining the carbon structural parameters of matrix-isolated organic species from relatively easily analyzed data even in the presence of large chemical shift anisotropy.

It has been demonstrated here that even for multiply-bonded species, the anisotropy in **J** only affects the ^{13}C dipolar spectra on the order of the experimental errors. Furthermore it cannot be independently observed unless **J** is completely anisotropic. In any case, for spin systems involving ^{13}C similar to those studied here, one can neglect **J** and still expect to get carbon–carbon bond lengths good to within ±0.02 Å.

In Table II the chemical shift tensors and their orientations are summarized. For the axially symmetric species the spectra confirm what is dictated by symmetry. In ethylene the dipolar spectrum allowed unequivocal assignment of σ_{22} along the C=C axis. Symmetry combined with theoretical and experimental precedents also allowed the assignment of σ_{11} and σ_{33}. For acetaldehyde, a rather complex second-order powder pattern results which is explained by using the orientation of the two ^{13}C shift tensors in Figure 11. These orientations were totally specified by the spectrum except for a single 180° rotation of the molecule about the carbon–carbon bond. With molecules such as these, where single-crystal NMR studies may be next to impossible, using the internal dipolar frame to establish the tensor axes is an attractive alternative. Especially with molecules that are small enough to be interesting to the theoretician, the dipolar spectrum of a matrix-isolated multiply-labeled species may often be the easiest way to experimentally obtain data.

In summary it has been demonstrated that reasonably accurate carbon bond lengths can be obtained from the dipolar spectrum of matrix-isolated species even when anisotropic chemical shift and indirect dipolar couplings are present and as such should be applicable to species stable only in noble-gas matrices. Furthermore the method allows the determination of the orientation of shift tensors relative to the molecular frame in molecules for which single crystals are not readily available. Anisotropy in the indirect ^{13}C dipolar coupling has also been shown typically to be no larger than the magnitude of the motional corrections to the direct dipolar coupling. The investigation of anisotropy in **J** in systems such as ethylene where it is rigorously separable from the direct dipolar coupling will provide future challenges to experimentalist and theorist alike. It is expected that future studies by dipolar spectroscopy of multiply-labeled matrix-isolated species will yield solutions to the structural enigmas that many of these species have presented and heretofore been insoluble.

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(44) Takao, I.; Tsuchiya, S. *J. Mol. Spectrosc.* **1972**, *44*, 88–107.

(45) Lynden-Bell, R. M.; Sheppard, N. *Proc. R. Soc. London, Ser. A.* **1962**, *269*, 285–403.

(46) **Note Added in Proof:** Readers will wish to become familiar with related work by Yannoni, C. S.; Kendrick, R. D. *J. Chem. Phys.* **1981**, *74*, 747 which has appeared since this paper was submitted.