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 C_{2v} nuclear configurations even though, in the case of the cation, it has been shown²⁷ that the linear form should be favored at long range by the monopole/induced-dipole interaction.

We observe that the structure of the dimer does not change substantially as a third niobium atom chemisorbs onto it. The binding energy of the niobium and niobium cation to the Nb_2 molecule is 0.39 and 1.77 eV, respectively. The neutral Nb– Nb_2 distance is slightly shorter than in the cation. We have prepared several animation sequences from our Nb_3 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 6A_1 state of the Nb_3 molecule upon ionization is very much delocalized. Also the increased bonding electron density between the Nb_2 and Nb^+ fragments is clearly evident. From the Mulliken populations we observe that the bonding in the 5A_1 state of the Nb_3^+ molecule is primarily through the mixing of the 5s orbital on the cation with a dimer orbital of considerable d_σ character. At the C_{2v} equilibrium geometry of the Nb_3 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 Nb_4 and Nb_4^+ 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 Nb_4 are essentially the same (both in C_{2h}). 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 Nb_4 very nearly coincides with the ionization potential we obtain for Nb_3 . We obtain a value of 1.07 and 1.68 eV for the dissociation energy of the neutral and cation of Nb_4 (dissociation of $Nb_4^{(+)}$ to $Nb_2^{(+)} + Nb_2$) 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 D_e 's because the Nb_4 rhombus SCF calculation did not dissociate properly to two identical Nb_2 molecules but instead dissociated asymmetrically.³⁵

From the Mulliken populations and the molecular orbitals it appears that the primary interaction that binds the two niobium dimers in the Nb_4 molecule is the interaction of the empty d_δ orbitals on one of the dimer molecules overlapping with the bonding electron density of the other dimer molecule. The NCSAImage animation sequences of the ionization of Nb_4 clearly show that the maximum bonding occurs between the atoms on the short diagonal and that this diagonal bonding is greater in all four cation states (obtained by ejecting in turn a B_u , B_g , A_g , and A_u electron, and this list is in the order of cation stabilities). The four ionization potentials are 3.98, 4.18, 5.07, and 5.80 eV, respectively, at the Hartree–Fock level. The animation sequences also reveal that the entire Nb_4 molecule is involved in the ionization so that it is not a localized phenomenon. The relatively strong influence that the niobium dimers have on each other via the empty d_δ – Nb_2 bond HOMO/LUMO interaction is suggestive of a similar interaction possibly being involved in the dehydrogenation chemistry of niobium clusters. Two Nb_4 molecules might exploit the remaining empty d_δ orbitals in the formation of a stable Nb_8 cluster.

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(35) Bauschlicher, C. W.; Taylor, P. R. *Theor. Chim. Acta* **1988**, *74*, 63.

Determination of Tensorial Orientation of Chemical Shift Anisotropy Interaction by Relaxation Studies of $2I_zS_z$ Spin Order in Solution[†]

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The observation of selective conversion of Zeeman order into a two-spin order, e.g., $2I_zS_z$, 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

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(1) Wokaun, A.; Ernst, R. R. *Mol. Phys.* **1987**, *36*, 317.

via transverse relaxation for degenerate spin systems has been applied to the study of slow molecular motion in macromolecules and molecular aggregates.^{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.^{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, this requirement places a rather strict limitation on the system suitable for such study. It may be removed by using the selective conversion of the Zeeman order into a heteronuclear two-spin order (e.g., $2I_zS_z$) to measure the cross relaxation of DD and CSA interactions in a ^{13}C - ^1H spin system in the fast motional region. The relaxation profile has been observed by Jaccard et al.,⁶ and the result was interpreted in terms of the orientation of the ^{13}C - ^1H internuclear vector with respect to the principal axes of the ^{13}C CSA tensor. However, the effect of ^{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 σ_{11} direction in comparison to the previous study from two-dimensional NMR powder spectra.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 ^{13}C nuclei is studied by invoking coherence transfer techniques to enhance the signal of two-spin order.^{8,9} The effect of ^{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 $2I_zS_z$ spin order basically invokes a coherence transfer sequence as the initial preparation of the spin system

$$(\pi/2)_x^H - 1/(2J_{\text{C-H}}) - (\pi/2)_\phi^H - t - (\pi/2)_y^C - (\text{FID})$$

where the spin-spin coupling constant $J_{\text{C-H}}$ is expressed in hertz. The first two-proton 90° pulses are used for generating $^1\text{H} \rightarrow ^{13}\text{C}$ coherence transfer and the last 90° pulse of ^{13}C converts the signal of two-spin order for observation. Since the period, $1/(2J_{\text{C-H}})$, 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 transfer⁸ is given by

$$\rho(t=0) \simeq (1/4)(1 + \hbar\omega_S S_z/kT \pm \hbar\omega_I(2S_z I_z)/kT) \quad (1)$$

where ω_S and ω_I are the Larmor frequencies of ^{13}C (denoted as S spin) and ^1H (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 ($\phi = \pm y$). Difference spectra of ^{13}C with $\phi = \pm y$ 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 of $2S_z I_z$ terms with signal enhancement by a factor of $\omega_I/\omega_S = \gamma_{\text{H}}/\gamma_{\text{C}} \simeq 4$ as compared with the normal ^{13}C spectra.⁸

The relaxation processes during time t in which the $2I_zS_z$ coherence evolves may be described by the Redfield theory¹⁰ with the consideration of CSA interaction at ^{13}C nuclei and DD interaction between ^{13}C and ^1H . 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_z , S_z , and $2I_zS_z$.^{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 ^{13}C - ^1H spin system with an axially symmetric shielding tensor by Bain and Lynden-Bell¹¹ and later modified for the general asymmetric shielding tensor by Jaccard et al.⁶ After the consideration of SR relaxation for ^{13}C , it becomes

$$\frac{d}{dt} \begin{bmatrix} \langle \Delta I_z(t) \rangle \\ \langle \Delta S_z(t) \rangle \\ \langle \Delta 2I_zS_z(t) \rangle \end{bmatrix} = \begin{bmatrix} A & D & 0 \\ D & B & E \\ 0 & E & C \end{bmatrix} \begin{bmatrix} \langle \Delta I_z(t) \rangle \\ \langle \Delta S_z(t) \rangle \\ \langle \Delta 2I_zS_z(t) \rangle \end{bmatrix} \quad (2)$$

where $\langle \Delta I_z(t) \rangle \equiv \langle I_z(t) \rangle - \langle I_z(\infty) \rangle$ and $\langle \Delta S_z(t) \rangle \equiv \langle S_z(t) \rangle - \langle S_z(\infty) \rangle$. The expectation values at infinite time denote their thermal equilibrium averages. The coupling coefficients are defined by

$$\begin{aligned} A &\equiv -(10/3)J_{IS,IS} \\ B &\equiv -(10/3)J_{IS,IS} - 4J_{S,S} - J_{\text{SR}} \\ C &\equiv -2J_{IS,IS} - 4J_{S,S} - J_{\text{SR}} \\ D &\equiv -(5/3)J_{IS,IS} \\ E &\equiv -4J_{IS,S} \end{aligned} \quad (3)$$

where $J_{IS,IS}$, $J_{S,S}$, J_{SR} , and $J_{IS,S}$ 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., $\omega\tau_c \ll 1$ and $\omega\tau_j \ll 1$ where τ_c and τ_j are 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

$$\begin{aligned} J_{IS,IS} &\equiv (3/10)\gamma_I^2\gamma_S^2\hbar^2r^{-6}\tau_c \\ J_{S,S} &\equiv (1/30)(\gamma_S B_0)^2 L(\sigma)\tau_c \\ J_{IS,S} &\equiv -(1/20)\gamma_I\gamma_S^2\hbar r^{-3}B_0 K(\sigma, \theta_{xz}, \theta_{yz})\tau_c \end{aligned} \quad (4)$$

where r is the proton-carbon internuclear distance. Also, we define

$$L(\sigma) \equiv \sigma_x^2 + \sigma_y^2 + \sigma_z^2 - \sigma_x\sigma_y - \sigma_y\sigma_z - \sigma_z\sigma_x \quad (5)$$

and

$$K(\sigma, \theta_{xz}, \theta_{yz}) \equiv (\sigma_x - \sigma_z)(3 \cos^2 \theta_{xz} - 1) + (\sigma_y - \sigma_z)(3 \cos^2 \theta_{yz} - 1) \quad (6)$$

where σ_x , σ_y , and σ_z are the principal components of shielding tensor. The angles θ_{xz} and θ_{yz} define the relative orientation between the IS internuclear vector (^1H - ^{13}C) with respect to the principal axes x and y of the σ tensor, respectively. Since we have considered that the relaxation of reorientational motion is in the Markoffian limit ($\tau_c \gg \tau_j$), the decoupling of orientation and angular momentum variables 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 τ_c and τ_j ,¹³ i.e.

$$\tau_j = I/(6kT\tau_c) \quad (7)$$

- (2) Kay, L. E.; Prestegard, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 3829.
- (3) Wong, T. C.; Wang, P. L.; Duh, D. M.; Hwang, L. P. *J. Phys. Chem.* **1989**, *93*, 1295.
- (4) Farrar, T. C.; Adams, B. R.; Grey, G. C.; Quintero-Arcaya, R. A.; Zuo, Q. *J. Am. Chem. Soc.* **1986**, *108*, 8190.
- (5) Hwang, L. P.; Wang, P. L.; Wong, T. C. *J. Phys. Chem.* **1988**, *92*, 4753.
- (6) Jaccard, G.; Wimpey, S.; Bodenhausen, G. *Chem. Phys. Letters* **1987**, *138*, 601.
- (7) Linder, M.; Höhener, A.; Ernst, R. R. *J. Chem. Phys.* **1980**, *73*, 4959.
- (8) Bulsing, J. M.; Doddrell, D. M. *J. Magn. Reson.* **1985**, *61*, 197.
- (9) Chang, W. T.; Wang, P. L.; Hwang, L. P. *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 417.

- (10) Redfield, A. G. *Adv. Magn. Reson.* **1965**, *1*, 1.
- (11) Bain, A. D.; Lynden-Bell, R. M. *Mol. Phys.* **1975**, *30*, 325.
- (12) Werbelow, L. G.; Grant, D. M. *Adv. Magn. Reson.* **1977**, *9*, 189.
- (13) Hubbard, P. S. *Phys. Rev.* **1963**, *131*, 1155.

The spectral density function for ^{13}C SR relaxation¹⁴ is represented by

$$J_{\text{SR}} = (2IkT/3\hbar^2)[C_{11}^2 + C_{22}^2 + C_{33}^2]\tau_j \quad (8)$$

where I is the moment of inertia of the molecule, and C_{11} , C_{22} , and C_{33} , expressed in s^{-1} , are the diagonal elements of the SR interaction tensor in the principal inertial axis system for carboxyl carbon of $\text{H}^{13}\text{COOCD}_3$.

The time evolution of $\langle\Delta S_z(t)\rangle$ may be solved from eq 2 with the known values of $\langle\Delta I_z(0)\rangle$, $\langle\Delta S_z(0)\rangle$, and $\langle 2I_zS_z(0)\rangle$ that may be calculated with the help of the initial density matrix given in eq 1 and the final equilibrium distribution. We obtain $\langle\Delta I_z(0)\rangle = -\hbar\omega_I/(4kT)$, $\langle\Delta S_z(0)\rangle = 0$, and $\langle 2I_zS_z(0)\rangle = \pm\hbar\omega_I/(4kT)$.

The difference in the intensity, denoted by ΔI_t , of the two (antiphase) lines at time t may be calculated from the difference in $\langle I_z(t)\rangle$ obtained with the variation of the sign in the $\langle 2I_zS_z(0)\rangle$ 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 $(\gamma_H/\gamma_C)\langle S_z(\infty)\rangle (= \hbar\omega_I/(4kT))$. Both of the following experimental and calculated results are expressed in terms of differential intensity ratio $\Delta I_t/I_0$.

Experimental Section

The measurement of $2I_zS_z$ spin order has been performed for the carboxyl carbon of methyl formate (HCOOCD_3), which was prepared by the esterification of formic acid with excess methanol- d_4 in the presence of trace sulfuric acid. A 15 vol % solution in methanol- d_4 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 150 s set for each scan. The temperatures are controlled within $\pm 0.5^\circ\text{C}$.

Results and Discussion

In the following calculation, $r = 1.101 \text{ \AA}$ is taken as the proton-carbon internuclear distance in methyl formate.¹⁵ The principal values of the carboxyl shielding tensor in methyl formate are obtained from solid-state powder spectra. They are $\sigma_{11} = -90.5$ ppm, $\sigma_{22} = 29.1$ ppm, and $\sigma_{33} = 61.5$ ppm with respect to the isotropic shift.⁷

It is found that the most shielded element of the tensor, σ_{33} , is nearly parallel to the normal to the COO plane. The orientations of the σ_{11} and σ_{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 σ_{22} closer to the C-O direction.¹⁶ Assignment of σ_{11} to σ_x , σ_{22} to σ_z , and σ_{33} to σ_y may be made,¹⁷ and $\theta_{xz} = 90^\circ$ is utilized in this work. The determination of the θ_{xz} angle is discussed in the following.

The various components of the SR interaction tensor for ^{13}C spins in $\text{H}^{13}\text{COOCD}_3$ are not known experimentally. They may be estimated on the basis of chemical shift data. From the experimental ^{13}C SR constant and the theoretical diamagnetic shielding constant of ^{13}CO , the average absolute shielding constant for a given ^{13}C nucleus may be expressed by¹⁸

$$\sigma = 261.8 + 0.779 \sum_{\beta} C_{\beta\beta} I_{\beta\beta} / 3 \quad (9)$$

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

$$\sigma_{\alpha\alpha} = 261.8 + 0.779 C_{\alpha\alpha} I_{\alpha\alpha} \quad (10)$$

Here, σ is in parts per million, $C_{\beta\beta}$ in kilohertz, and $I_{\beta\beta}$ 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

Figure 1. Plots of the calculated differential intensity ratio $\Delta I_t/I_0$ as a function of evolution time t . With $\theta_{xz} = 35^\circ$ (—) and 45° (---), curves A–C are obtained without the spin-rotation relaxations for $\tau_c = 10$, 5, and 2 ps, respectively.

Figure 2. Variation of differential intensity ratio $\Delta I_t/I_0$ as a function of evolution time t for HCOOCD_3 (15% v/v) in methanol- d_4 solution at 178, 193, 213, 258, and 273 K. Solid curves are calculated at the respective temperature with $\tau_c = 14.8$, 9.2, 3.6, 2.9, and 1.4 ps.

nucleus under consideration. This potential is relatively insensitive to the chemical environment of the atom since it is primarily determined by the core electrons and the nonbonded valence electron.¹⁸ Then, the diagonal component of the magnetic shielding tensor, relative to a specific reference, in the inertial axis system, may be calculated from eq 9 and 10. It may be expressed by

$$\sigma_{\alpha\alpha} - \sigma^{\text{ref}} = 0.779 (C_{\alpha\alpha} I_{\alpha\alpha} - \sum_{\beta} C_{\beta\beta} I_{\beta\beta}^{\text{ref}} / 3) \quad (11)$$

In eq 9–11, $C_{\alpha\alpha}$ (or $C_{\alpha\alpha}^{\text{ref}}$) and $I_{\alpha\alpha}$ (or $I_{\alpha\alpha}^{\text{ref}}$) are the diagonal components of the SR interaction tensor and the moment of inertia of the sample (or reference), respectively. Here, the methane molecule is chosen as the reference with $I_{\alpha\alpha}^{\text{ref}} = 5.22 \times 10^{-40} \text{ g cm}^2$ and $C_{\alpha\alpha}^{\text{ref}} = -15.94 \text{ kHz}$ ($\alpha = 1-3$) utilized.¹⁹

The calculation of the moment of inertia for $\text{H}^{13}\text{COOCD}_3$ may be made with the help of the structure information given by Curl.¹⁵ We obtain $I_1 = 47.36 \times 10^{-40} \text{ g cm}^2$, $I_2 = 136.03 \times 10^{-40} \text{ g cm}^2$, and $I_3 = 172.80 \times 10^{-40} \text{ g cm}^2$. The direction of the I_3 axis is perpendicular to the carboxyl plane. The I_1 direction lies in the ^{13}COH plane and makes an angle of 60.3° with the C-H direction. If the angle, θ_{xz} , between the $^{13}\text{C-H}$ bond and σ_{11} is known, the diagonal elements of σ in the principal inertial frame may be calculated and the corresponding elements of the SR interaction tensor may be obtained from eq 11. To fit the temperature-dependent relaxation data, a self-consistent calculation is obtained with the variation of θ_{xz} and τ_c values. As shown in Figure 1, the increasing magnitude of τ_c results in a shift of maximum intensity to a shorter time and an early decay profile. More

(14) Green, D. K.; Powles, J. G. *Proc. Phys. Soc., London* **1965**, *85*, 87.

(15) Curl, R. F., Jr. *J. Chem. Phys.* **1959**, *30*, 1529.

(16) Veeman, W. S. *Prog. NMR Spectrosc.* **1984**, *16*, 193, and pertinent references cited therein.

(17) Mehring, M. *High Resolution NMR Spectroscopy in Solids. NMR-Basic Principles and Progress*; Springer: New York, 1976; Vol. 11.

(18) (a) Burke, T. E.; Chan, S. I. *J. Magn. Reson.* **1970**, *2*, 120. (b) Schmidt, C. F., Jr.; Chan, S. I. *J. Magn. Reson.* **1971**, *5*, 15.

(19) Ozier, I.; Vitkevich, J. A.; Ramsey, N. F. *Abstracts of 27th Symposium on Molecular Structure and Spectroscopy*; The Ohio State University: Columbus, OH, 1972.

Figure 3. Plots of the obtained reorientational correlation times (O) and angular momentum correlation times (◇) at various temperatures under study. The relation of these two correlation times is given by eq 7. The dashed and dotted curves are obtained from the nonlinear regression of the corresponding data.

important, without the SR relaxation term, the magnitude of the differential intensity ratio is rather sensitive to the variations of the θ_{xz} values but not to the variation of τ_c . Without the CSA-DD cross-relaxation term, the calculated signal intensity of the $2I_z S_z$ spin order vanishes. Thus, the variation of the differential intensity ratio in the relaxation processes of the $2I_z S_z$ spin order demonstrates the importance of cross correlation in ^{13}C - ^1H spin interactions.

The measured $\Delta I/I_0$ values versus evolution time t at various temperatures are shown in Figure 2. The theoretical curves are also shown in the same figure for comparison. The best fitted curves for the temperature-dependent relaxation profile of two-spin order are obtained with $\theta_{xz} = 35^\circ$. Corresponding to this orientation, $C_{11} = -8.14$ kHz, $C_{22} = -2.12$ kHz, and $C_{33} = -1.26$ kHz are used in the calculations of relaxation profiles at various temperatures. The values of θ_{yz} and θ_{xz} utilized in this work agree well with $\theta_{yz} = 85^\circ$ and $\theta_{xz} = 33^\circ$ obtained by Linder et al. from

the study of two-dimensional NMR powder spectra.⁷ Our result indicates that σ_{22} is nearly parallel to the C=O bond.

In Figure 2, consistency of theoretical calculation with experiment is obtained at different temperatures. The decreases in the differential intensity ratio with increasing temperature indicate the effect of SR interaction. The temperature-dependent reorientational correlation times and angular momentum correlation times derived in this study are depicted in Figure 3. At 178 K, the obtained τ_c and τ_j are given by 14.8 and 5.4×10^{-3} ps, respectively, and the effect of SR interaction on the relaxation of two-spin order is negligibly small. However, at 273 K, the obtained τ_c and τ_j are given by 1.4 and 3.3×10^{-2} ps, respectively, and the effect of SR interaction is significant. The existence of this effect results in a 50% reduction of relaxation intensity. Without the SR relaxation term, the best fit of experimental data at 273 K may be obtained with $\tau_c = 2.7$ ps and $\theta_{xz} = 48^\circ$, which are essentially analogous to the results obtained previously by Jaccard et al.⁶ The discrepancy in θ_{xz} values demonstrates the important role of SR interaction in the relaxation of two-spin order.

Conclusion

It has been demonstrated that the cross correlation of DD and CSA interactions is responsible for the existence of the $2I_z S_z$ 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_2S

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The reaction of chlorine atoms with D_2S , forming DCl and DS , has been investigated by using time-resolved infrared diode laser absorption spectroscopic probing of both the D^{35}Cl and D^{37}Cl product. The rate constant obtained by using the pseudo-first-order method was found to be $3.2 (\pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The vibrational energy distribution in the DCl fragment was also determined, with 33 (± 7)% of the product DCl formed in $v = 0$, 56 (± 7)% in $v = 1$ and 11 (± 3)% in $v = 2$. These results are consistent with the known vibrational population inversion between the $v = 0$ and $v = 1$ states of DCl 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,¹ surface etching,^{2,3} and the production of chemical lasers.⁴ 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_2S where the primary reaction leads to the formation of HCl

The rates of the primary and secondary reactions in this system have been obtained by a number of different experimental techniques.⁵⁻⁹ The distribution of internal energy in the products is

- (1) Molina, M. J.; Rowland, F. S. *Nature* **1974**, *249*, 810.
- (2) Ritsko, J. J.; Ho, F.; Hurst, J. *Appl. Phys. Lett.* **1988**, *53*, 78.
- (3) Danner, D. A.; Hess, D. W. *J. Appl. Phys.* **1986**, *59*, 940.
- (4) Gross, R. W. F.; Bott, J. F., Eds. *Handbook of Chemical Lasers*; Wiley: New York, 1976.

- (5) Clyne, M. A. A.; Ono, Y. *Chem. Phys. Lett.* **1983**, *94*, 597.