# Effect of Nuclear Recoil on the Intermediate-State Reorientation of Oriented Nuclei

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The effect of a dynamic mechanism, namely, nuclear recoil, on the reorientation of oriented nuclei is treated via a model system. This system consists of a nucleus belonging to an iron-group ion $X$ in an $XY_5Z$ complex possessing $\mathcal{C}_{4v}$ symmetry. The numerical results clearly indicate that the nuclear recoil may become an important mechanism for reorientation when (i) there is no inversion symmetry and (ii) the electronic spin of the ion containing the nucleus is greater than $\frac{1}{2}$, allowing for the presence of $S^2q$ terms in the electron spin-vibrational coupling. For the particular examples considered, values of attenuation ranging from $-27\%$ to $+73\%$ have been found.

## I. INTRODUCTION

THE angular distribution and polarization of $\gamma$ rays emitted by oriented nuclei can be profoundly affected by the reorientation mechanisms that act on the nuclei in the $\gamma$-emitting intermediate state. The attenuation of angular anisotropies of $\gamma$ radiation from oriented nuclei have been reported in many experiments.[1] From the nature of the experimental parameters giving a value for attenuation, it is not possible to predict which particular mechanism is responsible for attenuation until results calculated on the basis of the mechanism assumed to be effective in the intermediate state agree with those found experimentally. The effect of static interactions on reorientation has been investigated in detail by Daniels and Misra.[2] They found that not all the cases considered by them could be satisfactorily explained on the basis of the static model alone. The effects of dynamic interactions on reorientation have not yet been explored. Attention has been called to two dynamic mechanisms[3]: the nuclear recoil that occurs during the emission of the $\beta$ particle and the electron shell deexcitation following electron-capture decay. That no significant nuclear reorientation takes place because of electron shell deexcitation following $K$ capture has been argued on theoretical grounds in Ref. 2.

In this paper the effect of nuclear recoil on reorientation is treated. The calculation is illustrated for a particular model system, consisting of a nucleus belonging to an iron-group ion $X$ in a complex of chosen symmetry. Orientation is effected by thermal-equilibrium methods at temperatures low enough so that, in the absence of nuclear recoil, only the ground-state modes of the vibrations of the complex are occupied. Physically, when a $\beta$ particle is emitted, the large recoil momentum of the nucleus excites the higher vibrational modes of its complex. These vibrational modes couple to the ion's electronic spin, which is in turn tightly coupled to the spin of the nucleus. In this way, $\beta$ emission may indirectly induce transitions between the nuclear sublevels, resulting in reorientation. The lattice vibrations are effectively not excited during the intermediate-state lifetime for two reasons: (a) The members of the complex are much more tightly bound with each other than with other members of the crystal lattice (the configuration of such complexes is maintained even in liquid solutions)[4]; (b) the nuclear lifetime is far shorter than the spin-lattice relaxation time. Consequently, the lattice vibrations here may be safely ignored. By invariance arguments (the recoil, being odd under inversion, only excites the odd modes of vibration of the complex, which have zero matrix elements between the $3d$ electron states), it is easily seen that there is no dynamic contribution to reorientation by a complex of octahedral symmetry. The case of $\mathcal{C}_{4v}$ symmetry, which is also of experimental interest, is then taken to be the working model of this paper. A complex with this symmetry is obtained simply by replacing one of the $Y$ molecules in the type $XY_6$ octahedral complex by a $Z$ molecule. An example of this type of complex is $X(\mathrm{Cl})_5\,\mathrm{H_2O}$, used experimentally in EPR work.[5]

In order to observe the effect of nuclear recoil, as distinct from static effects, we arrange the spin Hamiltonian in such a way that there is no reorientation on the basis of the static model; any reorientation will then

[1] M. A. Grace, C. E. Johnson, R. G. Scurlock, and R. T. Taylor, Phil. Mag. **2**, 1079 (1957); J. M. Daniels, J. L. G. Lamarche, and M. A. R. LeBlanc, Can. J. Phys. **36**, 997 (1958); W. W. Strohm, Jr., and R. C. Sapp, Phys. Rev. **132**, 207 (1963); E. Ambler, R. P. Hudson, and G. M. Temmer, *ibid.* **97**, 1212 (1955); G. A. Westenbarger and D. A. Shirley, *ibid.* **123**, 1812 (1961); M. Kaplan, J. Blok, and D. A. Shirley, *ibid.* **184**, 1177 (1969); P. H. Barrett and D. A. Shirley, *ibid.* **184**, 1181 (1969). A brief summary of experimental data on attenuation of angular anisotropies is as follows. Daniels *et al.* found complete attenuation in the 396-keV, 3.4-nsec state of $Lu^{175}$ in cerium magnesium nitrate (CMN) following decay of oriented $Yb^{175}$. Strohm, Jr., *et al.* found an attenuation in the 136-keV, 9-nsec state of $Fe^{57}$ in cerium zinc nitrate following decay of oriented $Co^{57}$. Ambler *et al.* found complete attenuation in the 91-keV state of $Pm^{147}$, 2.4-nsec state in CMN following decay of $Nd^{147}$. Blok *et al.* found considerable attenuation for the 61-keV, 3-nsec state of $Pm^{145}$ in CMN. Barrett *et al.* found substantial ($\sim$60%) but not complete attenuation of the 91-keV, 2.4-nsec state of $Pm^{147}$ in CMN.

[2] J. M. Daniels and S. K. Misra, Can. J. Phys. **44**, 1965 (1966).

[3] D. A. Shirley, Ann. Rev. Nucl. Sci. **16**, 89 (1966); W. W. Strohm, Jr., and R. C. Sapp, Phys. Rev. **132**, 207 (1963).

[4] B. N. Figgs, *Introduction to Ligand Fields* (Wiley-Interscience, Inc., New York, 1967), p. 217.

[5] M. Amitay, Ph.D. thesis, Carnegie Institute of Technology, 1965 (unpublished); H. Wesemeyer, Ph.D. thesis, The University of British Columbia 1958 (unpublished).

be due solely to nuclear recoil. This is done by giving the parameters appearing in the spin Hamiltonian (Sec. IV) the same values before and after decay.[2] However, the present scheme incorporates the case when the parameters of the spin Hamiltonian do change during decay.

The general theory of reorientation will be given in Sec. II, and the initial-time density matrix in Sec. III. The effective Hamiltonian for the $XY_5Z$ complex will be discussed in Sec. IV; in particular, the contribution from the coupling of the ion's electronic spin to the vibrations of the $Y_5Z$ cluster[6] surrounding the ion will be determined. To estimate the effect of nuclear recoil on reorientation, relevant parameters must be evaluated; this will be done in Sec. V. Further implications of the theory will be discussed in Sec. VI.

## II. GENERAL THEORY

An assembly of oriented nuclei is best described in terms of a density matrix $\rho_n$. The orientation parameters $M_r^s$, which are the quantities of experimental interest, are the coefficients in the expansion of $\rho_n$ in the basis spherical tensors $\mathcal{Y}_r^s$. While this expansion is useful theoretically, it is found that, when calculations are to be carried out on a digital computer, a different orthonormal basis is more suitable. This basis is constructed from the eigenvectors of the effective Hamiltonian of the problem $\mathcal{H}_{\text{eff}}$. The coefficients in the expansion of $\rho_n$ in this new basis can easily be related to the orientation parameters $M_s^r$.

The procedure to be followed here is essentially the same as developed in Ref. 2, with the following differences. First, there is here a functional dependence of $\mathcal{H}_{\text{eff}}$ on the normal coordinates $q_\lambda{}^\mu$ (which transform as the representation $\Gamma_\lambda$ of the symmetry group) of the cluster. This dependence is absent in the static model. Second, in this paper the initial-time ($t=0+$, i.e., immediately after $\beta$ emission) density matrix takes into account the excitations to higher cluster vibrational modes due to nuclear recoil. With these modifications, the result of the formulation of Ref. 2, to be taken as the framework for all further calculations in this paper, is as follows. The time average of the axially symmetric orientation parameters, in accordance with the radioactive decay law, is given by

$$\bar{M}_r{}^0=\sum_a M_{aa}(0+)\langle a|\,\mathcal{Y}_r{}^0(\mathbf{I})\mathbf{1}(\mathbf{S})\textstyle\prod_{\lambda\mu}\mathbf{1}(q_\lambda{}^\mu)\,|a\rangle + \sum_{ab,\,b>a}\frac{2M_{ab}(0+)\langle b|\,\mathcal{Y}_r{}^0(\mathbf{I})\mathbf{1}(\mathbf{S})\prod_{\lambda\mu}\mathbf{1}(q_\lambda{}^\mu)\,|a\rangle}{\{1+(E_a-E_b)^2\tau^2/\hbar^2\}}, \quad (2.1)$$

where $|a\rangle$, $|b\rangle$ are the eigenvectors of $\mathcal{H}_{\text{eff}}(\mathbf{S},\mathbf{I},q_\lambda{}^\mu)$, with eigenvalues $E_a$ and $E_b$ in the composite direct-product space of electronic spin $\mathbf{S}$, nuclear spin $\mathbf{I}$, and cluster vibrational coordinates $q_\lambda{}^\mu$; $\mathbf{1}(\mathbf{S})$ and $\mathbf{1}(q_\lambda{}^\mu)$ are the unit matrices in the electronic-spin space and the space of the $q_\lambda{}^\mu$ mode of vibration, respectively. $M_{ab}(0+)$ are the coefficients in the initial-time expansion

$$\rho(0+)=\textstyle\sum_{ab} M_{ab}(0+)\,|a\rangle\langle b| \quad (2.2)$$

of $\rho(0+)$ in terms of the orthonormal basis $|a\rangle\langle b|$.

The hard-core (hc) values, or the long-time averages, of the orientation parameters are obtained by letting $\tau\to\infty$ in Eq. (2.1):

$$\bar{M}_r{}^0(\text{hc}) = \sum_a M_{aa}(0+)\langle a|\,\mathcal{Y}_r{}^0(\mathbf{I})\mathbf{1}(\mathbf{S})\prod_{\lambda\mu}\mathbf{1}(q_\lambda{}^\mu)\,|a\rangle. \quad (2.3)$$

## III. INITIAL-TIME DENSITY MATRIX

$\rho(0+)$ is the direct product

$$\rho(0+)=\rho_s\otimes\rho_v, \quad (3.1)$$

where $\rho_s$ is the density matrix in the composite electron-nuclear-spin space, and $\rho_v$ is the density matrix in the vibrational space of the complex. $\rho_s$ is related to $\rho_s{}^{(p)}$, the density matrix for the parent state, in the following manner:

$$\rho_s=U\rho_s{}^{(p)}U^{-1}, \quad (3.2)$$

where $U$ is a unitary matrix consisting of Clebsch-Gordan coefficients which depend on the parent- and intermediate-state nuclear spins and on the angular momentum carried off by the $\beta$ particle.[7] For the thermal-equilibrium methods used for nuclear orientation,

$$\rho_s{}^{(p)}=\textstyle\sum_n \exp(-\epsilon_n/kT)(|\,\epsilon_n\rangle\langle\epsilon_n|)/\sum_n\exp(-\epsilon_n/kT), \quad (3.3)$$

where $\epsilon_n$ and $|\,\epsilon_n\rangle$ are, respectively, the eigenvalues and eigenvectors of the spin Hamiltonian responsible for the nuclear orientation of the parent state. $\rho_v$ can be written

$$\rho_v=\textstyle\prod_{\lambda\mu}\rho_v{}^{(\lambda\mu)}, \quad (3.4)$$

with the matrix elements[8]

$$(\rho_v{}^{(\lambda\mu)})_{mn}=\frac{\exp(-P_{\lambda\mu}{}^2/\omega_{\lambda\mu}\hbar)H_m[P_{\lambda\mu}/\sqrt{(\omega_{\lambda\mu}\hbar)}]H_n[P_{\lambda\mu}/\sqrt{(\omega_{\lambda\mu}\hbar)}]}{\sqrt{(\pi\omega_{\lambda\mu}\hbar 2^{m+n}m!n!)}}. \quad (3.5)$$

[6] The words "complex" and "cluster" will hereafter be used for $XY_5Z$ complex and $Y_5Z$ cluster, respectively.
[7] L. C. Biedenharn and M. E. Rose, Rev. Mod. Phys. **25**, 729 (1953).
[8] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), p. 68.

Here $P_{\lambda\mu}$ and $\omega_{\lambda\mu}$ are, respectively, the momentum received during $\beta$ emission and the simple-harmonic-oscillator frequency of vibration of $q_\lambda{}^\mu$, and $H_m$ is the Hermite polynomial of degree $m$. $P_{\lambda\mu}$ are determined from the following equation:

$$P_{\lambda\mu}=\sum_{\alpha=x,y,z}\mathfrak{D}_{\lambda\mu 0\alpha}p_{0\alpha}/m_0\,, \tag{3.6}$$

where $\mathbf{p}_0$ is the nuclear-recoil momentum, and $\mathfrak{D}$ is the matrix connecting $Q_\lambda{}^\mu$, the normal coordinates for the complex, to the displacement vectors $\mathbf{u}_i'$ of the members of the complex ($i=0$ refers to the ion; $i=1,2,\cdots$ to the members of the cluster):

$$Q_\lambda{}^\mu=\sum_{\substack{i=0,1,\cdots\\ \alpha=x,y,z}}\mathfrak{D}_{\lambda\mu i\alpha}u_{i\alpha}{}'\,. \tag{3.7}$$

The normal coordinates $Q_\lambda{}^\mu$ and $q_\lambda{}^\mu$ for the complex $XY_5Z$ and the cluster $Y_5Z$ are listed in the Appendix.

Since $\mathbf{p}_0$ shows a continuous spectrum of values over its allowed range, in a complete theory this recoil momentum would be taken account of in a statistical fashion, involving the distributions of $\beta$-particle and neutrino momenta. However, the accuracy to which the present calculations can be carried out at this time does not warrant the effort. For example, since the spring constants for the vibrations of the complex are unknown, the present calculation can be illustrated only with the help of typical values chosen for $\omega_{\lambda\mu}$. Typical values, then, will be chosen for $\mathbf{p}_0$ as well. In addition, noting from Eq. (3.5) that the matrix elements $(\rho_v{}^{(\lambda\mu)})_{mn}$ fall off very rapidly for increasing $m$ and $n$, the approximation is made that all the $(\rho_v{}^{(\lambda\mu)})_{mn}$ that have $m,n\geqslant$ a certain maximum, depending on $P_{\lambda\mu}{}^2/\omega_{\lambda\mu}\hbar$, can be neglected.

## IV. EFFECTIVE HAMILTONIAN

The effective Hamiltonian can be written

$$\mathfrak{IC}_{\rm eff}=\mathfrak{IC}_s(\mathbf{H},\mathbf{S},\mathbf{I})+\mathfrak{IC}_{sv}(\mathbf{H},\mathbf{S},q_\lambda{}^\mu)+\mathfrak{IC}_{\rm vib}(q_\lambda{}^\mu,p_\lambda{}^\mu)\,, \tag{4.1}$$

where $p_\lambda{}^\mu$ are the momenta conjugate to $q_\lambda{}^\mu$, and $\mathbf{H}$ is the external magnetic field. $\mathfrak{IC}_s$ is the spin Hamiltonian for the ion, $\mathfrak{IC}_{sv}$ is the contribution to $\mathfrak{IC}_{\rm eff}$ arising from the coupling of the ion's electronic spin to the cluster vibrations, and $\mathfrak{IC}_{\rm vib}$ is the purely vibrational energy of the cluster. The specialization of these terms to the ion $X$ belonging to the $XY_5Z$ complex will now be discussed in detail.

### A. Spin Hamiltonian $\mathfrak{IC}_s$ of the Ion

For the purpose of the present calculations, we will consider a $D$-state ion with a nondegenerate lowest orbital level and an effective electronic spin $S=2$, for example, $Fe^{++}$ $[(3d)^6;{}^5D]$. A cubic field splits the $^5D$ quintuplet into an upper doublet and a lower triplet. A field of $\mathcal{C}_{4v}$ symmetry further splits the doublet into singlets (belonging to the representations $A_1$ and $B_2$ of the $\mathcal{C}_{4v}$ symmetry group) and the triplet into an upper doublet (belonging to the representation $E$) and a lower singlet (belonging to the representation $B_1$). The energy levels and the corresponding real normalized wave functions are given in Table I. The spin Hamiltonian of the ion has the general form

TABLE I. Normalized real wave functions for $^5$D ion in a field of $\mathcal{C}_{4v}$ symmetry (the designation is according to transformation under rotation).

| Energy level | Wave function |
|---|---|
| $\epsilon_{B_2}$ | $\lvert B_2\rangle=(Y_2{}^2+Y_2{}^{-2})/\sqrt{2}$ |
| $\epsilon_{A_1}$ | $\lvert A_1\rangle=Y_2{}^0$ |
| $\epsilon_E$ | $\lvert E_x\rangle=(Y_2{}^1-Y_2{}^{-1})/\sqrt{2}i$ |
| | $\lvert E_y\rangle=(Y_2{}^1+Y_2{}^{-1})/\sqrt{2}$ |
| $\epsilon_{B_1}=\epsilon_0$ (ground level) | $\lvert 0\rangle=(Y_2{}^2-Y_2{}^{-2})/\sqrt{2}i$ |

$$\mathfrak{IC}_s(\mathbf{H},\mathbf{S},\mathbf{I})=g_{\rm II}\mu_B H_zS_z+g_\perp\mu_B(H_xS_x+H_yS_y)+AS_zI_z+B(S_xI_x+S_yI_y)\,, \tag{4.2}$$

where the symmetry axis is taken to be the $z$ axis, and $\mu_B$ is the Bohr magneton.

The constants $g_{\rm II}$, $g_\perp$, $A$, and $B$ appearing in Eq. (4.2) for the $^2D$ ion in a $\mathcal{C}_{4v}$ field are then calculated to have the expressions

$$g_{\rm II}=2(1-4\lambda D_{B_2})\,, \tag{4.3}$$

$$g_\perp=2(1-\lambda D_E)\,, \tag{4.4}$$

$$A=-P(\kappa+8\lambda D_{B_2})\,, \tag{4.5}$$

$$B=-P(\kappa+2\lambda D_E)\,, \tag{4.6}$$

where $\lambda$ is the spin-orbit coupling constant $P=2\gamma\mu_B\mu_N/\langle r\rangle_{\rm av}{}^3$, $\gamma$ is the nuclear gyromagnetic factor in units of $e/2Mc$, $\mu_N$ is the nuclear magneton, $\langle r\rangle_{\rm av}$ is an effective radius of the $3d$ shell, and $\kappa$ is a numerical factor representing the admixture of configurations with unpaired $s$ electron and $D_n=(\epsilon_n-\epsilon_0)^{-1}$ (the subscript 0 refers to the ground level). For the sake of simplicity, the nuclear quadrupole moment is assumed to be negligible.

### B. Electron Spin-Vibrational Coupling

The term $\mathfrak{IC}_{sv}$ can be obtained from the matrix elements of the perturbation $V'$, which is the potential energy of the ion due to the fluctuating part of the cluster. Following the results of the detailed discussion presented by Van Kranendonk and Lee[9] for a nondegenerate ground orbital level,

$$\mathfrak{IC}_{sv}=2g\mu_B\lambda\mathbf{A}\cdot(\mathbf{H}\times\mathbf{S})+\mu_B\lambda(\mathbf{H}\cdot\mathfrak{L}\cdot\mathbf{S}+\mathbf{S}\cdot\mathfrak{L}\cdot\mathbf{H})+\mu_B{}^2\lambda^2\mathbf{S}\cdot\mathfrak{L}\cdot\mathbf{S}\,, \tag{4.7}$$

where

$$\mathbf{A}=-i\textstyle\sum_n{}'D_n{}^2\langle 0|V'P_n\mathbf{L}|0\rangle \tag{4.8}$$

[9] J. Van Kranendonk and Y. Y. Lee, Can. J. Phys. **44**, 1613 (1966).

(a prime over the summation sign indicates $n\neq 0$, and $P_n=|n\rangle\langle n|$),

$$\mathfrak{L}=\mathfrak{L}'+\mathfrak{L}''+\mathfrak{L}''',$$

$$\mathfrak{L}'=\sum_{mn}{}' D_mD_n\langle 0|\mathbf{L}P_mV'P_n\mathbf{L}|0\rangle,$$

$$\mathfrak{L}''=\sum_{mn}{}' D_mD_n(\langle 0|\mathbf{L}P_m\mathbf{L}|n\rangle +\langle m|\mathbf{L}|n\rangle\langle 0|\mathbf{L}|m\rangle)\langle n|V'|0\rangle, \tag{4.9}$$

$$\mathfrak{L}'''=-\sum_m{}' D_m{}^2\langle 0|\mathbf{L}P_m\mathbf{L}P_0V'|0\rangle.$$

Calculation of $\mathfrak{L}$ and $\mathbf{A}$ in terms of $q_\lambda{}^\mu$ will now be considered. The field $V'$ for the $Y_5Z$ cluster can be expressed in terms of the displacements $\mathbf{u}_i$ of the members of the cluster from their equilibrium positions,

$$V'(\mathbf{r})=\sum \mathbf{V}_i(\mathbf{r})\cdot\mathbf{u}_i, \tag{4.10}$$

where only the terms linear in $\mathbf{u}_i$ are retained in the Taylor-series expansion for $V'$. Alternatively, in terms of the normal coordinates $q_\lambda{}^\mu$ of the cluster,

$$V'(\mathbf{r})=\sum_{\lambda\mu} V_\lambda{}^\mu(\mathbf{r})q_\lambda{}^\mu, \tag{4.11}$$

which also serves to define the $V_\lambda{}^\mu$. Since $V'(\mathbf{r})$ is a scalar, and $q_\lambda{}^\mu$ are real, $V_\lambda{}^\mu$ transform as the representation $\Gamma_\lambda$. Selection rules for the matrix elements $\langle m|V_\lambda{}^\mu|n\rangle$ are easily determined from group-theoretical considerations. If the eigenstates $|m\rangle$ and $|n\rangle$ belong to the representations $\Gamma_m$ and $\Gamma_n$, respectively, $\langle m|V_\lambda{}^\mu|n\rangle$ will be zero if $\Gamma_\lambda$ is not contained in the decomposition of the direct product $\Gamma_m\otimes\Gamma_n$.

Since the only $q_\lambda{}^\mu$ excited by the nuclear recoil are $q^{A_1}$, $q^{E_x}$, and $q^{E_y}$ (Appendix), (4.11) becomes

$$V'(r)=V^{A_1}q^{A_1}+V^{E_x}q^{E_x}+V^{E_y}q^{E_y}. \tag{4.12}$$

The potentials $V^{A_1}$, $V^{E_x}$, and $V^{E_y}$ for the present case are

$$V^{A_1}=\frac{-(e''-e')e_0}{a^2\sqrt{(m_1+5m)}}\left(\frac{3(3z^2-r^2)}{2a^2}+\frac{5(35z^4-30z^2r^2+3r^4)}{8a^4}\right), \tag{4.13}$$

$$V^{E_x}=\frac{(e''-e')e_0}{a^2\sqrt{(m_1+5m)}}\left(\frac{3}{a^2}xz+\frac{5xz(7z^2-3r^2)}{2a^4}\right), \tag{4.14}$$

$$V^{E_y}=\frac{(e''-e')e_0}{a^2\sqrt{(m_1+5m)}}\left(\frac{3}{a^2}yz+\frac{5yz(7z^2-3r^2)}{2a^4}\right), \tag{4.15}$$

where a point-charge model of the complex has been assumed with $e_0$, $e'$, and $e''$, respectively, as the effective charges of the $X$, $Y$, and $Z$ ions; $a$ the distance of any of the $Y$ or $Z$ ions from the central $X$ ion; and $m$, $m_1$, respectively, the masses of the $Y$, $Z$ ions. In Eqs. (4.13)–(4.15) the odd terms and those of degree higher than the fourth are deliberately omitted, as they have zero matrix elements between the $3d$ electron states. The evaluation of the matrix elements is facilitated if the above potentials are expressed in the operator equivalent forms. The vector $\mathbf{A}$ and the tensor $\mathfrak{L}$ are then

$$A_x=A_y=A_z=\mathfrak{L}_{xy}=\mathfrak{L}_{yx}=\mathfrak{L}_{zz}=0, \tag{4.16}$$

$$\mathfrak{L}_{xx}=\mathfrak{L}_{yy}=\frac{(e''-e')e_0q^{A_1}D_{B_2}{}^2}{21a^2\sqrt{(m_1+5m)}}\left(-27\frac{\langle r^2\rangle_{\rm av}}{a^2}+25\frac{\langle r^4\rangle_{\rm av}}{a^4}\right), \tag{4.17}$$

$$\mathfrak{L}_{xz}/q^{E_x}=\mathfrak{L}_{zx}/q^{E_x}=\mathfrak{L}_{yz}/q^{E_y}=\mathfrak{L}_{zy}/q^{E_y}=\frac{(e''-e')e_0D_E}{7a^2\sqrt{(m_1+5m)}}\times\left[D_E\left(-3\frac{\langle r^2\rangle_{\rm av}}{a^2}+\frac{5(13\sqrt{3}-27)\langle r^4\rangle_{\rm av}}{36a^4}\right)+D_{B_2}\left(-12\frac{\langle r^2\rangle_{\rm av}}{a^2}+\frac{5(13\sqrt{3}-15)\langle r^4\rangle_{\rm av}}{18a^4}\right)\right]. \tag{4.18}$$

Finally, from Eqs. (4.7) and (4.16)–(4.18) one writes simply

$$\mathfrak{IC}_{sv}=l_\perp(H_xS_x+H_yS_y)q^{A_1}+l_\perp\lambda(\mathbf{S}^2-S_z{}^2)q^{A_1}/\mu_\beta +l_z[(H_zS_x+H_xS_z)q^{E_x}+(H_zS_y+H_yS_z)q^{E_y}] +l_z\lambda[(S_zS_x+S_xS_z)q^{E_x}+(S_zS_y+S_yS_z)q^{E_y}]/\mu_\beta, \tag{4.19}$$

where

$$l_\perp=\frac{2\mu_\beta\lambda(e''-e')e_0D_{B_2}{}^2}{21a^2\sqrt{(m_1+5m)}}\left(-27\frac{\langle r^2\rangle_{\rm av}}{a^2}+25\frac{\langle r^4\rangle_{\rm av}}{a^4}\right), \tag{4.20}$$

$$l_z=\frac{2\mu_\beta\lambda(e''-e')e_0D_E}{7a^2\sqrt{(m_1+5m)}}\times\left[D_E\left(-3\frac{\langle r^2\rangle_{\rm av}}{a^2}+\frac{5(13\sqrt{3}-27)\langle r^4\rangle_{\rm av}}{36a^4}\right)+D_{B_2}\left(-12\frac{\langle r^2\rangle_{\rm av}}{a^2}+\frac{5(13\sqrt{3}-15)\langle r^4\rangle_{\rm av}}{18a^4}\right)\right]. \tag{4.21}$$

The next step now is to calculate the matrix elements of $q_\lambda{}^\mu$. Let $\xi_\lambda{}^\mu$ and $\xi_\lambda{}^{\mu\dagger}$ be the annihilation and creation operators for the vibrations of the normal coordinate $q_\lambda{}^\mu$. Then, in the occupation-number-space representation, the operator $q_\lambda{}^\mu(=\xi_\lambda{}^\mu+\xi_\lambda{}^{\mu\dagger})$ has the matrix elements

$$\langle n'|q_\lambda{}^\mu|n''\rangle=(n''\hbar/2\omega^{\lambda\mu})^{1/2}\delta_{n',n''+1} +(n'\hbar/2\omega^{\lambda\mu})^{1/2}\delta_{n',n''+1}. \tag{4.22}$$

### C. Vibrational Energy ($\mathfrak{IC}_{\rm vib}$)

$\mathfrak{IC}_{\rm vib}$ includes only the vibrational energy of those modes that play an effective role in the mechanism of

TABLE II. Orientation parameter $A_2(=\langle \mathcal{Y}_0^0(S=2)\mathcal{Y}_2^0(I=1)\rangle)$ for various values of recoil momentum, nuclear lifetime, and vibrational frequency of $q^E$ mode of vibration for $Fe^{++}$ in a $\mathcal{C}_{4v}$ symmetry. Initial orientation is assumed to be effected at 0.003 and 0°K. The superscripts $i$, $\infty$, and $\tau$ refer to initial, hard-core, and nuclear lifetime averages, $A_2^i(T=0°K)=-1.18\times10^{-1}$, $A_2^i(T=0.003°K)=-1.11\times10^{-1}$.

| | | | $T=0°K$ | | | | $T=0.003°K$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $x$ $[=P^E/\sqrt{(\omega^E\hbar)}]$ | $\nu^E$ (cps) | $\tau$ (nsec) | $A_2^\tau$ $\times10$ | % Attenuation $(1-A_2^\tau/A_2^i)$ $\times100$ | $A_2^\infty$ $\times10$ | % Attenuation $(1-A_2^\infty/A_2^i)$ $\times100$ | $A_2^\tau$ $\times10$ | % Attenuation $(1-A_2^\tau/A_2^i)$ $\times100$ | $A_2^\infty$ $\times10$ | % Attenuation $(1-A_2^\infty/A_2^i)$ $\times100$ |
| 0.5 | $10^{12}$ | 1 | −1.47 | −25 | −1.07 | 10 | −0.608 | 45 | −0.452 | 60 |
| | | 10 | −1.46 | −24 | −1.07 | 10 | −0.607 | 45 | −0.452 | 60 |
| | | 100 | −1.46 | −24 | −1.07 | 10 | −0.603 | 46 | −0.452 | 60 |
| | $10^{13}$ | 1 | −1.43 | −21 | −1.39 | −18 | −0.729 | 34 | −0.707 | 36 |
| | | 10 | −1.44 | −22 | −1.39 | −18 | −0.726 | 35 | −0.707 | 36 |
| | | 100 | −1.44 | −22 | −1.39 | −18 | −0.726 | 35 | −0.707 | 36 |
| 1.0 | $10^{12}$ | 1 | −1.47 | −25 | −1.30 | −10 | −0.649 | 42 | −0.583 | 47 |
| | | 10 | −1.47 | −25 | −1.30 | −10 | −0.648 | 42 | −0.583 | 47 |
| | | 100 | −1.47 | −25 | −1.30 | −10 | −0.647 | 42 | −0.583 | 47 |
| | $10^{13}$ | 1 | −1.49 | −26 | −1.38 | −17 | −0.750 | 32 | −0.713 | 36 |
| | | 10 | −1.50 | −27 | −1.38 | −17 | −0.752 | 32 | −0.713 | 36 |
| | | 100 | −1.50 | −27 | −1.38 | −17 | −0.754 | 32 | −0.713 | 36 |
| 4.0 | $10^{12}$ | 1 | −1.40 | −19 | −0.386 | 68 | −0.702 | 37 | −0.300 | 73 |
| | | 10 | −1.39 | −18 | −0.386 | 68 | −0.699 | 37 | −0.300 | 73 |
| | | 100 | −1.36 | −15 | −0.386 | 68 | −0.687 | 38 | −0.300 | 73 |
| | $10^{13}$ | 1 | −1.42 | −20 | −1.34 | −14 | −0.699 | 37 | −0.668 | 40 |
| | | 10 | −1.43 | −21 | −1.34 | −14 | −0.698 | 37 | −0.668 | 40 |
| | | 100 | −1.43 | −21 | −1.34 | −14 | −0.698 | 37 | −0.668 | 40 |

reorientation. In the present dynamic model, the electronic spin of the ion couples only to the $q^{A_1}$, $q^{E_x}$, and $q^{E_y}$ vibrations during the nuclear recoil. Then

$$\mathcal{H}_{\rm vib}=\hbar\omega^{A_1}(\xi^{A_1\dagger}\xi^{A_1}+\tfrac{1}{2}) + \hbar\omega^{E}(\xi^{E_x\dagger}\xi^{E_x}+\xi^{E_y\dagger}\xi^{E_y}+1). \quad (4.23)$$

In writing Eq. (4.23), use has been made of the fact that the $q^{E_x}$ and $q^{E_y}$ vibrations are degenerate (both vibrate with the same frequency $\omega^E$).

## V. NUMERICAL CALCULATIONS

The first step in the numerical evaluation of reorientation consists in estimating the various parameters that appear in $\mathcal{H}_{\rm eff}=\mathcal{H}_s+\mathcal{H}_{sv}+\mathcal{H}_{\rm vib}$. The spin Hamiltonian $\mathcal{H}_s$ is characterized by $g_{\parallel}$, $g_\perp$, $A$, $B$, and $\mathbf{I}$. For simplicity, the nuclear spin $\mathbf{I}$ will be assumed to be unity, as this is the smallest spin capable of exhibiting the property of alignment. From Eqs. (4.3)–(4.6), it is seen that $g_{\parallel}$, $g_\perp$, $A$, and $B$ depend on the values of $\lambda$, $P$, $\kappa$, $D_E$, and $D_{B_2}$. $\lambda$ will be chosen to be $-100$ cm$^{-1}$, which is the value for $Fe^{++}$. The values for $P$ and $\kappa$ are not available for $Fe^{++}$. We then arbitrarily use the $Co^{++}$ values $P=0.0225$ cm$^{-1}$ and $\kappa=0.351$. A typical value of 15 000 cm$^{-1}$ for divalent iron-group ions in a cubic field is assumed for the spacing $1/D_{B_2}$. A value of 200 cm$^{-1}$ will be assumed for $1/D_E$, as it corresponds to a nonzero splitting only when the cubic symmetry is lowered to a $\mathcal{C}_{4v}$ symmetry. One then has the following values for the spin-Hamiltonian parameters $g_{\parallel}=2.054$, $g_\perp=3.0$, $A=-0.0067$ cm$^{-1}$, and $B=+0.0146$ cm$^{-1}$. Two values of temperature, viz., 0.003 and 0°K, will be assumed to be effecting the initial nuclear orientation. For the evaluation of the parameters $l_\perp$ and $l_z$ appearing in $\mathcal{H}_{sv}$, one needs to know the values of $a$, $\langle r^2\rangle_{\rm av}/a^2$, $\langle r^4\rangle_{\rm av}/a^4$, $(e''-e')$, $e_0$, $m_1$, and $m$. The following typical values will be assumed: $a=2$ Å, $\langle r^2\rangle_{\rm av}/a^2=\frac{1}{4}$, $\langle r^4\rangle_{\rm av}/a^4=\frac{1}{16}$, $(e''-e')=\frac{1}{3}e$, $e_0=2e$, $m_1=4m=72m_p$, where $e$ and $m_p$ are, respectively, the electron's charge and the proton's mass. Then $l_\perp=-5.28$ erg cm$^{-1}$ g$^{-1/2}$ G$^{-1}$, and $l_z=-1.36\times10^4$ erg cm$^{-1}$ g$^{-1/2}$ G$^{-1}$.

As $|l_\perp|\ll|l_z|$, the terms containing $l_\perp$ in $\mathcal{H}_{sv}$ will be neglected. The $S^2q$ terms in $\mathcal{H}_{sv}$ are larger than the $HSq$ terms by a factor of the order of $\lambda/\mu_\beta H\approx10^2$ for $\lambda=10^2$ cm$^{-1}$ and $H=10^4$ G, as seen from Eq. (4.7). We shall therefore neglect the $HSq$ terms. Only the effect of the term containing $q^{E_x}$ in $\mathcal{H}_{sv}$ is taken into account, for the following reasons. With $I=1$, $S=2$, and with only the first four vibrational levels of $q^{E_x}$ excited, we have to deal with matrices of the order of $60\times60$ and the computation of the results given in Table II takes, in all, about 300 min, even on a computer as big as CDC-6400. If the term containing $q^{E_y}$ were considered at the same time, we would have to manipulate matrices of the order of $240\times240$, which would presumably take more than a day's computer time.

It is easily seen, however, that inclusion of the $q^{E_y}$ term would not vitiate our results, but would rather result in an increase in the magnitude of the attenuation percentages given in Table II. This is due to the axial symmetry of the problem, whereby the effect on the axial parameters $M_r^0$ of the $q^{E_y}$ term considered separately will be the same as that of the $q^{E_x}$ term; when the $q^{E_x}$ and $q^{E_y}$ terms are considered together, there will be an interference effect, which will presumably not reduce the $M_r^0$ values below those obtained from the $q^{E_x}$ term alone.

The numerical evaluations will be made separately

for $\nu^{Ex}=10^{12}$ cps and $10^{13}$ cps, values typical of molecular vibrations, and for $P^{Ex}/\sqrt{(\omega^E\hbar)}=0.5$, 1, and 4. The calculations will be illustrated for nuclear lifetimes of 1 nsec, 10 nsec, and 100 nsec. We shall assume that the nucleus decays without any change in spin. Since we do not know what physical change to expect in the electronic shell, it will be assumed that there is no change in the electronic shell during decay, so that the parameters $A$, $B$, $g_{\parallel}$, and $g_{\perp}$ appearing in $\mathcal{H}_s$, and the electronic spin $S$ are the same before and after decay. It is to be noted, however, that in a calculation dealing with a real physical case, the nuclear spin and the charged state of the electronic shell do change, and the corresponding changes in the parameters should be duly taken into account. One can only expect at the outset that changes in the electronic shell and nuclear spin will lead to greater reorientation. The results of the present calculations are summarized in Table II.

## VI. DISCUSSION

The main features of the numerical results are as follows: (i) The reorientation is quite sensitive to the typical vibrational frequency of the participating mode; the attenuation of alignment is, in most cases, found to be much larger for $\nu^E=10^{12}$ cps than for $\nu^E=10^{13}$ cps (see Table II). The reorientations for smaller values of $\nu^E$ (not included in Table II) have been separately evaluated, and it was found that the attenuation increased with decreasing frequency, with almost complete attenuation of alignment for $\nu^E=10^8$ cps. These latter frequencies do not correspond to typical infrared spectra. Nevertheless, if the spring constants and spacings of the members of the complex allow for frequencies smaller than $10^{12}$ cps, larger attenuations than those given in Table II may be expected on the basis of our model. (ii) The attenuation of alignment is dependent on the momentum received by a participating mode of vibration, e.g., the maximum attenuation for $x(=P^E/(\omega^E\hbar)^{1/2})=0.5$ is 60%, for $x=1.0$ it is 47%, and for $x=4.0$ it is 73% (see Table II). (iii) The attenuation depends on whether or not $S>\frac{1}{2}$. We have calculated reorientation for the case (not included in Table II) when the $S^2q$ terms in $\mathcal{H}_{sv}$ are absent, leaving the $HSq$ terms responsible for the dynamic effects. This occurs when $S=\frac{1}{2}$. As expected from the discussion in Sec. V of the relative magnitudes of the $HSq$ and $S^2q$ terms, we found a negligible attenuation for $\nu^E=10^{12}$ and $10^{13}$ cps. This is the reason that we have chosen $Fe^{++}(3d^6,S=2)$ to be the ion containing the nucleus rather than $Ti^{+++}(3d^1,S=\frac{1}{2})$ for illustration, even though the latter would have been simpler for calculation, requiring manipulation of much smaller (24×24) matrices. (iv) The attenuation is not always positive. For example, in Table II there are several momentum and frequency values for which the attenuation is negative; these values correspond to an enhancement of alignment due to nuclear recoil. A similar result was found in the static case.[2]

The results of the present calculations indicate that the nuclear recoil becomes an important dynamical mechanism for reorientation when (i) there is absence of inversion symmetry for the nucleus at its site in the complex, and (ii) the electronic spin of the ion containing the nucleus is greater than one-half ($S>\frac{1}{2}$). As a consequence, cases normally characterized by octahedral symmetry become vulnerable to the dynamical reorientation if this symmetry is somehow broken. This may occur if there is a distortion of the octahedron, or if the atoms of any two molecules symmetrically situated in the complex are isotopically different.

For computational reasons, it was not possible to investigate reorientation for many more values of recoil momentum than those presented in Table II; a complete theory would require an averaging over all values that correspond to the momentum distribution of the $\beta$ particle. The values of the parameters appearing in $\mathcal{H}_{\text{eff}}$ are also not known, particularly the frequencies of vibration of the participating modes. We hope to close these gaps in the treatment as more experimental data and faster computers become available.

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## APPENDIX

Let the ion $X$ be situated at the center of the cube and the $Y$ and $Z$ molecules at the face centers; subscript 0 refers to the coordinates of the ion $X$, subscript 1 to the coordinates of ion $Z$, and subscripts 2, 3, 4, 5, 6 to the coordinates of the $Y$ ions. From the character table for the symmetry group $\mathcal{C}_{4v}$, it is seen that the representation constituted by the displacement vectors of the complex reduces to $5A_1\oplus A_2\oplus B_1\oplus B_2\oplus 6E$. By inspection, the symmetry coordinates can be written down. The normal coordinates of the complex, $Q_\lambda{}^\mu$, can then be determined by the use of the Schmidt orthogonalization procedure. They are listed below:

$$Q^{Ex}(1)=[1/(\sqrt{M})][(\sqrt{m_0})x_0+(\sqrt{m_1})x_1+(\sqrt{m})\times(x_2+x_3+x_4+x_5+x_6)], \quad \text{(A1)}$$

$$Q^{Ey}(1)=[1/(\sqrt{M})][(\sqrt{m_0})y_0+(\sqrt{m_1})y_1+(\sqrt{m})\times(y_2+y_3+y_4+y_5+y_6)], \quad \text{(A2)}$$

$$Q^{E_x}(2)=[1/(3+\alpha^2)^{1/2}][\alpha y_1-y_2+z_4-z_6], \quad \text{(A3)}$$

$$Q^{E_y}(2)=[1/(3+\alpha^2)^{1/2}][\alpha x_1-x_2+z_3-z_5], \quad \text{(A4)}$$

$$Q^{E_x}(3)=[M(M-m_0)]^{-1/2}\times[x_0(M-m_0)-(\sqrt{m_0})((\sqrt{m_1})x_1+(\sqrt{m})\times(x_2+x_3+x_4+x_5+x_6))], \quad \text{(A5)}$$

$$Q^{E_y}(3)=[M(M-m_0)]^{-1/2}\times[y_0(M-m_0)-(\sqrt{m_0})((\sqrt{m_1})y_1+(\sqrt{m})\times(y_2+y_3+y_4+y_5+y_6))], \quad \text{(A6)}$$

$$Q^{E_x}(4)=\left(\frac{14mm_1}{(3m_1+m)(M-m_0)}\right)^{1/2}x_1+\frac{\sqrt{2}(2m-m_1)}{[7(5m+m_1)(3m_1+m)]^{1/2}}x_2-\left(\frac{5m+m_1}{14(3m_1+m)}\right)^{1/2}(z_3-z_5)-\left(\frac{3m_1+m}{14(5m_1+m)}\right)^{1/2}(x_3+x_4+x_5+x_6), \quad \text{(A7)}$$

$$Q^{E_y}(4)=\left(\frac{14mm_1}{(3m_1+m)(M-m_0)}\right)^{1/2}y_1+\frac{\sqrt{2}(2m-m_1)}{[7(5m+m_1)(3m_1+m)]^{1/2}}y_2-\left(\frac{5m+m_1}{14(3m_1+m)}\right)^{1/2}(z_4-z_6)-\left(\frac{3m_1+m}{14(5m_1+m)}\right)^{1/2}(y_3+y_4+y_5+y_6), \quad \text{(A8)}$$

$$Q^{E_x}(5)=(2/\sqrt{7})x_2+(1/2\sqrt{7})(z_3-z_5)-(1/2\sqrt{7})(x_3+x_4+x_5+x_6), \quad \text{(A9)}$$

$$Q^{E_y}(5)=(2/\sqrt{7})y_2+(1/2\sqrt{7})(z_4-z_6)-(1/2\sqrt{7})(y_3+y_4+y_5+y_6), \quad \text{(A10)}$$

$$Q^{E_x}(6)=\tfrac{1}{2}(x_3-x_4+x_5-x_6), \quad \text{(A11)}$$

$$Q^{E_y}(6)=\tfrac{1}{2}(y_3-y_4+y_5-y_6), \quad \text{(A12)}$$

$$Q^{A_1}(1)=(1/\sqrt{M})[(\sqrt{m_0})z_0+(\sqrt{m_1})z_1+(\sqrt{m})\times(z_2+z_3+z_4+z_5+z_6)], \quad \text{(A13)}$$

$$Q^{A_1}(2)=[M(M-m_0)]^{-1/2}\times[z_0(M-m_0)-(\sqrt{m_0})((\sqrt{m_1})z_1+(\sqrt{m})\times(z_2+z_3+z_4+z_5+z_6))], \quad \text{(A14)}$$

$$Q^{A_1}(3)=[(M-m_0)(M-m_0-m_1)]^{-1/2}\times[z_1(M_1-m_0-m_1)-(\sqrt{(mm_1)}\times(z_2+z_3+z_4+z_5+z_6))], \quad \text{(A15)}$$

$$Q^{A_1}(4)=\tfrac{1}{2}(x_3+y_4-x_5-y_6), \quad \text{(A16)}$$

$$Q^{A_1}(5)=[1/2(\sqrt{5})][4z_2-(z_3+z_4+z_5+z_6)], \quad \text{(A17)}$$

$$Q^{B_2}(1)=\tfrac{1}{2}(x_3-y_4-x_5+y_6), \quad \text{(A18)}$$

$$Q^{B_2}(2)=\tfrac{1}{2}(z_3-z_4+z_5-z_6), \quad \text{(A19)}$$

$$Q^{A_2}=\tfrac{1}{2}(y_3-x_4-y_5+x_6), \quad \text{(A20)}$$

and

$$Q^{B_1}=\tfrac{1}{2}(y_3+x_4-y_5-x_6). \quad \text{(A21)}$$

Here $M=m_0+m_1+5m$, $\alpha=\sqrt{(m/m_1)}$; $m_0$, $m_1$, and $m$ are, respectively, the masses of $X$, $Z$, and $Y$ ions. All the coordinates are in the mass-weighted scale; for example, by $x_i$ is understood $x_i(\sqrt{m_i})$. The normal coordinates $q_\lambda{}^\mu$ of the cluster can be obtained from those of the complex $Q_\lambda{}^\mu$ by simply substituting 0 for $x_0$, $y_0$, and $z_0$ in Eqs. (A1)–(A21) and choosing any 18 independent equations. In particular, the vibrational modes of the cluster excited by nuclear recoil are

$$q^{E_x}=(m_1+5m)^{-1/2}[(\sqrt{m_1})x_1+(\sqrt{m})(x_2+x_3+x_4+x_5+x_6)], \quad \text{(A22)}$$

$$q^{E_y}=(m_1+5m)^{-1/2}[(\sqrt{m_1})y_1+(\sqrt{m})(y_2+y_3+y_4+y_5+y_6)], \quad \text{(A23)}$$

$$q^{A_1}=(m_1+5m)^{-1/2}[(\sqrt{m_1})z_1+(\sqrt{m})(z_2+z_3+z_4+z_5+z_6)]. \quad \text{(A24)}$$