

Differential Line Broadening in the Presence of Quadrupolar–CSA Interference

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The formalism for calculating the lineshape of a spin 1/2 J -coupled to a high-spin nucleus undergoing quadrupolar and chemical shift anisotropy (CSA) relaxations is derived in the case where the tensors of both interactions are noncoincident and nonaxial. The expressions show that the CSA–quadrupolar interference term which is responsible for the asymmetry of lines involves a term depending on tensorial parameters. The effect of this term on the lineshapes is discussed with respect to three cases, namely coincident–axially symmetric, noncoincident–axially symmetric, and general noncoincident quadrupolar and CSA tensors. These cases are considered in the analysis of the lineshape of the ^1H -decoupled spectra of the ^{31}P nucleus J -coupled to the ^{59}Co nucleus encountered in the tetrahedral cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$. © 1998 Academic Press

formalism for calculating the lineshapes in a more general case in order to perform a more correct analysis. In this paper, we will present the formalism and the results of analysis and of reinvestigations carried out on the tetrahedral cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$ (Fig. 1). Initially, we shall briefly outline the different steps for calculating the lineshapes.

BASIC THEORY

For an IS spin system, where the spin- $\frac{1}{2}$ S is J -coupled to the I quadrupolar nucleus, the usual well-resolved S multiplet can be changed, by relaxation processes, into a broad or coalesced pattern without any clear multiplet structure (11). Using the stochastic approach based on an analogy with the chemical exchange (12, 13), the lineshape $I(\omega)$ of the NMR pattern of the S nucleus of spin $\frac{1}{2}$, J -coupled to one I quadrupolar nucleus, is expressed by (11)

$$I(\omega) \propto \mathbf{W} \cdot (i\Omega + \mathbf{A})^{-1} \cdot \mathbf{1}, \quad [1]$$

where \mathbf{W} is a row vector with components proportional to the a priori probabilities of the $2I + 1$ spin states of the I nucleus (all equal to 1); $\mathbf{1}$ is a $(2I + 1)$ unit column vector; and Ω is a $(2I + 1) \times (2I + 1)$ diagonal matrix with elements given by the expression

$$\Omega_{m,m'} = (\omega_0 - \omega + J_{SI}m)\delta_{m,m'}, \quad [2]$$

where ω_0 is the Larmor frequency of spin S ; m is the state of spin I ; J_{SI} is the SI scalar coupling constant; and $\delta_{m,m'}$ is the Kronecker delta.

The elements of the $(2I + 1) \times (2I + 1)$ matrix \mathbf{A} are given by

$$A_{m,m'} = (-1/T_2(S) - 1/\tau_m)\delta_{m,m'} + R_{m,m'}, \quad [3]$$

where $(1/\pi T_2(S))$ is the natural linewidth of any one of the $(2I + 1)$ components of the S multiplet in the absence of the relaxation of the spin I ; $R_{m,m'}$ is the total probability per

INTRODUCTION

Recently we reported (1) the first investigation and analysis of the effects of interference terms on the lineshape of a spin $\frac{1}{2}$ J -coupled to a high-spin nucleus undergoing quadrupolar and chemical shift anisotropy (CSA) relaxations. Such interference terms arising from these two interactions of rank 2 when they have the same correlation times lead to differential line broadening giving rise to asymmetric lineshapes. This was observed on the spectra of the ^{31}P nucleus J -coupled to a ^{59}Co nucleus in some tetrahedral clusters $\text{HFeCo}_3(\text{CO})_{11}\text{L}$ with a phosphorus ligand bound to a cobalt atom. The lineshape analysis of ^{31}P spectra was carried out with the formalism derived by Werbelow *et al.* (2) which is suited to the case of a high-spin nucleus having coincident and axially symmetric quadrupolar and CSA tensors. This situation is presumably not fulfilled for the spin system encountered in tetrahedral carbonyl clusters, as has been reported (3) in a recent solid-state ^{59}Co NMR study showing that both tensors are noncoincident and nonaxial.

The lineshapes in the case of general noncoincident quadrupolar and CSA tensors have not been studied in contrast to the widely studied case (4–6) of dipolar and CSA tensors for which it has been shown that the lineshapes depend on tensorial parameters (5, 7–10). Hence, we have derived a

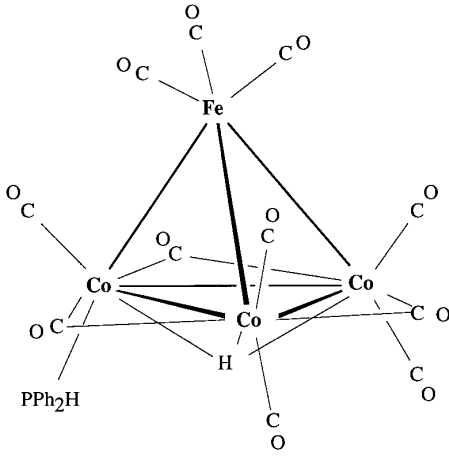


FIG. 1. Spatial view of the cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$.

unit time of transitions occurring between the states m and m' of the spin I ; and τ_m is the average lifetime of the state m of spin I expressed by

$$\tau_m^{-1} = \sum_{m'}^{m' \neq m} R_{m,m'}. \quad [4]$$

Depending on the strengths of the interactions of spin I and also of the molecular motion the transition probabilities $R_{m,m'}$ ($m \neq m'$) are given by

$$R_{m,m'} = \int_{-\infty}^{+\infty} \overline{\langle m | H(t) | m' \rangle \langle m | H(t + \tau) | m' \rangle^*} e^{-i\omega_{m,m'}\tau} d\tau. \quad [5]$$

The bar denotes an ensemble average; $H(t)$ is the time-dependent relaxation Hamiltonian which may be written as the sum of all relaxation interactions μ involving the spin I : $H(t) = \sum_{\mu} H_{\mu}(t)$. These various interactions, in terms of spherical irreducible tensors, are expressed in the laboratory frame (Lab) by

$$H_{\mu}(t) = \xi_{\mu} \sum_{q=-L}^L (-1)^q T_{L,q}^{(\mu)} F_{L,-q}^{(\mu)}(\text{Lab}, t), \quad [6]$$

where ξ_{μ} is a constant related to the strength of interaction μ , $T_{L,q}^{(\mu)}$ involves spin operators, and $F_{L,-q}^{(\mu)}$ is a function of space coordinates. The subscript L defines the tensor rank and will be set equal to 2 since we shall limit ourselves to tensors of rank 2, which correspond to the mechanisms considered in this work. By substitution of this equation into Eq. [5], the transition probabilities $R_{m,m'}$ can be readily expressed by

$$R_{m,m'} = \sum_{\mu, \mu'} \sum_{q, q'=-2}^2 (-1)^{q+q'} \langle m | T_{2,q}^{(\mu)} | m' \rangle \times \langle m | T_{2,q'}^{(\mu')} | m' \rangle^* J_{-q,-q'}^{\mu, \mu'}(\omega_{m,m'}), \quad [7]$$

$J_{-q,-q'}^{\mu, \mu'}(\omega_{m,m'})$ being the so-called spectral density function given by

$$J_{-q,-q'}^{\mu, \mu'}(\omega_{m,m'}) = \xi_{\mu} \xi_{\mu'} \int_{-\infty}^{+\infty} \sum_{i,j=-2}^2 F_{2,i}^{(\mu)} F_{2,j}^{(\mu')*} \times \overline{D_{-q,i}^{2*}(\Omega_{\text{Lab},\mu}(t)) D_{-q',j}^2(\Omega_{\text{Lab},\mu'}(t + \tau))} e^{-i\omega_{m,m'}\tau} d\tau. \quad [8]$$

$F_{2,i}^{(\mu)}$ are the irreducible coupling tensor elements in the principal axis system of the interaction μ . They are constant and their orientation dependence is contained in the second-rank Wigner rotation matrix elements $D_{-q,i}^2(\Omega_{\text{Lab},\mu}(t))$. $\Omega_{\text{Lab},\mu}(t)$ is defined by three Eulerian angles ($\alpha_{\text{Lab},\mu}$, $\beta_{\text{Lab},\mu}$, $\gamma_{\text{Lab},\mu}$) and describes the orientation of the principal axes of the tensor μ , relative to laboratory fixed axes, Lab. The other symbols involving μ' have the same meaning.

At this point, we will consider that both μ and μ' are molecular fixed axis systems and have the same motions. Accordingly the choice of the molecular fixed system is arbitrary. If we choose the principal axis system μ' and use Wigner rotation matrices (14) we obtain

$$J_{-q,-q'}^{\mu, \mu'}(\omega_{m,m'}) = \xi_{\mu} \xi_{\mu'} \int_{-\infty}^{+\infty} \sum_{i,j=-2}^2 F_{2,i}^{(\mu)} F_{2,j}^{(\mu')*} \times \sum_{k=-2}^2 \overline{D_{k,j}^2(\Omega_{\mu,\mu'}) D_{-q,i}^{2*}(\Omega_{\text{Lab},\mu}(t)) D_{-q',k}^2(\Omega_{\text{Lab},\mu}(t + \tau))} e^{-i\omega_{m,m'}\tau} d\tau, \quad [9]$$

where $\Omega_{\mu,\mu'}$ brings the μ system into coincidence with the μ' system.

In the following we limit ourselves to the case of isotropic molecular motion described by a single time correlation τ_c in the extreme narrowing conditions, and in the case of an isotropic medium where the orthogonality property of the Wigner elements matrices can be used (15). In this case we can show that the spectral density functions $J_{-q,-q'}^{\mu, \mu'}(\omega_{m,m'})$ are independent of the index q and may be expressed by

$$J^{\mu, \mu'} = \xi_{\mu} \xi_{\mu'} \sum_{i,j=-2}^2 F_{2,i}^{(\mu)} F_{2,j}^{(\mu')*} D_{i,j}^2(\Omega_{\mu,\mu'}) \frac{2\tau_c}{5}. \quad [10]$$

It follows that $R_{m,m'}$ can be readily replaced by the simple expression

$$R_{m,m'} = \sum_{\mu, \mu'} S_{m,m'}^{\mu, \mu'} J^{\mu, \mu'}, \quad [11]$$

where the quantity $S_{m,m'}^{\mu,\mu'}$ is a spin operator given by

$$S_{m,m'}^{\mu,\mu'} = \sum_{q=-2}^2 \langle m | T_{2,q}^{(\mu)} | m' \rangle \langle m | T_{2,q}^{(\mu')} | m' \rangle^*. \quad [12]$$

This expression will reduce considerably the computational task of evaluating the transition probabilities $R_{m,m'}$. This will be shown below in the case of interest in the present work, namely the case of the quadrupolar and chemical shift anisotropy interactions.

In this case, the total relaxation Hamiltonian is $H(t) = H_Q(t) + H_{CSA}(t)$. The subscripts Q and CSA refer, respectively, to the quadrupolar and chemical shift anisotropy interactions. The interaction constants introduced in Eq. [6] in terms of the quadrupole moment (Q) and the shift anisotropy ($\Delta\sigma$) are defined as $\xi_Q = (\frac{1}{4})\sqrt{\frac{3}{2}}(1/I(2I-1)) (e^2qQ/\hbar)$ and $\xi_{CSA} = (1/\sqrt{6})\gamma B_0\Delta\sigma$, where the symbols have their usual meaning.

According to the conventions used in this work (Eq. [6]), the spin operators and the irreducible coupling tensor elements in the principal axis system introduced in Eq. [8] are defined through the relationships given elsewhere (16).

The quadrupolar and CSA interactions give rise to relaxation mechanisms characterized, respectively, by the relaxation times (T_{1Q}, T_{2Q}) and (T_{1CSA}, T_{2CSA}). Under the conditions of extreme narrowing and single correlation time τ_c they are given by (11)

$$\frac{1}{T_{1Q}} = \frac{1}{T_{2Q}} = \frac{4}{5} (2I-1)(2I+3) \left(1 + \frac{\eta_Q^2}{3}\right) \xi_Q^2 \tau_c$$

$$\frac{1}{T_{1CSA}} = \frac{6}{7} \frac{1}{T_{2CSA}} = \frac{4}{5} \left(1 + \frac{\eta_{CSA}^2}{3}\right) \xi_{CSA}^2 \tau_c, \quad [13]$$

η_Q and η_{CSA} being the asymmetry parameters of the quadrupolar and CSA coupling tensors, respectively.

According to Eq. [7] and using relation [11], the transition probabilities $R_{m,m'}$ are defined as the sum of three terms:

$$R_{m,m'} = S_{m,m'}^Q J^Q + S_{m,m'}^{CSA} J^{CSA} + 2S_{m,m'}^{Q,CSA} J^{Q,CSA}. \quad [14]$$

The first two terms are the usual contributions of quadrupolar and CSA interactions and involve, respectively, the autocorrelation spectral densities J^Q and J^{CSA} . The third term is the CSA–quadrupolar interference term which involves the cross-correlation spectral density $J^{Q,CSA}$. The calculations of J^Q and J^{CSA} lead to the well-known expressions (11)

$$J^Q = \xi_Q^2 \left[1 + \frac{\eta_Q^2}{3}\right] \frac{2\tau_c}{5}$$

$$J^{CSA} = \xi_{CSA}^2 \left[1 + \frac{\eta_{CSA}^2}{3}\right] \frac{2\tau_c}{5}. \quad [15]$$

The calculation of $J^{Q,CSA}$ using relation [10] for a given orientation of the CS tensor relative to the quadrupolar tensor specified by $\Omega_{Q,CSA} = (\alpha, \beta, \gamma)$ yields the following expression:

$$J^{Q,CSA} = \xi_Q \xi_{CSA} \frac{\tau_c}{5} \times \left[(3 \cos^2 \beta - 1) \right. \\ \left. - \sin^2 \beta (\cos(2\alpha)\eta_Q + \cos(2\gamma)\eta_{CSA}) \right. \\ \left. + ((\cos^2 \beta + 1)\cos(2\alpha)\cos(2\gamma)) \right. \\ \left. - 2 \sin(2\alpha)\cos(\beta)\sin(2\gamma) \right] \frac{\eta_Q \eta_{CSA}}{3}. \quad [16]$$

Note that if it concerns a single interaction (Q or CSA) this expression with the three Euler angles equal to zero ($\alpha = 0, \beta = 0, \gamma = 0$) gives those of Eq. [15].

For the calculations of $S_{m,m'}^Q, S_{m,m'}^{CSA}$, and $S_{m,m'}^{Q,CSA}$ according to Eq. [12], the use of the expressions of spin operators (16) and of their properties yields the following nonzero terms:

$$S_{m,m\pm 1}^Q = \langle m | T_{2,\mp 1}^Q | m \pm 1 \rangle^2 \\ = (2m \pm 1)^2 (I \pm m + 1)(I \mp m)$$

$$S_{m,m\pm 2}^Q = \langle m | T_{2,\mp 2}^Q | m \pm 2 \rangle^2 \\ = (I \pm m + 2)(I \mp m - 1)(I \pm m + 1)(I \mp m)$$

$$S_{m,m\pm 1}^{CSA} = \langle m | T_{2,\mp 1}^{Q,CSA} | m \pm 1 \rangle^2 \\ = (I \pm m + 1)(I \mp m)$$

$$S_{m,m\pm 1}^{Q,CSA} = \langle m | T_{2,\mp 1}^Q | m \pm 1 \rangle \langle m | T_{2,\mp 1}^{CSA} | m \pm 1 \rangle \\ = (2m \pm 1)(I \pm m + 1)(I \mp m). \quad [17]$$

Finally, the calculation using these expressions and those of spectral densities (Eqs. [15] and [16]) yields, in terms of transversal relaxation times (Eq. [13]), the following non-zero transition probabilities,

$$R_{m,m\pm 2} = \frac{(I \pm m + 2)(I \mp m - 1)(I \pm m + 1)(I \mp m)}{2(2I + 3)(2I - 1)} \frac{1}{T_{2Q}}$$

$$R_{m,m\pm 1} = \frac{(I \pm m + 1)(I \mp m)}{2} \\ \times \left[\frac{(2m \pm 1)^2}{(2I + 3)(2I - 1)} \frac{1}{T_{2Q}} + \frac{6}{7} \frac{1}{T_{2CSA}} \right. \\ \left. + \phi K \sqrt{\frac{6}{7}} \frac{(2m \pm 1)}{\sqrt{(2I + 3)(2I - 1)}} \frac{1}{\sqrt{T_{2Q} T_{2CSA}}} \right]$$

$$\begin{aligned}
K = & \frac{1}{\sqrt{(1 + \eta_Q^2/3)(1 + \eta_{CSA}^2/3)}} \\
& \times \left[(3 \cos^2 \beta - 1) - \sin^2 \beta (\cos(2\alpha) \eta_Q \right. \\
& + \cos(2\gamma) \eta_{CSA}) + ((\cos^2 \beta + 1) \cos(2\alpha) \\
& \times \cos(2\gamma) - 2 \sin(2\alpha) \cos(\beta) \sin(2\gamma)) \frac{\eta_Q \eta_{CSA}}{3} \left. \right], \quad [18]
\end{aligned}$$

ϕ being equal to +1 if the sign of the product of the quantities $\chi = e^2qQ/h$ and $\Delta\sigma$ is positive and equal to -1 for the opposite case. The two equations correspond to the probability that a nucleus in state m undergoes two-quantum and one-quantum transitions, respectively. The one-quantum transition involves, in addition to the contribution of quadrupolar and CSA interactions, the CSA–quadrupolar interference term which arises since the two interactions have the same rank and the same correlation time. The incidence of this interference term on the lineshape $I(\omega)$ (Eq. [1]) of the NMR pattern of the S nucleus of spin $\frac{1}{2}$ can be explained by the linewidth of components of the S multiplet. To simplify, we can say that the linewidth is defined by the diagonal elements of matrix \mathbf{A} (Eq. [3]) which depend on the relaxation time, $T_2(S)$, and also on the relaxation of spin I since τ_m is a function of the relaxation times of I (Eqs. [4] and [18]). The contribution of $T_2(S)$ to the linewidth of the components of the S multiplet is the same and can be ignored in this discussion. In the case of a symmetric multiplet each pair of lines related to the states m and $-m$ (the low-frequency component and its corresponding high-frequency component) has the same linewidth. As the width of each line of the multiplet is inversely proportional to the average lifetime of the state corresponding to the transition, the symmetry of the spectrum implies $\tau_m = \tau_{-m}$. This occurs in the cases where the spin I undergoes only one relaxation mechanism or several relaxation mechanisms without interference between them. In the case of relaxation mechanisms giving rise to interference terms, τ_m and τ_{-m} are different and consequently the spectrum is asymmetric. The difference between τ_m and τ_{-m} leads to a quantity involving only interference terms. This is easily shown with the aid of Eqs. [4] and [18] in the case of a quadrupolar nucleus with $I = 1$.

The above equations show that the interference term contains a factor defined by K which depends on the asymmetry parameters η_Q and η_{CSA} and also on the orientation of the CS tensor relative to the quadrupolar tensor specified by the three Euler angles (α , β , γ). The dependence of the interference term on the tensorial parameters will have a direct effect on the lineshapes, notably on their asymmetry. This will be discussed in the following section where three

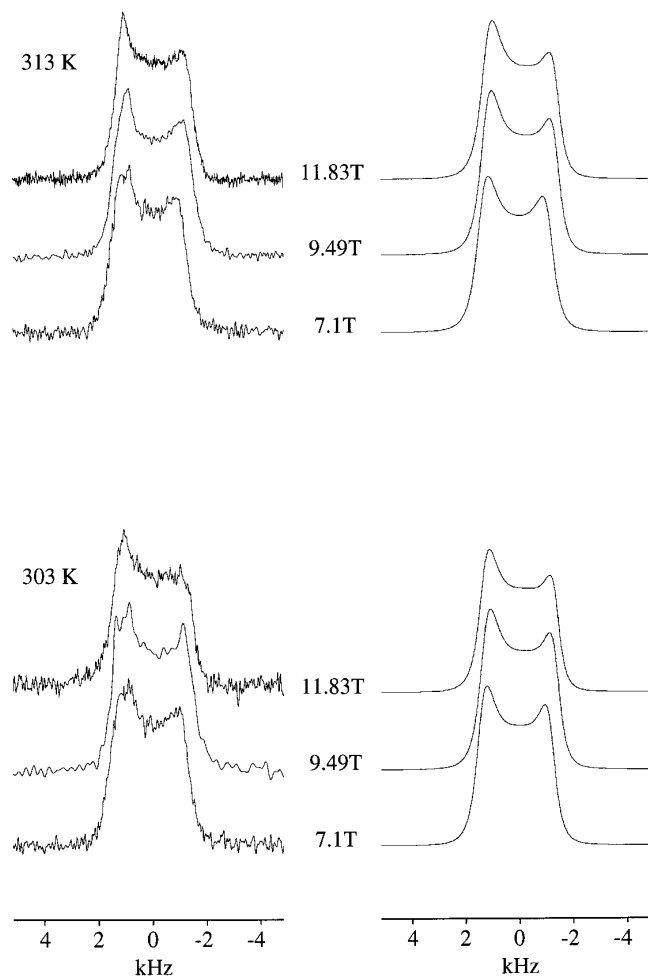


FIG. 2. Experimental $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$ in CD_2Cl_2 at 303 K (bottom) and 313 K (top) at three different fields. The calculated spectra were obtained with the parameters listed in Table 1.

cases are considered, namely coincident–axially symmetric, noncoincident–axially symmetric, and general noncoincident quadrupolar and CSA tensors. Equally, these cases will be considered in the analysis of the spectra of the ^{31}P nucleus J -coupled to a ^{59}Co nucleus encountered in the tetrahedral cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$ with the phosphine ligand bound to a cobalt atom. The ^{31}P spectra are displayed in Fig. 2 along with the temperature and field values used. Experimental conditions for observing these spectra are given elsewhere (I).

ANALYSIS AND DISCUSSION

For the case of interest in the present work, a spin- $\frac{1}{2}$ nucleus (^{31}P) J -coupled to a spin- $\frac{7}{2}$ nucleus (^{59}Co), the transition probabilities required for the calculations were obtained from Eq. [18] for $I = \frac{7}{2}$, yielding the following nonzero transition probabilities:

$$\begin{aligned}
R_{\pm 7/2, \pm 5/2} &= \frac{21}{10} \left[\frac{1}{T_{2Q}} + \frac{10}{7} \frac{1}{T_{2CSA}} \pm \phi K \sqrt{\frac{10}{7} \frac{1}{\sqrt{T_{2Q} T_{2CSA}}}} \right] \\
R_{\pm 7/2, \pm 3/2} &= \frac{7}{10} \frac{1}{T_{2Q}} \\
R_{\pm 5/2, \pm 3/2} &= \frac{8}{5} \left[\frac{1}{T_{2Q}} + \frac{45}{14} \frac{1}{T_{2CSA}} \pm \phi K \sqrt{\frac{45}{14} \frac{1}{\sqrt{T_{2Q} T_{2CSA}}}} \right] \\
R_{\pm 5/2, \pm 1/2} &= \frac{3}{2} \frac{1}{T_{2Q}} \\
R_{\pm 3/2, \pm 1/2} &= \frac{1}{2} \left[\frac{1}{T_{2Q}} + \frac{90}{7} \frac{1}{T_{2CSA}} \pm \phi K \sqrt{\frac{90}{7} \frac{1}{\sqrt{T_{2Q} T_{2CSA}}}} \right] \\
R_{\pm 3/2, \mp 1/2} &= 2 \frac{1}{T_{2Q}} \\
R_{\pm 1/2, \mp 1/2} &= \frac{48}{7} \frac{1}{T_{2CSA}}. \tag{19}
\end{aligned}$$

Under the assumption that other broadening mechanisms of the spin S nucleus are negligible ($1/T_2(S) = 0$), $I(\omega)$ depends on the S chemical shift (ω_S), the coupling constant J_{SI} , the relaxation times of I (T_{2Q} , T_{2CSA}), ϕ ($= \pm 1$), and the value of K . In the following, these cases will be discussed and used to analyze the ^{31}P spectra. In this analysis, (a) it has been assumed that the P–Co system is an IS spin system and (b) the Co relaxation is described with the assumptions of an extreme narrowing, single correlation time.

To analyze the lineshapes, an iterative nonlinear least-squares fitting of the experimental lineshapes has been developed, using the Powell method (17) from the Numerical Recipes package (18). The accuracy of each parameter was determined using the Harwell subroutine SV02A. Computations were performed on a Silicon Graphics computer with a FORTRAN program Quad-CSA written by the authors. The parameters used in the fit of the experimental lineshapes are the coupling constant $J(^{31}\text{P} - ^{59}\text{Co})$, the ^{59}Co relaxation times (T_{2Q} , T_{2CSA}), and the ^{31}P chemical shift $\omega_{31\text{P}}$. In the lineshape analysis we have taken into account the parameter K considering three different cases of quadrupolar and CSA tensors which will now be presented.

Coincident and Axially Symmetric Tensors

In this case where $\eta_Q = 0$, $\eta_{CSA} = 0$, and ($\alpha = 0$, $\beta = 0$, $\gamma = 0$), the quantity K is reduced to 2. For this particular case, the transition probabilities were first calculated for a spin $\frac{1}{2}$ J -coupled to a nucleus of spin $\frac{3}{2}$ (19). Recently, the theoretical lineshape of a spin $\frac{1}{2}$ J -coupled to a nucleus of integer or half-integer spins has been presented and the transition probabilities $R_{m,m'}$ have been calculated up to $I = \frac{9}{2}$

(2). In the work cited, the case of a quadrupolar nucleus with spin $\frac{5}{2}$ has been discussed in detail. More recently, the above explicit expressions with ($K = 2$) were reported along with a discussion of the lineshapes in the case of a spin $\frac{7}{2}$ as the results of lineshape analysis of experimental data (1).

For the compound $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$, the fit using the program Quad-CSA was done for the spectra recorded at three different magnetic fields and two different temperatures. They are displayed in Fig. 2 along with spectra calculated with the fit parameters. The values of the latter with those of relaxation times of the related cobalt nucleus directly measured are listed in Table 1 where $\omega_{31\text{P}}$ is replaced by $\delta_{31\text{P}}$ which corresponds to ^{31}P chemical shifts relative to external H_3PO_4 in H_2O . A discussion of these results in this case of coincident and axially symmetric quadrupolar and CSA tensors has formed the subject of our recent publication (1); here other cases will be examined.

Noncoincident and Axially Symmetric Tensors

For this case where $\eta_Q = 0$ and $\eta_{CSA} = 0$, the quantity K (Eq. [18]) becomes

$$K = (3 \cos^2 \beta - 1)^2. \tag{20}$$

β is the angle between the principal axes of the two tensors. In Fig. 3, the effect of β on the lineshapes through the CSA–quadrupolar interference is illustrated using, in the calculations of $I(\omega)$, a set of values corresponding to those found experimentally on tetrahedral carbonyl clusters. The plots in Fig. 3 are generated for $J_{SI} = 450$ Hz, $T_{2Q} = 500$ μs , $T_{2CSA} = 5$ ms, $\phi = -1$ and for different values of β . These simulations show that the eight lines of the multiplet collapse into a broad pattern. The lack of multiplet structure is due to the combined effects of the relaxation of the quadrupolar nucleus I and of the scalar relaxation of the second kind (11) of the I nucleus on the S nucleus.

The asymmetry of the lineshapes arises from the CSA–quadrupolar interference term. As can be seen in Fig. 3, the asymmetry is maximum for $\beta = 0^\circ$, vanishes for $\beta = 54.7^\circ$ (magic angle), appears with a reversed sense for values $> 54.7^\circ$, and reaches another maximum for $\beta = 90^\circ$. This behavior reflects the dependence of K on β since the asymmetry of lineshapes is directly modulated by K . The values of the latter are between 2 and -1 which correspond to the two maxima of the asymmetry of spectra. The spectrum calculated with $\beta = 0^\circ$ ($K = 2$) is more asymmetrical than that calculated with $\beta = 90^\circ$ ($K = -1$). For values of β increasing from 90° to 180° , the asymmetry will decrease, vanish for $\beta = \pi - 54.7^\circ$ (magic angle), increase with a reversed sense, and reach another maximum for $\beta = 180^\circ$. It must be noted that due to the form of the β dependence of K , the spectra corresponding to β and to its complement $-\beta$ are similar. The result is that, as in solid-state NMR, it

TABLE 1
Parameters Obtained from the Analysis of $^{31}\text{P}\{^1\text{H}\}$ Spectra of the Cluster $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$ along with the Results of the Longitudinal Relaxation-Time Measurements (T_1) of a Cobalt Nucleus Bound to Phosphorus

Temperature (K)	Field (T)	$\delta_{31\text{p}}^a$ (ppm)	$J(^{31}\text{P}-^{59}\text{Co})$ (Hz)	$T_{2\text{Q}}$ (μs)	$T_{2\text{CSA}}$ (ms)	$K/\sqrt{T_{2\text{CSA}}}$ ($\text{ms}^{-1/2}$)	T_1 (μs)
303	7.1	13.2 ± 0.2	450 ± 8	450 ± 40	14 ± 7	0.53	500 ± 40
	9.46	12.6 ± 0.2	454 ± 7	520 ± 50	8 ± 3	0.71	555 ± 20
	11.83	13.0 ± 0.2	452 ± 8	500 ± 50	5 ± 2	0.9	510 ± 20
313	7.1	13.1 ± 0.1	448 ± 5	550 ± 40	17 ± 8	0.49	620 ± 20
	9.46	12.9 ± 0.2	454 ± 8	550 ± 70	10 ± 6	0.63	630 ± 20
	11.83	13.5 ± 0.2	452 ± 5	600 ± 60	7 ± 2	0.76	605 ± 20

^a Relative to external H_3PO_4 in H_2O .

is impossible to distinguish between the two values of the angle between the principal axes of the two tensors.

In Fig. 4, the effect of β on the lineshapes is presented for a poorly resolved multiplet. The spectra correspond to a spin- $\frac{1}{2}$ nucleus J -coupled to a spin- $\frac{7}{2}$ nucleus calculated for $J_{SI} = 450$ Hz, $T_{2\text{Q}} = 50$ μs , $T_{2\text{CSA}} = 50$ ms, $\phi = -1$ and for different values of β varying from 0° to 180° . These simulations show that for values of β increasing from 0° to 54.7° the resolution of the multiplet and the asymmetry decrease, leading to a symmetric shape. The opposite behavior of the lineshape of the multiplet is obtained for values of β increasing until $\beta = 90^\circ$. For values of β between 90° and 180° the lineshapes behave as indicated in the above case. As can be seen in Figs. 3 and 4, the change of the sense of the asymmetry of the lineshape is linked to the sign of the K values. This point will be tackled after a brief discussion about the general case.

For the $^{31}\text{P}-^{59}\text{Co}$ spin system in $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$, since the relaxation of the ^{59}Co nucleus by the CSA mechanism is weaker than the quadrupolar mechanism (I) as in the case of other clusters (20–22), the transition probabilities $R_{m,m'}$ and consequently the lineshapes will depend on $1/T_{2\text{Q}}$ and $K/\sqrt{T_{2\text{Q}}T_{2\text{CSA}}}$ but not on $1/T_{2\text{CSA}}$. The result is that the lineshape analysis may provide only $T_{2\text{Q}}$ and the ratio $K/\sqrt{T_{2\text{CSA}}}$. As the values of K and $T_{2\text{CSA}}$ are found to be correlated, the recourse to a new fitting of the experimental lineshapes is useless since $K/\sqrt{T_{2\text{CSA}}}$ can be determined using the results obtained in the case of coincident and axially symmetric quadrupolar and CSA tensors. For $K = 2$, the values of the ratio are presented in Table 1. Of course the values of the other parameters, except $T_{2\text{CSA}}$ which is undetermined, are the same. Since K is between -1 and 2 , $T_{2\text{CSA}}$ is therefore inferior or equal to that obtained in the case of coincident and axially symmetric quadrupolar and CSA tensors (Table 1). However, the presence of the asymmetry of the lineshapes enables us to exclude values of K close to zero and as a consequence we conclude that β is far from the magic angle. In the same way, we can eliminate the low values of K which lead to low values of $T_{2\text{CSA}}$ in the range

of the $T_{2\text{Q}}$ values since the CSA contribution to the cobalt relaxation must remain weak. Further discussions on these parameters of the $^{31}\text{P}-^{59}\text{Co}$ spin system require information, not available to date, about the two quadrupolar and CSA tensors. These conclusions are equally true for the lineshape analysis of the case of general noncoincident quadrupolar and CSA tensors which will now be presented.

General Noncoincident Tensors

For this case, the CSA–quadrupolar interference term involves a quantity K depending on the asymmetry parameters η_{Q} and η_{CSA} and also on the three Euler angles (α , β , γ). As in the above case, the lineshapes are determined by $T_{2\text{CSA}}$ and $T_{2\text{Q}}$ and also by the value of K . The expression of K shows that the values of K range from -1 to 2 and that a given value of K corresponds to several sets of the values of η_{Q} , η_{CSA} , and the three Euler angles (α , β , γ). This indicates that the lineshape analysis may lead to K but not to the values of each tensorial parameter.

For the $^{31}\text{P}-^{59}\text{Co}$ spin system in $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$, using this case of general noncoincident CSA and quadrupolar tensors, the lineshape analysis leads to the same results as in the above case. Hence, only the values of the ratio $K/\sqrt{T_{2\text{CSA}}}$, obtained above and listed in Table 1, are accessible. The $T_{2\text{CSA}}$ value must be inferior or equal to that obtained in the former case of coincident and axially symmetric quadrupolar and CSA tensors. The values of K cannot be close to zero and the other parameters remain unchanged. As stated above, the lack of information about the two related tensors limits our discussion.

The last point to consider in this section concerns the sense of the asymmetry of the lines. This point has been also discussed in the case of dipolar and CSA interactions (8, 23–25) which presents similarities with the related case. For the quadrupolar and CSA interactions, the sense of the asymmetry depends on the sign of the three quantities J_{SI} , ϕ , and K . Since the sign of ϕ depends on the product of $\chi = e^2qQ/h$ and $\Delta\sigma$, the sense of the asymmetry will depend on the product of the four quantities. The general rule for

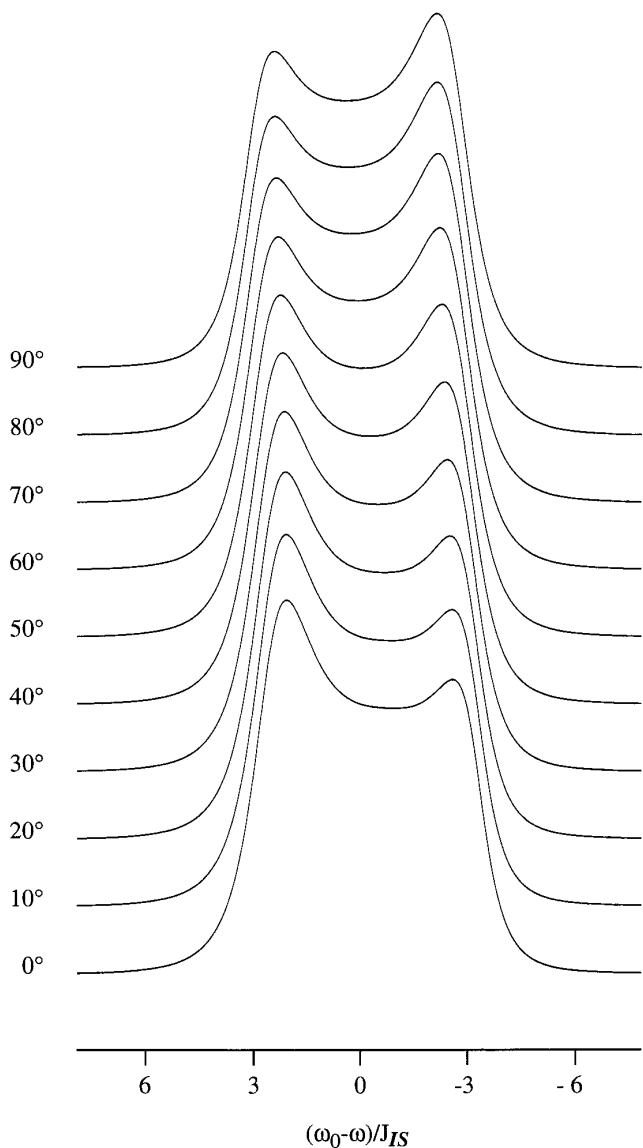


FIG. 3. Theoretical spectra for a spin-1/2 nucleus J -coupled to a spin-7/2 nucleus in the case of noncoincident and axially symmetric tensors. The plots versus reduced frequency $(\omega_0 - \omega)/J_{SI}$ correspond to $J_{SI} = 450$ Hz, $T_{2Q} = 500 \mu\text{s}$, $T_{2CSA} = 5$ ms, $\phi = -1$ and to different values of β (left side).

the sense of the asymmetry of the spectrum is as follows. If the quantity $J \cdot \chi \cdot \Delta\sigma \cdot K$ is negative, the spectrum is asymmetrical with the highest maximum on the low-frequency side of the pattern, and with the asymmetry reversed if the sign of $J \cdot \chi \cdot \Delta\sigma \cdot K$ is positive. The spectra displayed in Fig. 3 are calculated for positive values of the product $J \cdot \chi \cdot \Delta\sigma$. The highest maximum is on the left side if K is positive and is on the right side if K is negative.

The asymmetry of the ^{31}P spectra shows that the sign of the product $J \cdot \chi \cdot \Delta\sigma \cdot K$ is negative. Since the coupling constant between phosphorus and cobalt nuclei seems to be

positive (26), the sign of $\chi \cdot \Delta\sigma \cdot K$ is therefore negative. For the case of coincident and axially symmetric quadrupolar and CSA tensors K is positive ($K = 2$) and consequently the sign of $\chi \cdot \Delta\sigma$ is negative. The absolute sign of these two quantities requires supplementary information which is not available.

Throughout this paper we have used the model of isotropic molecular motion described by a single correlation time. This model allows a complete calculation of the lineshape and shows the influence of the relative orientation of the related tensors on the lineshapes. Nevertheless it is clear that the presence of anisotropic interactions often implies a nonisotropic molecular motion described by multiple correlation times. This situation introduces a complexity in the calculation of lineshapes.

CONCLUSION

In this paper, we have derived a formalism for calculating the lineshapes of a spin $\frac{1}{2}$ J -coupled to a high-spin nucleus undergoing quadrupolar and chemical shift anisotropy relaxations in the case of general noncoincident quadrupolar and CSA tensors. The expressions show that the CSA–quadrupolar interference term which is responsible for the asymmetry of lines involves a factor K depending on the asymmetry parameter η_Q and η_{CSA} and on the three Euler angles (α , β ,

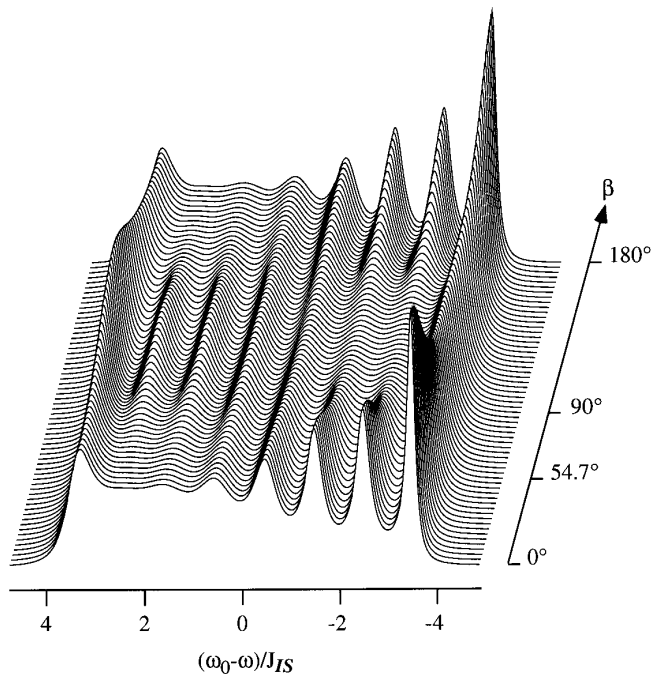


FIG. 4. Theoretical spectra for a spin-1/2 nucleus J -coupled to a spin-7/2 nucleus in the case of noncoincident and axially symmetric tensors. The plots versus reduced frequency $(\omega_0 - \omega)/J_{SI}$ correspond to $J_{SI} = 450$ Hz, $T_{2Q} = 50 \mu\text{s}$, $T_{2CSA} = 50$ ms, $\phi = -1$ and to values of β varying from 0° to 180° .

γ). The values of K range from -1 to 2 . The value $K = 2$ corresponds to the case of coincident and axially symmetric quadrupolar and CSA tensors. For the case of axially symmetric quadrupolar and CSA tensors with the magic angle between the principal axes K is equal to zero and the line-shapes are symmetric.

Using this general formalism, the lineshape analysis of the ^{31}P spectra in $\text{HFeCo}_3(\text{CO})_{11}\text{PPh}_2\text{H}$ confirms the results obtained considering the case of coincident and axially symmetric quadrupolar and CSA tensors (I). The same values are obtained for the ^{31}P chemical shift $\delta_{31\text{P}}$, $J(^{31}\text{P}-^{59}\text{Co})$, and $T_{2\text{Q}}(^{59}\text{Co})$. However, $T_{2\text{CSA}}(^{59}\text{Co})$ and K are found to be correlated and only the ratio $K/\sqrt{T_{2\text{CSA}}(^{59}\text{Co})}$ is provided by the lineshape analysis. The measure of $T_{2\text{CSA}}(^{59}\text{Co})$ requires information about the two tensors. For this work, solid-state NMR can be useful.

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