coupling that leads to increased bonding. In the absence of such obvious spin-coupling alternatives, we have continued with calculations on states that can dissociate to ground-state fragments. The geometries were restricted to essentially the same (both in induced-dipole interaction. A few animation sequences from our Nb3 calculations for the rhombus-like arrangement. The planar equilibrium geometry of the dimer cation is 0.39 and 1.77 eV, respectively. The neutral Nb-Nb distance is slightly shorter than in the cation. We have prepared several animation sequences from our Nb3 calculations for the Macintosh II machine using visualization software developed at the NCSA. (These animation sequences are available from the author upon request.) In these sequences it is easily seen that the electron density that leaves the 4A1 state of the Nb3 molecule upon ionization is very much delocalized. Also the increased bonding electron density between the Nb2 and Nb* fragments is clearly evident. From the Mulliken populations we observe that the bonding in the 4A1 state of the Nb3* molecule is primarily through the mixing of the 5s orbital on the cation with a dimer orbital of considerable d4 character. At the C2v equilibrium geometry of the Nb3 cation the Nb that is chemisorbed onto the dimer supports a net positive charge of only 0.4 and possesses 2.76 s and 3.83 d electrons (the atomic values are 3.00 s and 4.00 d electrons). Hence a large amount of charge has transferred to the chemisorbed Nb. Considering the trimer molecule to be made of a dimer molecule and a chemisorbed Nb atom, one can construct an MO diagram by taking plus and minus combinations of the dimer orbitals with the atomic orbitals. This simple MO picture leads to the conclusion that the 5s electron on the atom (which leaves upon ionization) must go into an antibonding orbital. This explains the increased bonding upon ionization.

We have performed calculations on the planar Nb2 and Nb3* systems, and we find minimum energy configurations for both systems in the rhombus arrangement. The planar equilibrium structures we obtain for the neutral and cation of Nb3 are essentially the same (both in C2v). There is a significant lengthening of the shortest Nb-Nb distance as compared to the dimer bond length, and, the two sides of the rhombus are different by only 0.3 Å. The value of the acute rhombus angle in the equilibrium structure is 64°. The value of 4.31 eV we obtain from our RECP-CISD calculations for the ionization potential of Nb3 very nearly coincides with the ionization potential we obtain for Nb2. We obtain a value of 1.07 and 1.68 eV for the dissociation energy of the neutral and cation of Nb4 (dissociation of Nb34Â to Nb34 Â + Nb3) by subtracting the RECP-CISD energy of the rhombus configuration at equilibrium from the RECP-CISD energy we obtain for the rectangular configuration at infinite separation. This was necessary to get an estimate of the Dc's because the Nb3 rhombus SCF calculation did not dissociate properly to two identical Nb3 molecules but instead dissociated asymmetrically. From the Mulliken populations and the molecular orbitals it appears that the primary interaction that binds the two niobium dimers in the Nb3 molecule is the interaction of the empty d6 orbitals on one of the dimer molecules overlapping with the bonding electron density of the other dimer molecule.

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Determination of Tensorial Orientation of Chemical Shift Anisotropy Interaction by Relaxation Studies of 2I(S2) Spin Order in Solution†

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The observation of selective conversion of Zeeman order into a two-spin order, e.g., 2I(S2), of the C-H moiety is made with a coherence transfer technique for measuring the cross correlation of chemical shift anisotropy and dipole–dipole interactions. The temperature-dependent relaxation profiles of the two-spin order are investigated to examine the effect of spin–rotation interaction, which was neglected in a previous study, and subsequently to determine the tensorial orientation of chemical shift anisotropy interaction. Results show excellent agreement with the study from two-dimensional NMR powder spectra.

Introduction

Nuclear magnetic resonance relaxation studies are an important tool for the study of molecular dynamics in liquids. Recent advances in both the NMR theory and the experimental techniques have substantially increased its level of information. The development of multiple quantum relaxation1 has paved new ways to study the molecular dynamics in liquids. The advent of multiple quantum relaxation experiments opens the possibility to select the appropriate spin interaction that generates only a certain order of multiple quantum relaxation. Multiple quantum relaxation

via transverse relaxation for degenerate spin systems has been applied to the study of slow molecular motion in macromolecules and molecular aggregates.\(^\text{2,3}\)

Recently, the development of the theory of differential line broadening may be applied to the study of the cross relaxation between the chemical shift anisotropy (CSA) and the dipole–dipole (DD) interactions.\(^\text{4,5}\) However, both the differential line broadening effect and the generation of the "forbidden" multiple quantum coherence depend on the slow motional correlation time of the system. For those effects to be experimentally observable, via transverse relaxation for degenerate spin systems has been discussed. The effect of I\(^{13}\)C spin-rotation (SR) interaction in the I\(^{13}\)C-IH spin system in the fast motional region. The relaxation profile has been observed by Jaccard et al., and the result was interpreted in terms of the orientation of the I\(^{13}\)C-H internuclear vector with respect to the principal axes of the I\(^{13}\)C CSA tensor. However, the effect of I\(^{13}\)C spin–rotation (SR) interaction was not taken into account in their study. They predicted a somewhat larger value in the angle between the C–H axis and the \(\sigma_{11}\) direction in comparison to the previous study from twodimensional NMR powder spectra.\(^\text{7}\) Also, the use of the enriched carbon-13 sample in their work requires specific labeling that may be too laborious to apply their technique to most cases. Therefore, in this work, a dilute solution of methyl formate with naturally abundant I\(^{13}\)C nuclei is studied by invoking coherence transfer techniques to enhance the signal of two-spin order.\(^\text{8,9}\) The effect of I\(^{13}\)C SR interaction on the relaxation of the two-spin order is discussed, and the tensorial orientation of CSA interaction is reexamined.

### Theory

The pulse sequence used for measuring the relaxation of the 2I\(_{13C}\)S I nuclei basically invokes a coherence transfer sequence as the initial preparation of the spin system

\[
(\pi/2)^{H}_{x} - 1/(2I_{13C-H}) - (\pi/2)^{H}_{y} - 1 - (\pi/2)^{C}_{z} - (\text{FID})
\]

where the spin–proton coupling constant \(J_{C-H}\) is expressed in hertz. The first two-proton 90° pulses are used for generating \(\hat{H} \rightarrow \hat{I}^{13C}\) coherence transfer and the last 90° pulse of I\(^{13}\)C converts the signal of two-spin order for observation. Since the period, \(1/(2I_{13C-H})\), for generating coherence transfer is much shorter than \(T_1\) of the system, it is noted that spin relaxation during this period is neglected. Thus, the initial density matrix just after the preparation of the spin system with coherence transfer is given by

\[
\rho(t=0) \approx (1/4)(1 + \omega_{S}\hat{S}_{z}/kT \pm \omega_{S}(2S_{1/2})/kT) \quad (1)
\]

where \(\omega_{S}\) and \(\omega_{C}\) are the Larmor frequencies of I\(^{13}\)C (denoted as S spin) and \(^{1}\)H (denoted as I spin) nuclei, respectively. The plus/minus sign in the third term of eq 1 is taken according to the phase of the second 90° pulse of proton (\(\phi = \pm \omega_{C}\)). Difference spectra of I\(^{13}\)C with \(\phi = \pm \omega_{C}\) are recorded for each value of the evolution time \(t\) in the pulse sequence. Antiphase doublet spectral lines are observed. As expressed in eq 1, the difference in the intensity of the two (antiphase) lines is related to the evolution time \(2S_{1/2}\) with signal enhancement by a factor of \(\omega_{C}/\omega_{S} \approx \gamma_{I}^{13C}/\gamma_{H} \approx 4\) as compared with the normal I\(^{13}\)C spectra.\(^\text{8}\)

The relaxation processes during time \(\tau\) in which the 2I\(_{13C}\)S coherence evolves may be described by the Redfield theory\(^\text{10}\) with the consideration of CSA interaction at I\(^{13}\)C nuclei and DD interaction between I\(^{13}\)C and \(^{1}\)H. To account for the NMR relaxation processes, the populations of an IS system with two nonequivalent spin-1/2 nuclei may be described by the density matrix operator or in terms of the expectation values of the three operators \(I_{x}, I_{y},\) and \(2I_{13C}S_{z}\).\(^\text{11,12}\) A straightforward calculation based on Redfield’s scheme yields the coupling coefficients that determine the time evolution of these expectation values. The equation of motion has been given explicitly for the I\(^{13}\)C–I\(^{1}\)H spin system with an axially symmetric shielding tensor by Bain and Lynden-Bell\(^\text{13}\) and later modified for the general asymmetric shielding tensor by Jaccard et al.\(^\text{14}\) After the consideration of SR relaxation for I\(^{13}\)C, it becomes

\[
\frac{d}{dt} \left[ \begin{array}{c} \Delta I_{x(t)} \\ \Delta I_{y(t)} \\ \Delta I_{z(t)} \end{array} \right] = \left[ \begin{array}{ccc} A & D & 0 \\ D & B & E \\ 0 & E & C \end{array} \right] \left[ \begin{array}{c} \Delta I_{x(t)} \\ \Delta I_{y(t)} \\ \Delta I_{z(t)} \end{array} \right] \quad (2)
\]

where \(\Delta I_{x(t)} = \langle I_{x}(t) \rangle - \langle I_{x}(\infty) \rangle\) and \(\Delta I_{z(t)} = \langle S_{z}(t) \rangle - \langle S_{z}(\infty) \rangle\). The expectation values at infinite time denote their thermal equilibrium averages. The coupling coefficients are defined by

\[
\begin{align*}
A &= -(10/3)J_{IS,IS} \\
B &= -(10/3)J_{IS,SS} - J_{SR} \\
C &= -2J_{IS,IS} - 4J_{SS} - J_{SR} \\
D &= -(5/3)J_{IS,IS} \\
E &= -4J_{IS}
\end{align*}
\]

where \(J_{IS,IS}, J_{IS,SS}, J_{SR}\), and \(J_{IS,JS}\) represent the spectral density functions for the DD, CSA, SR, and DD-CSA cross relaxations, respectively. For simplicity, only isotropic motion with an extreme narrowing condition is considered, e.g., \(\omega_{C} \gg 1\) where \(\tau_{C} \rightarrow \infty\) and \(\tau_{C} \rightarrow 1\) where \(\tau_{C}\). The reorientation and the angular momentum correlation times of the molecules considered. Other relaxation mechanisms such as remote intramolecular and intermolecular DD interactions are neglected. Thus, the spectral density functions may be simplified into the following expressions

\[
\begin{align*}
J_{IS,IS} &= (3/10)\gamma_{I}^{13C}2\gamma_{H}^{2}h^{2}r^{2}\tau_{c} \\
J_{SS} &= (1/30)\gamma_{S}\gamma_{S}2L(\sigma r) \\
J_{IS,JS} &= -(1/20)\gamma_{I}^{13C}s_{I}^{5}h^{2}r^{3}B_{0}(k\sigma_{xS}\sigma_{yS})\tau_{c} \\
L(\sigma) &= \sigma_{x}^{2} + \sigma_{y}^{2} + \sigma_{z}^{2} - \sigma_{x}\sigma_{y} - \sigma_{x}\sigma_{z} - \sigma_{y}\sigma_{z} \\
K(\sigma_{xS},\sigma_{yS}) &= (\sigma_{x} - \sigma_{y})(3\cos^{2}\theta_{xy} - 1) + (\sigma_{y} - \sigma_{z})(3\cos^{2}\theta_{yz} - 1)
\end{align*}
\]

where \(\sigma_{x}, \sigma_{y},\) and \(\sigma_{z}\) are the principal components of shielding tensor. The angles \(\theta_{xy}\) and \(\theta_{yz}\) define the relative orientation between the IS internuclear vector (\(^{13}\)C–\(^{1}\)H) with respect to the Markoffian limit (\(r_{I} \gg r_{C}\)), the decoupling of orientation and angular moment correlation times leads to the vanishment of the cross-relaxation term of SR interaction with DD or CSA interactions and also gives rise to a relation between \(\tau_{r}\) and \(\tau_{p,13}\) i.e.

\[
\tau_{r} = 1/(6k\tau_{p})
\]
Relaxation Studies of 2JCS Spin Order in Solution

The spectral density function for 13C SR relaxation is represented by

$$J_{SR} = (2kT/3\hbar^2)[C_{11} + C_{22} + C_{33}]t_f$$

where \( I \) is the moment of inertia of the molecule, and \( C_{11}, C_{22}, \) and \( C_{33} \), expressed in \( \text{g cm}^2 \), are the diagonal elements of the SR interaction tensor in the principal inertial axis system for carboxyl carbon of HCOOCD3.

The time evolution of \( \langle \Delta S_i(t) \rangle \) may be solved from eq 2 with the known values of \( \langle \Delta I(O) \rangle \), \( \langle \Delta S_i(O) \rangle \), and \( 2JCS(O) \) that may be calculated with the help of the initial density matrix given in eq 1 and the final equilibrium distribution. We obtain \( \Delta I(O) = -h\omega_s/(4kT) \), \( \Delta S_i(O) = 0 \), and \( 2JCS(O) = \pm h\omega_s/(4kT) \).

The difference in the intensity, denoted by \( \Delta l_0 \), of the two (antiphase) lines at time \( t \) may be calculated from the difference in \( I_0(t) \) obtained with the variation of the sign in the \( 2JCS(O) \) term. It may be shown that the initial intensity, denoted by \( I_0 \), of the individual spectral line in the antiphase doublet is directly proportional to \( \langle \gamma \langle \gamma \rangle \rangle \rangle = (\pm h\omega_s/(4kT)) \). Both of the experimental and calculated results are expressed in terms of differential intensity ratio \( \Delta l/\Delta l_0 \).

**Experimental Section**

The measurement of 2JCS spin order has been performed for the carboxyl carbon of methyl formate (HCOOCD3), which was prepared by the esterification of formic acid with excess methanol-d4 in the presence of trace sulfuric acid. A 15 vol % solution in methanol-d4 was sealed in vacuo in a 10-mm tube after three freeze-pump-thaw cycles. Carbon-13 spectra were measured at various temperatures with a Bruker MSL-300 spectrometer operating at 7.05 T after 48 scans with a relaxation delay of 1.50 s set for each scan. The temperatures are controlled within \( \pm 0.5^\circ \text{C} \).

**Results and Discussion**

In the following calculation, \( \tau = 1.101 \text{ Å} \) is taken as the proton–carbon internuclear distance in methyl formate. The principal values of the carboxyl shielding tensor in methyl formate are obtained from solid-state powder spectra. They are \( \sigma_{11} = -90.5 \text{ ppm} \), \( \sigma_{22} = 29.1 \text{ ppm} \), and \( \sigma_{33} = 61.5 \text{ ppm} \) with respect to the isotropic shift.

It is found that the most shielded element of the tensor, \( \sigma_{33} \), is nearly parallel to the normal to the COO plane. The orientations of the \( \sigma_{11} \) and \( \sigma_{22} \) axes are much more sensitive to the local structure around the carboxyl group. It appears that increasing the double-bond character of the C–O bond moves \( \sigma_{22} \) closer to the C–O direction. Assignment of \( \sigma_{11} \) to \( \sigma_{22} \) and \( \sigma_{33} \) to \( \sigma_n \) may be made, and \( \theta_{se} = 90^\circ \) is utilized in this work. The determination of the \( \theta_{se} \) angle is discussed in the following.

The various components of the SR interaction tensor for 13C spins in HCOOCD3 are not known experimentally. They may be estimated on the basis of chemical shift data. From the experimental 13C SR constant and the theoretical diagonal magnetic shielding constant of 13CO, the average absolute shielding constant for a given 13C nucleus may be expressed by

$$\sigma = 261.8 + 0.779C_{13CO}/3$$

A similar expression may be obtained for the diagonal components of the magnetic shielding tensor. It yields

$$\sigma_{an} = 261.8 + 0.779C_{13CO}_{an}$$

Here, \( \sigma \) is in parts per million, \( C_{13CO} \) in kilohertz, and \( I_{an} \) in 10^{-40} g cm^2. The first term on the right-hand side of eq 9 and 10 is the contribution due to the total electrostatic potential at the

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important, without the SR relaxation term, the magnitude of the differential intensity ratio is rather sensitive to the variations of the $\delta_{sr}$ values but not to the variation of $\tau_r$. Without the CSA–DD cross-relaxation term, the calculated signal intensity of the $2^1S_0$ spin order vanishes. Thus, the variation of the differential intensity cross-relaxation term, the calculated signal intensity of the $2^1S_0$ spin order, which can be implemented to determine the tensorial orientation of CSA interaction. However, it is noted that certain inherent limitations do exist. The effect of SR interaction not only accelerates the relaxation but also significantly reduces the relaxation intensity. In applying this method, large $^{13}$C random field interactions may sequester two-spin order. Therefore, proper preparation of the sample by minimizing the effect of intermolecular spin interactions and making the measurements at temperatures as low as possible is required for the application of this method.

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Kinetics and Product Vibrational Energy Disposal Dynamics in the Reaction of Chlorine Atoms with D$_2$S

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The reaction of chlorine atoms with D$_2$S, forming DCI and DS, has been investigated by using time-resolved infrared diode laser absorption spectroscopic probing of both the D$^{33}$Cl and D$^{34}$Cl product. The rate constant obtained by using the pseudo-first-order method was found to be $3.2 (\pm 0.3) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The vibrational energy distribution in the DCI fragment was also determined, with $33 (\pm 7)$% of the product DCI formed in $v = 0$, $56 (\pm 7)$% in $v = 1$ and $11 (\pm 3)$% in $v = 2$. These results are consistent with the known vibrational population inversion between the $v = 0$ and $v = 1$ states of DCI previously observed for this reaction. The advantage of using infrared absorption measurements, rather than infrared emission, to determine vibrational distributions is that the $v = 0$ population can be directly measured. The relative vibrational populations were modeled by using two different prior functions, both of which led to linear surprisal plots.

Introduction

Gas-phase chlorine atoms play critical roles in atmospheric chemistry, surface etching, and the production of chemical lasers. One important class of chlorine reactions is the abstraction of hydrogen atoms from a wide variety of precursors. The fundamental issues in these systems involve the determination of reaction rates as well as the characterization of the energy disposal dynamics in the reaction products. One well-studied example is the reaction of chlorine atoms with H$_2$S where the primary reaction leads to the formation of HCI.

The rates of the primary and secondary reactions in this system have been obtained by a number of different experimental techniques. The distribution of internal energy in the products is

\begin{equation}
\text{Cl} + \text{H}_2\text{S} \rightarrow \text{HCl} + \text{HS}
\end{equation}