Field spectroscopy of hyperfine interactions and spin-modification conversion in molecules with C_{3v} symmetry

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(Submitted 30 September 1994)
Zh. Éksp. Teor. Fiz. **107**, 704–731 (March 1995)

We examine an alternative approach to the spectroscopy of hyperfine interactions in molecules with C_{3v} symmetry, namely field spectroscopy of the disruption of hyperfine coupling. We describe the field dependence of a nonlinear resonance in components of an IR spectrum in which the axial projection of the rotational angular momentum $K=1$; this dependence stems from hyperfine parity doubling. In addition, we consider spin-modification conversion in these molecules. Explicit expressions are derived for all varieties of the hyperfine contribution to conversion, enabling one under certain conditions to determine which tensor spin–rotation constants do not contribute to the spectrum. We point out the need to allow for K-doubling in the parity of rotational levels with $K=3$ when describing conversion. We discuss the corresponding field structure of the nonlinear optical spectrum. © *1995 American Institute of Physics.*

1. INTRODUCTION

The appearance of the present paper has been facilitated by at least two circumstances. The first is the existence of a body of anticipatory work geared to a description of the hyperfine structure of field spectra of a nonlinear optical resonance in spherical top molecules.[1,2] One would naturally like to extend the types of molecules treated to symmetric tops. The second is the availability of experimental data[3] on spin-modification conversion in molecules with C_{3v} symmetry and subsequent attempts to calculate those modifications theoretically,[4] which still await further development. One novel aspect of the calculation was that tensor spin–rotation interactions were taken into consideration.

We know that in symmetric top molecules, tensor interactions of off-axis nuclear spins with rotational angular momentum and with on-axis directed nuclear spins result in parity doubling of levels for which the axial projection of the rotational angular momentum is $K=1$.[5] Hyperfine doubling is manifested is a specific fashion in the magnetic field spectrum of a nonlinear optical resonance in radiative absorption, which can be used to determine the pertinent interaction constants. It has turned out that not all newly considered interactions contribute to the spectrum, and there are certain cases in which the analysis of spin-modification conversion can help fill the gap.

On the other hand, it has turned out to be necessary in considering conversion to allow for the doubling of levels with $K=3$ due to centrifugal distortions of initially "rigid" molecules (Ref. 6, Section 8.3). Information on the magnitude of K doubling is not always available (see, for example, the recent work on fluoroform[7,8]), but we will show that it can be obtained from the electric-field absorption spectrum of a nonlinear optical resonance.

Rather than occupy ourselves with the foregoing applications, we give here the general characteristics of hyperfine interactions in molecules with C_{3v} symmetry, starting with the assignment of basis elements in irreducible representation spaces, and concluding with a calculation of the reduced matrix elements of the hyperfine Hamiltonian.

2. SYMMETRY BASIS ELEMENTS

The symmetry group for the Hamiltonian of a molecule that contains identical nuclei is a direct product $O_3 \otimes G$, where $O_3 = SO_3 \otimes C_i$ is the group of arbitrary molecular rotations and inversions in the laboratory frame of reference, and G is the permutation group of the spatial and spin coordinates of identical nuclei, which is isomorphic to the spatial symmetry group G of the core of the "rigid" molecule.[9] The group elements of the latter are finite rotations and inversions relative to a coordinate system attached to the molecule[1)] ($G \subset O_3$).

In the present paper we consider molecules with C_{3v} symmetry ($G = C_{3v}$ and $G = S_3$), particularly the halogenated methanes—halomethane CH_3–Hal (methyl halide) and trihalomethane CH–Hal_3 (haloform), where Hal $\in$ (F,Cl,Br,I). These molecules can all be represented by the chemical formula XY_3Z.

It is convenient to take the spatial configuration of the XY_3Z to be that of a right-handed screw. The numbering of the Y molecules is then taken to be such that a right-handed rotation C_3, which leaves the molecule unchanged ($C_3 \in G$), corresponds to a permutation of the Y molecular coordinates $(123)\underline{123}=\underline{321}$, where $(123) \in G$.

Let the origin of the molecule-fixed coordinate system (right-handed reference frame) be at the molecule's center of mass. The $\mathbf{u}_z$ axis points along the X–Z bond in the Z direction. The orientation of the remaining axes is given by the x and y components of the vectors $\mathbf{r}^{hp}$, extended from the h nuclei ($h \in (X,Z)$) toward the Y^p nuclei:

$$\mathbf{r}^{hp}=r_{h\mathrm{H}}\mathbf{n}^{hp}=-r_{Oh}\mathbf{u}_z+r_{O\mathrm{H}}\mathbf{n}^p, \quad r_{ij}=|\mathbf{r}^{ij}|,$$

with $(\mathbf{n}^p \cdot \mathbf{u}^z)=0,\binom{x}{y}$ the other components[2)] are

 1063-7761/95/030400-15$10.00

$$\mathbf{n}^1=\begin{pmatrix}1\\0\end{pmatrix},\quad \mathbf{n}^2=\begin{pmatrix}\bar{c}\\s\end{pmatrix},\quad \mathbf{n}^3=\begin{pmatrix}\bar{c}\\\bar{s}\end{pmatrix},\tag{1}$$

$$c+is=\exp(i\pi/3)=(1+i\sqrt{3})/2.$$

The point O is at the center of the base of the XY_3 pyramid with vertex at X.

To describe the structure of the Hamiltonian for spin-dependent interactions we use the two-sided tensor coupling operators $\hat{\mathbf{T}}^{\lambda}_{\kappa_\rho}$, which are referred to a particular basis of the irreproducible representations of the group $O_3 \otimes S_3$:

$$\left[\hat{S}^{\lambda'}_{k'_{\rho'}}\otimes\hat{T}^{\lambda''}_{\kappa''_{\rho''}}\right]^{\lambda\dot{s}}_{k_{\rho}\dot{q}}=\sum_{q'q''}^{s's''}\left\langle\begin{matrix}\lambda s\\ \kappa_\rho q\end{matrix}\middle|\begin{matrix}\lambda' s'\ \lambda'' s''\\ \kappa'_{\rho'}q'\,\kappa''_{\rho''}q''\end{matrix}\right\rangle\hat{S}^{\lambda'\dot{s}'}_{\kappa'_{\rho'}\dot{q}'}\hat{T}^{\lambda''\dot{s}''}_{\kappa''_{\rho''}\dot{q}''}.\tag{2}$$

The upper pair of indices $\lambda_{\dot{s}}$ corresponds to the group $S_3 \cong C_{3v}$, and the lower, $\kappa_\rho\dot{q}$, to O_3 (the subscript ρ corresponds to its subgroup C_i). In these pairs, the first entry is the index of the irreducible space, and the second in the index of the basis element in that space.[3)] For coupling we use the two-sided Wigner coefficients, which are products of the customary ones:

$$\left\langle\begin{matrix}\lambda s\\ \kappa_\rho q\end{matrix}\middle|\begin{matrix}\lambda' s'\ \lambda'' s''\\ \kappa'_{\rho'}q'\,\kappa''_{\rho''}q''\end{matrix}\right\rangle=\langle\kappa q|\kappa' q'\,\kappa'' q''\rangle\langle\rho|\rho'\rho''\rangle\times\langle\lambda s|\lambda' s'\lambda'' s''\rangle.\tag{3}$$

The Wigner coefficients for the groups C_{3v} and C_i are described in Appendix A.

Since the symmetry properties of the Wigner coefficients depend on the choice of basis for the representations of O_3 and C_{3v}, it is convenient to make this choice consistently, for example on a set of spherical basis functions.[10,11] An explicit realization of basis elements can be obtained by projecting polar ($\mathbf{n}$) or axial ($\hat{\mathbf{J}}=-i\mathbf{n}\times\nabla_{\mathbf{n}}$) vectors (vector operators) onto the spaces of the various irreducible representations:

1) C_i—the space inversion group,

$$v^{(\rho)}_j=\begin{cases}n_j, & \rho=u(A_u),\\ \hat{J}_j, & \rho=g(A_g).\end{cases}\tag{4}$$

The parity is $p=(-1)^\rho j\in(x,y,z)$.

2) O_3—the rotation–inversion group,

$$|\kappa 1_\rho q\rangle=1_\rho q=(-i)^\kappa\sum_j v^{(\rho)}_j{}_sD_{j\dot{q}}=\sum_j v^{(\rho)}_j{}_aD_{jq}.\tag{5}$$

Here the standard transformation matrices are

$$({}_sD_{j\dot{q}})=\begin{pmatrix}{}_s\hat{d} & 0\\ 0 & 1\end{pmatrix},\quad {}_s\hat{d}=\frac{1}{\sqrt{2}}\begin{pmatrix}\bar{1} & 1\\ \bar{i} & \bar{i}\end{pmatrix}.$$

The ordering of the indices of ${}_sD$ is

$$j\in\begin{pmatrix}x\\y\\z\end{pmatrix},\quad \dot{q}\in(+1,-1,0).$$

3) C_{3v}—the molecular symmetry group,

$$|\lambda s\rangle=(-i)^\lambda\times\begin{cases}v^{(u)}_z, & |\lambda s\rangle=|A_1 0\rangle=|00\rangle,\\ v^{(g)}_z, & |\lambda s\rangle=|A_2 0\rangle=|10\rangle,\\ (v^\rho_x+isv^{(\rho)}_y)/\sqrt{2}, & |\lambda s\rangle=|E,\pm1\rangle=|2,\pm1\rangle.\end{cases}\tag{6}$$

Besides the letter designators of the irreducible representations we have used numerical designators here that properly reflect the parity of the representation.[12,13] The power to which the phase factor $(-i)$ is raised is chosen such that the two-sided tensor operators remain hermitian under coupling:[14]

$$(\hat{T}^{\lambda\dot{s}}_{\kappa_\rho q})^\dagger=(-1)^{\lambda+\kappa+q}\cdot\hat{T}^{\lambda\bar{\dot{s}}}_{\kappa_\rho\bar{q}}\hat{T}^{\lambda_s}_{\kappa_\rho q}.\tag{7}$$

Similarly, for the basis vectors $\mathbf{u}^{\lambda\dot{s}}_{1_\rho\dot{q}}\equiv\mathbf{u}_{1_\rho\dot{q}}\otimes\mathbf{u}^{\lambda\dot{s}}$ of the representation of the group $O_3\otimes S_3$,

$$(\mathbf{u}^{\lambda\dot{s}}_{1\rho\dot{q}})^*=(-1)^{\lambda+1+q}\mathbf{u}^{\lambda\bar{\dot{s}}}_{1\rho\bar{\dot{q}}}\equiv\mathbf{u}^{\lambda_s}_{1\rho q}.\tag{8}$$

We call this the alternative (a) basis, lacking as it does the phase factors $(-i)^{\lambda+\kappa}$ of the standard (s) basis. The type of basis (a or s) is indicated, as required, to the left of the corresponding term at the appropriate sub- or superscript level.

We can obtain a useful realization of the basis for the group C_{3v} using the previously introduced vectors $\mathbf{n}^p$,

$$\mathbf{u}^{\Gamma\dot{\sigma}}=(-i)^\Gamma\sum^p\mathbf{n}^p\cdot{}^sU^{p\Gamma\dot{\sigma}}=\sum^p\mathbf{n}^p\cdot{}^aU^{p\Gamma\dot{\sigma}},\tag{9}$$

or the spin operators, if we replace $\mathbf{n}^p$ with $\hat{\mathbf{I}}^p$. For the sake of convenience, as with ${}_sD$, we take the transformation matrices ${}^sU$ to be unitary:

$$({}^sU^{p\Gamma\dot{\sigma}})=\frac{1}{\sqrt{3}}\begin{pmatrix}1 & 1 & 1\\ \epsilon_+ & \epsilon_- & 1\\ \epsilon_- & \epsilon_+ & 1\end{pmatrix}.$$

The indices of this matrix are ordered as follows:

$$p\in\begin{pmatrix}1\\2\\3\end{pmatrix},\quad \Gamma\dot{\sigma}\in(E+1,E-1,A_1 0).$$

The matrix elements are $\epsilon_\sigma=\exp(i\sigma 2\pi/3)=\bar{c}+i\sigma s$ where $\sigma=\pm1$.

The vectors

$$\mathbf{n}^{p_1p_2}=(\mathbf{n}^{p2}-\mathbf{n}^{p1})/\sqrt{3}=m^{p3},$$

$$\mathbf{m}^{(1)}=\begin{pmatrix}0\\1\end{pmatrix},\quad \mathbf{m}^{(2)}=\begin{pmatrix}s\\c\end{pmatrix},\quad \mathbf{m}^{(3)}=\begin{pmatrix}\bar{s}\\c\end{pmatrix}\tag{10}$$

provide an alternative construction if we associate the side (p_1p_2) of a right triangle with vertices at the Y nuclei with the vertex p_3 according to the rule $p_3(p_1p_2)\in\{1(23),2(31),3(12)\}$.

Other concepts will be introduced as needed.

TABLE I. E Representation Matrices for C_{3v}.

g	S_g	$\Delta^E(g)_{cart}$	$\Delta^E(g)$	$\hat{\mathcal{U}}_g$	$\hat{\mathcal{U}}_g\|^{J_\nu}_{M\underline{M}}\rangle$
(1)(2)(3)	E	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\hat{1}$	1
(123)	C_3	$\begin{bmatrix}\bar{c}&\bar{s}\\s&\bar{c}\end{bmatrix}$	$\begin{bmatrix}\varepsilon^*&0\\0&\varepsilon\end{bmatrix}$	$\hat{\underline{R}}\left(\frac{2\pi}{3},0,0\right)$	$\varepsilon_{\bar{K}}\cdot\|^{J_\nu}_{M\underline{M}}\rangle$
(132)	C_3^{-1}	$\begin{bmatrix}\bar{c}&s\\\bar{s}&\bar{c}\end{bmatrix}$	$\begin{bmatrix}\varepsilon&0\\0&\varepsilon^*\end{bmatrix}$	$\hat{\underline{R}}\left(-\frac{2\pi}{3},0,0\right)$	$\varepsilon_K\cdot\|^{J_\nu}_{M\underline{M}}\rangle$
(1)(23)	σ_v^1	$\begin{bmatrix}1&0\\0&\bar{1}\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\hat{I}_{nv}0\hat{\underline{R}}(0,\pi,0)$	1
(2)(31)	σ_v^2	$\begin{bmatrix}\bar{c}&\bar{s}\\\bar{s}&c\end{bmatrix}$	$\begin{bmatrix}0&\varepsilon\\\varepsilon^*&0\end{bmatrix}$	$\hat{I}_{nv}\cdot\hat{\underline{R}}\left(\frac{2\pi}{3},\pi,-\frac{2\pi}{3}\right)$	$\varepsilon_{\bar{K}}\cdot(-1)^{\nu+\underline{M}}\|^{J_\nu}_{M\underline{\bar{M}}}\rangle$
(3)(12)	σ_v^3	$\begin{bmatrix}\bar{c}&s\\s&c\end{bmatrix}$	$\begin{bmatrix}0&\varepsilon^*\\\varepsilon&0\end{bmatrix}$	$\hat{I}_{nv}\cdot\hat{\underline{R}}\left(-\frac{2\pi}{3},\pi,\frac{2\pi}{3}\right)$	$\varepsilon_K\cdot(-1)^{\nu+\underline{M}}\|^{J_\nu}_{M\underline{\bar{M}}}\rangle$

3. HYPERFINE INTERACTION HAMILTONIAN

Hyperfine interaction components, in a general discussion, are transformed to an invariant coupling form in two-sided tensor operators. The required expansion in irreducible components of the second-rank tensors of the groups SO_3 and S_3 is described in Appendix B. We further propose a perfectly well-defined ordering of the spin subsystems, $\mathbf{J}\oplus\mathbf{I}\oplus\mathbf{I}^h=\mathbf{F}^h$.

3.1. Spin–rotation Hamiltonian

3.1.1. Since the angular velocity $\mathbf{\Omega}$ of a molecule with C_{3v} symmetry may not point in the same direction as its angular momentum $\hbar\hat{\mathbf{J}}=\mathsf{I}\cdot\mathbf{\Omega}$ (I is the inertia tensor in the center of mass system), the spin–rotation interaction can be written out in two ways:

$$-\hat{H}_{sr}=\sum^{p}\mathsf{M}^p{:}\hat{\mathbf{J}}\hat{\mathbf{I}}^p=\sum^{p}\mathsf{R}^p{:}\hat{\Omega}\hat{I}^p,$$

$$\mathsf{M}^p=\tilde{\mathsf{B}}\cdot\mathsf{R}^p,\quad \tilde{\mathsf{B}}=2\mathsf{B}=\hbar\cdot\mathsf{I}^{-1},\quad B_\perp\leqslant 2B_z. \tag{11}$$

A colon denotes contraction over corresponding (Cartesian) indices of the O_3 tensors, yielding a scalar. The tensor $\mathsf{R}^{(p)}$ is dimensionless.

In the first case, the tensor M^p is not symmetric ($\mathsf{M}^p\neq\mathsf{M}^{p\mathsf{T}}$), but to make up for that, $\hat{\mathbf{J}}$ is diagonal in J. In the second case, R^p is symmetric, but the matrix elements of the operator $\hat{\Omega}$ are not diagonal in J. The asymmetry of M^p is due in general to the fact that $\hat{\mathbf{J}}$ is tied to the center of mass, which lies outside the nuclei p, while $\hat{\Omega}$ is coordinate-free and can be translated to any of the nuclei unaltered.

C_{3v} symmetry yields the following:

$$\mathsf{R}^p=\begin{bmatrix}\underline{R}^{A_1}_{\perp}\cdot 1_2+\underline{R}^{E}_{\perp}\cdot\sigma_v^p\underline{R}^{E}_{z}\cdot\underline{\mathbf{n}}^p\\ \underline{R}^{E}_{z}\cdot\underline{\mathbf{n}}^{p\mathsf{T}}\qquad \underline{R}^{A_1}_{z}\end{bmatrix}={}_{(n)}\underline{R}^p+{}_{(e)}\underline{R}^p. \tag{12}$$

Here the Cartesian components of the two-dimensional column vector $\mathbf{n}^p$ are defined in Eq. (1). The matrices σ_v^p in Cartesian (Δ^E_{cart}) and spherical (Δ^E) bases are given in Table I. The right-hand side of (12) is given in terms of the conventional nuclear (n) and electronic (e) components of this tensor, with

$$(n)\underline{\mathsf{R}}^{p_1}=-\sum^{p_2\neq p_1}R_{p_1p_2}(\underline{1}_3-\underline{\mathbf{n}}^{p_1p_2}\otimes\underline{\mathbf{n}}^{p_1p_2}),$$

$$R_{p_1p_2}=\frac{\mu_{p_1}q_{p_2}}{\hbar c r_{p_1p_2}}. \tag{13}$$

The electronic component depends on rotational excitation of the valence electrons.[15] Using the two-sided tensor operators introduced above, we can write the same Hamiltonian in invariant-coupling form:

$$-\hat{H}_{sr}=\sum_{\kappa}^{\lambda}[\tilde{\mathsf{M}}^{\lambda\otimes}_{(11)\kappa\otimes}\hat{\mathbf{J}}^{A_1\otimes}_{1\otimes}\hat{\mathbf{I}}^{\lambda}_{1}]^{A_1 0}_{0_+0}$$

$$=\sum_{\kappa}^{\lambda}[\tilde{\mathbf{R}}^{\lambda\otimes}_{(11)\kappa\otimes}\hat{\Omega}^{A_1\otimes}_{1\otimes}\hat{\mathbf{I}}^{\lambda}_{1}]^{A_1 0}_{0_+0}. \tag{14}$$

The significance of the tilde over a tensor is that, for example, $\tilde{\mathsf{M}}^{\lambda}_{\kappa}=\sqrt{[\lambda][\kappa]}\mathsf{M}^{\lambda}_{\kappa}$. Hereafter, symbols in brackets (e.g., $[\lambda]$) correspond to the dimension of their respective representations.[4] The spherical components of tensors (a is the alternative basis) can be expressed in terms of Cartesian components:

$${}^{a}M^{A_1 0}_{(11)0,\dot{0}}=M^{A_1}_{z}+2M^{A_1}_{\perp},\quad M^{A_1}_{z}=\tilde{B}_z R^{A_1}_{z},$$

$$M^{A_1}_{\perp}=\tilde{B}_\perp R^{A_1}_{\perp},\quad {}^{a}M^{A_1\dot{0}}_{(11)1,\dot{0}}=0,$$

$${}^{a}M^{A_1\dot{0}}_{(11)2,\dot{0}}=-\sqrt{2}(M^{A_1}_{z}-M^{A_1}_{\perp}),$$

$${}^{a}M^{E\dot{\sigma}}_{(11)1,\dot{\sigma}}=\sqrt{3}M^{E}_{(-)z},\quad M^{E}_{(\pm)z}=\tilde{B}_{(\pm)}R^{E}_{z},$$

$$\tilde{B}_{(\pm)}=(\tilde{B}_z\pm\tilde{B}_\perp)/2,\quad {}^{a}M^{E\dot{\sigma}}_{(11)2,\dot{\sigma}}=\sqrt{3}\sigma M^{E}_{(+)z},$$

$${}^{a}M^{E\dot{\sigma}}_{(11)2,\underline{2\sigma}}=\sqrt{3}M^{E}_{\perp},\quad M^{E}_{\perp}=\tilde{B}_\perp R^{E}_{\perp}, \tag{15}$$

$$ {}^{a}R^{A_1\dot{0}}_{(11)0,\underline{\dot{0}}}=R^{A_1}_{\underline{z}}+2R^{A_1}_{\underline{\perp}}, \quad {}^{a}R^{A_1\dot{0}}_{(11)2,\underline{\dot{0}}}=-\sqrt{2}(R^{A_1}_{\underline{z}}-R^{A_1}_{\underline{\perp}}), $$

$$ {}^{a}R^{E\dot{\sigma}}_{(11)2,\underline{\tilde{\sigma}}}=-\sqrt{3}\sigma R^{E}_{\underline{z}}, \quad {}^{a}R^{E\dot{\sigma}}_{(11)2,\underline{2\sigma}}=\sqrt{3}R^{E}_{\underline{\perp}}. \tag{16} $$

Four constants are required for a description of spin–rotation interaction; only the scalar constants (A_1)are usually known. example, in $^{12}CH_3F$ (Ref. 16),

$$ M^{A_1}_{\underline{\perp}}=0.8\pm1.5 \text{ kHz}, \quad M^{A_1}_{\underline{z}}=14.66\pm0.7 \text{ kHz}. $$

3.1.2. For on-axis spins, the corresponding structure of the spin–rotation interaction has only scalar (A_1) components:

$$ -\hat{H}^{h}_{sr}=\mathsf{M}^{h}:\hat{\mathbf{J}}\hat{\mathbf{I}}^{h}=\sum_{\kappa}[\tilde{\mathbf{M}}^{h}_{(11)\kappa}\otimes\hat{\mathbf{J}}_1\otimes\hat{\mathbf{I}}^{h}_1]^{A_1 0}_{0_+ 0}. \tag{17} $$

Here

$$ \mathsf{M}^{h}=\tilde{\mathsf{B}}\cdot\mathsf{R}^{h}, \quad \underline{\mathsf{R}}^{h}=\begin{bmatrix} R^{hA_1}_{\underline{\perp}}\cdot\hat{1}_2 & 0 \\ 0 & R^{hA_1}_{\underline{z}} \end{bmatrix}={}_{(n)}\underline{\mathsf{R}}^{h}+{}_{(e)}\underline{\mathsf{R}}^{h}. \tag{18} $$

For example, in $^{12}CH_3F$ (Ref. 16),

$$ M^{\mathsf{F}A_1}_{\underline{\perp}}=4.0\pm1.9 \text{ kHz}, $$

$$ M^{\mathsf{F}A_1}_{\underline{z}}=-51.1\pm1.3 \text{ kHz}. $$

3.2. Spin–spin Hamiltonian

We assume here that spin–spin interaction are mostly direct (nuclear). Interactions mediated by electron spins are cited for completeness, but are not taken into consideration: ${}_{(e)}\mathsf{S}^{p_1p_2}\simeq 0$.

3.2.1. Spin-spin interactions between off-axis spins ($p\in(1,2,3)$) and on-axis spins ($h\in(C,Z)$).

$$ \hat{H}^{h}_{ss}=\sum^{p}\mathsf{S}^{hp}:\hat{\mathbf{I}}^{p}\hat{\mathbf{I}}^{h}=\sum^{\lambda}_{\kappa}[\tilde{\mathsf{S}}^{h\lambda}_{\kappa}\otimes\hat{\mathbf{I}}^{\lambda}_1\otimes\mathbf{I}^{hA_1}_1]^{A_1 0}_{0_+ 0}, \tag{19} $$

$$ \mathsf{S}^{hp}=\begin{bmatrix} S^{hA_1}_{\underline{\perp}}\cdot 1_2+S^{hE}_{\underline{\perp}}\cdot\sigma^{p}_{v} & S^{hE}_{\underline{z}}\cdot\mathbf{n}^{p} \\ S^{hE}_{\underline{z}}\cdot\mathbf{n}^{p\overline{T}} & S^{hA_1}_{\underline{z}} \end{bmatrix} $$

$$ ={}_{(n)}\mathbf{S}^{hp}+{}_{(e)}\mathbf{S}^{hp}. \tag{20} $$

This tensor has structure similar to $\underline{\mathsf{R}}^{p}$, and

$$ {}_{(n)}\underline{\mathsf{S}}^{hp}=S_{hp}(\underline{1}_3-3\underline{\mathbf{n}}^{hp}\otimes\underline{\mathbf{n}}^{hp}), \quad \hbar S_{ij}=\mu_i\mu_j/r^{3}_{ij}\ ; \tag{21} $$

$$ {}^{a}S^{hA_1\dot{0}}_{(11)0,\underline{\dot{0}}}=0, $$

$$ {}^{a}S^{hA_1\dot{0}}_{(11)2,\underline{\dot{0}}}=-\frac{3}{\sqrt{2}}S_{hH}[1-3(r_{Oh}/r_{hH})^2], $$

$$ {}^{a}S^{hE\dot{\sigma}}_{(11)2,\underline{\dot{\sigma}}}=\sigma\cdot 3\sqrt{3}S_{hH}r_{Oh}r_{OH}/r^{2}_{hH}, $$

$$ {}^{a}S^{hE\dot{\sigma}}_{(11)2,\underline{2\sigma}}=-\frac{3}{2}\sqrt{3}S_{hH}(r_{OH}/r_{hH})^2. \tag{22} $$

3.2.2. Interactions among off-axis spins

$$ \hat{H}_{ss}=\sum^{(p_1p_2)}\mathsf{S}^{(p_1p_2)}:\hat{\mathbf{I}}^{p_1}\hat{\mathbf{I}}^{p_2} $$

$$ =\sum^{(\lambda_1\lambda_2)\lambda}_{\kappa}[\tilde{\mathsf{S}}^{(\lambda_1\lambda_2)\lambda}_{(11)\kappa}\otimes\hat{\mathbf{I}}^{\lambda_1}_1\otimes\hat{\mathbf{I}}^{\lambda_2}_1]^{A_1 0}_{0_+ 0}. \tag{23} $$

Here we have employed the alternative structure (10) in the vectors $\mathbf{m}^{p_3}=\mathbf{n}^{p_1p_2}$:

$$ \underline{\mathsf{S}}^{(p_3)}_{p_1p_2}=\begin{bmatrix} \underline{S}^{A_1}_{\perp}\cdot\hat{1}_2+S^{E}_{\underline{\perp}}\cdot\sigma^{p_3}_{v}S^{E}_{\underline{z}}\cdot\underline{\mathbf{m}}^{p_3} \\ S^{E}_{\underline{z}}\cdot\underline{\mathbf{m}}^{p_3\mathsf{T}} \quad S^{A_1}_{\underline{z}} \end{bmatrix}={}_{(n)}\underline{\mathsf{S}}^{p_1p_2}+{}_{(e)}\underline{\mathsf{S}}^{p_1p_2}, \tag{24} $$

$$ {}_{(n)}\underline{\mathsf{S}}^{p_1p_2}=S_{p_1p_2}(\underline{1}_3-3\underline{\mathbf{n}}^{p_1p_2}\otimes\underline{\mathbf{n}}^{p_1p_2}); \tag{25} $$

$$ {}^{a}S^{(A_1A_1)A_1\dot{0}}_{(11)2,\underline{\dot{0}}}=-\sqrt{\frac{2}{3}}S_{HH}, $$

$$ {}^{a}S^{(EE)A_1\dot{0}}_{(11)2,\underline{\dot{0}}}=-\frac{1}{\sqrt{2}}\cdot{}^{a}S^{(A_1A_1)A_1\dot{0}}_{(11)2,\underline{\dot{0}}}, $$

$$ {}^{a}S^{(A_1E)E\dot{\sigma}}_{(11)2,\underline{2\dot{\sigma}}}=-\frac{3}{4}S_{HH}, $$

$$ {}^{a}S^{(EE)E\dot{\sigma}}_{(11)2,\underline{2\dot{\sigma}}}=2\cdot{}^{a}S^{(A_1E)E\dot{\sigma}}_{(11)2,\underline{2\dot{\sigma}}}. \tag{26} $$

3.2.3. Interactions among on-axis spins ($h_1\neq h_2$) and quadrupole interactions ($h_1=h_2$):[17]

$$ \hat{H}^{h_1h_2}_{ss}=\mathsf{S}^{h_1h_2}: \quad \hat{\mathbf{I}}^{h_1}\hat{\mathbf{I}}^{h_2}=\sum_{\kappa}[\tilde{\mathsf{S}}^{h_1h_2}_{(11)\kappa}\otimes\hat{\mathbf{I}}^{h_1}_1\otimes\hat{\mathbf{I}}^{h_2}_1]^{A_1 0}_{0_+}\ . \tag{27} $$

4. WAVE FUNCTIONS

Rotational and spin wave functions can be transformed to symmetry-adapted form using the projection operators for finite groups (C_{3v} and S_3, respectively).

4.1. Rotational wave functions

The rotational wave functions of a symmetric top can be defined in terms of the elements of the orthogonal matrix $C\in O_3$, as described in Ref. 10:

$$ \langle C|^{J\nu}_{M\underline{M}}\rangle_a=(-i)^{J+\nu}\langle C|^{J\nu}_{M\underline{M}}\rangle_s=(-i)^{J+\nu}\sqrt{\frac{[J]}{8\pi^2}} $$

$$ \times(-1)^{\underline{M}}D^{J\nu *}_{M\dot{\underline{M}}}(C), $$

$$ |^{J_p}_{M\underline{M}}\rangle^{*}_{a}=p(-1)^{M+\underline{M}}|^{J_p}_{\overline{M}\ \underline{\overline{M}}}\rangle_a, \quad [J]=2J+1. \tag{28} $$

In these equations, $D^{J\nu}_{M\underline{M}}(C)=(\det C)^{\nu}\cdot D^{J}_{M\underline{M}}(C)$.

The results of operating on these functions with the angular momentum operators ${}_{a}\hat{J}_{1\underline{q}}$ and ${}_{a}\hat{J}_{1\dot{\underline{q}}}$ have the same form, and the inversion operator $\hat{I}_{n\nu}$ is diagonal:

$$ {}_{a}\hat{J}_{10}|^{J\nu}_{M\underline{M}}\rangle_a=(-i)M|^{J\nu}_{M\underline{M}}\rangle_a, $$

$$ {}_a\hat{J}_{1\pm1}|^{J\nu}_{M\underline{M}}\rangle_a=(-i)\times\left(\mp\frac{1}{\sqrt{2}}\right)\sqrt{(J\mp M)(J\pm M+1)}|^{J\nu}_{M\pm1\underline{M}}\rangle_a; \quad (29) $$

$$ {}_a\hat{J}_{10}|^{J\nu}_{M\underline{M}}\rangle_a=(-i)\underline{M}|^{J\nu}_{M\underline{M}}\rangle_a, $$

$$ {}_a\hat{J}_{1\pm1}|^{J\nu}_{M\underline{M}}\rangle_a=(-i)\left(\mp\frac{1}{\sqrt{2}}\right)\times\sqrt{(J\mp\underline{M})(J\pm\underline{M}+1)}|^{J\nu}_{M\underline{M}\pm1}\rangle_a; \quad (30) $$

$$ \hat{I}_{n\nu}|^{J\nu}_{M\underline{M}}\rangle_a=(-1)^{J+\nu}|^{J\nu}_{M\underline{M}}\rangle_a=p|^{Jp}_{M\underline{M}}\rangle, $$

and $p=(-1)^{\tau}=(-1)^{J+\nu}$ is the parity. The representation of O_3 in symmetric-top function can be written in terms of the D functions of Ref. 9:

$$ \hat{\mathscr{H}}^c_s\langle C|^{J\nu}_{M\underline{M}}\rangle=\langle S^{-1}C|^{J\nu}_{M\underline{M}}\rangle=\sum_{M_1}\langle C|^{J\nu}_{M_1\underline{M}}\rangle D^{J\nu}_{M_1M}(S). \quad (31) $$

When there is no inversion, $\hat{\mathscr{H}}^c_s$ reduces to

$$ \hat{\mathscr{R}}(\alpha,\beta,\gamma)=\hat{\mathscr{R}}_z(\alpha)\cdot\hat{\mathscr{R}}_y(\beta)\cdot\hat{\mathscr{R}}_z(\gamma), $$

$$ \hat{\mathscr{R}}_j(\varphi)=\exp(-i\varphi\hat{J}_j), \quad j\in(x,y,z). $$

Similarly for $O_{\underline{3}}$,

$$ \hat{\mathscr{H}}^c_{\underline{s}}\langle C|^{J\nu}_{M\underline{M}}\rangle=\langle C\underline{S}|^{J\nu}_{M\underline{M}}\rangle=\langle\underline{S}^{-1}\underline{C}|^{J\nu}_{\underline{M}M}\rangle=\sum_{\underline{M}_1}\langle C|^{J\nu}_{M\underline{M}_1}\rangle D^{J\nu}_{\underline{M}_1\underline{M}}(\underline{S}). \quad (32) $$

Here $\underline{C}\equiv C^{-1}$. With no inversions, $\hat{\mathscr{H}}^c_{\underline{s}}$ reduces to

$$ \hat{\underline{\mathscr{R}}}(\alpha,\beta,\gamma)=\hat{\underline{\mathscr{R}}}_z(\alpha)\cdot\hat{\underline{\mathscr{R}}}_y(\beta)\cdot\hat{\underline{\mathscr{R}}}_z(\gamma), $$

$$ \hat{\underline{\mathscr{R}}}_j(\varphi)=\exp(-i\varphi\hat{\underline{J}}_j), \quad \underline{j}\in(\underline{x},\underline{y},\underline{z}). $$

Symmetry-adapted functions can be obtained using the rotational projection operator[5)]

$$ \underline{P}^{\Gamma\sigma(\sigma')}_J=\frac{[\Gamma]}{[G]}\sum_{g\in G}\Delta^{\Gamma*}_{\sigma\sigma'}(g)\underline{\mathscr{U}}_g. $$

E-representation matrices $\Delta^E(g)$ for $g\in S_3$ and the corresponding action of $\underline{\mathscr{U}}_g$ on the rotational wave functions are given in Table I (where dots denote vanishing matrix elements):

$$ |(K_r)^{\Gamma\sigma}_{J_\nu M}\rangle_a=\frac{1}{\sqrt{2(2+\delta_{K,0}-\delta_{r,0})}}\{(1-\sigma(-1)^r)|^{J\nu}_{MK}\rangle_a+(1+\sigma(-1)^r)(-1)^{\Gamma+\nu+K}|^{J\nu}_{M\tilde{K}}\rangle_a\}, \quad \nu\in(g,u). \quad (33) $$

Here and elsewhere $K=|\underline{M}|$, and the subscript $r=r_3=\mathrm{Rest}(K/3)$ is the remainder after division. The transformation from the standard to the alternative basis is

$$ \langle C|(K_r)^{\Gamma\sigma}_{J_\nu M}\rangle_a=(-i)^{\Gamma+J}\langle C|(K_r)^{\Gamma\sigma}_{J_\nu M}\rangle_s. $$

Complex conjugation of the wave functions is consistent with hermitian conjugation of the two-sided operators defined in (7):

$$ |(K_r)^{\Gamma\sigma}_{J_pM}\rangle^*_a=(-1)^{\Gamma+J+M}|(K_r)^{\Gamma\bar{\sigma}}_{J_pM}\rangle_a. \quad (34) $$

It is assumed here that $|p\rangle^*=|p\rangle$.

4.2. Spin wave functions

We employ the alternative choice of phase for the spin wave functions and spin operators of the nuclei p:

$$ |I^p,M^p\rangle_a=(-i)^{Ip}|I^p,M^p\rangle_s, $$

$$ {}_a\hat{I}^p_{10}|I^p,M^p\rangle_a=(-i)M^p|I^p,M^p\rangle_a, $$

$$ {}_a\hat{I}^p_{1\pm1}|I^p,M^p\rangle_a=(-i)\left(\mp\frac{1}{\sqrt{2}}\right)\times\sqrt{(I^p\mp M^p)(I^p\pm M^p+1)}|I^p,M^p\pm1\rangle_a. \quad (35) $$

Here M^p is the projection of $\hat{\mathbf{I}}^p$ on the $\mathbf{u}_z$ axis, which is fixed in space.

Let $I^p=1/2$ and $M^p=\sigma/2$, where $\sigma=\pm1$. For the nonsymmetric wave functions of the three equivalent nuclei we use the shorthand notation

$$ \langle\underline{M}^1,\underline{M}^2,\underline{M}^3|M^1,M^2,M^3\rangle=\langle\underline{M}^1|1/2,M^1\rangle\otimes\langle\underline{M}^2|1/2,M^2\rangle\otimes\langle\underline{M}^3|1/2,M^3\rangle. $$

The spin-projection operator acting on these wave functions yields the symmetry-adapted functions

$$ \underline{P}^{\Gamma\sigma(\sigma')}_J=\frac{[\Gamma]}{[G]}\sum_{g\in G}\Delta^{\Gamma*}_{\sigma\sigma'}(g)\underline{g}. $$

Here the $\underline{g}$ are the spin arguments of $\underline{\mathbf{M}}^p$,[18] so the action of the spin projection operator is consistent with that of the rotation operator. As a result, we obtain the symmetrized combinations of wave functions

$$ \left|\begin{matrix}A_1 & 0\\ 3/2 & 3M\end{matrix}\right\rangle_a=|M,M,M\rangle_a, \quad (M=\pm1/2), \quad (36) $$

$$ \left|\begin{matrix}A_1 & 0\\ 3/2 & M\end{matrix}\right\rangle_a=\frac{1}{\sqrt{3}}\{|\overline{M},M,M\rangle_a+|M,\overline{M},M\rangle_a+|M,M,\overline{M}\rangle_a\}, \quad (37) $$

$$ \left|\begin{matrix}E_1 & \sigma\\ 1/2 & M\end{matrix}\right\rangle_a=\frac{2M}{\sqrt{3}}\{|\overline{M}M,M\rangle_a+\varepsilon_\sigma|M,\overline{M},M\rangle_a+\varepsilon_\sigma|M,M,\overline{M}\rangle_a\}. \quad (38) $$

The phase factor $2M=\pm1$ is required in the last equation for the total spin operator, ${}_s\hat{\mathbf{I}}=\Sigma^p{}_s\hat{\mathbf{I}}^p$ to act in standard fashion:

$$ \left\langle\begin{matrix}E & \sigma\\ 1/2 & 1/2\end{matrix}\right|{}_s\hat{I}_+\left|\begin{matrix}E & \sigma\\ 1/2 & -1/2\end{matrix}\right\rangle=1, \quad \hat{I}_\pm=\hat{I}_x\pm i\hat{I}_y. $$

Symmetrized spin operators can be obtained similarly, in accordance with (9).

4.3. Total wave functions satisfying the Pauli exclusion principle

The Pauli exclusion principle requires that

$$|(K_r)^{(\Gamma_J\Gamma_I)A_20}_{(J_\nu I)M_JM_I}\rangle=\sum^{\sigma_J\sigma_I}\langle A_20|\Gamma_J\sigma_J\Gamma_I\sigma_I\rangle|(K_r)^{\Gamma_J\sigma_J}_{J_\nu M_J}\rangle|^{\Gamma_I\sigma_I}_{IM_I}\rangle. \tag{39}$$

Using Appendix A, we obtain

$$\langle A_20|A_20A_10\rangle=1,\quad \langle A_20|E\tilde{\sigma}E\sigma\rangle=\sigma/\sqrt{2}.$$

The total wave functions behave as before under the operators ${}_a\hat{J}_{1\dot{q}}$, ${}_a\hat{I}_{1\dot{q}}$, and $\hat{I}_{n\nu}$, but not ${}_a\hat{J}_{1\dot{q}}$ and ${}_a\hat{I}^p_{1\dot{q}}$. The possible rotational states with various K for the electronic and vibrational ground states of XY_3Z molecules are analogous to those of NH_3 discussed by Landau and Lifshitz.[19] On account of the Pauli principle, XY_3Z molecules have no states corresponding to those of atoms. Indeed, atomic states must have parity $p=(-1)^J$, and are obtained with $K=0$, but in the present case we have $\nu=1$, i.e., $p=(-1)^{J+1}$.

5. MATRIX ELEMENTS OF HYPERFINE INTERACTIONS

Below we make use of the following factorization of matrix elements of two-sided tensor operators (the Wigner–Eckart theorem):[14]

$$\langle(\alpha')^{\Gamma'\sigma'}_{J'_{\nu'}M'}|\hat{T}^{\lambda s}_{\kappa_\eta q}|(\alpha)^{\Gamma\sigma}_{J_\nu M}\rangle=\left\langle\begin{matrix}\Gamma'\sigma' & \lambda s & \Gamma\sigma\\ J'_{\nu'}M' & \kappa_\eta q & J_\nu M\end{matrix}\right\rangle \times\frac{[(\alpha')^{\Gamma'}_{J'_{\nu'}}\|\hat{\mathbf{T}}^\lambda_{\kappa_\eta}\|(\alpha)^\Gamma_{J_\nu}]}{\sqrt{[\Gamma']\cdot[J']}}. \tag{40}$$

If the operator is hermitian, then its reduced matrix element satisfies

$$[(\alpha')^{\Gamma'}_{J'_{\nu'}}\|\hat{\mathbf{T}}^\lambda_{\kappa_\eta}\|(\alpha)^\Gamma_{J_\nu}]=(-1)^{-J'+\kappa+J-\Gamma'+\lambda+\Gamma}\times[(\alpha')^{\Gamma'}_{J'_{\nu'}}\|\hat{\mathbf{T}}^\lambda_{\kappa_\eta}\|(\alpha)^\Gamma_{J_\nu}]^*. \tag{41}$$

All required applications of the Wigner–Eckart theorem can be found in Ref. 10. One need only note that the reduced matrix element defined in the latter is

$$\langle(\alpha')_{J'}\|\hat{\mathbf{T}}_\kappa\|(\alpha)_J\rangle=\frac{(-1)^{-J'+\kappa+J}}{\sqrt{[J']}}[(\alpha')_{J'}\|\hat{\mathbf{T}}_\kappa\|(\alpha)_J]. \tag{42}$$

It is straightforward to adapt the discussion to C_{3v}.

5.1. Auxiliary spin matrix elements

$$[{}^{\Gamma_J}_I\|\hat{\mathbf{I}}^{A_1}_1\|^{\Gamma_I}_I]=i(\sqrt{5}\,\delta_{\Gamma_JA_1}+\delta_{\Gamma_JE}),$$

$$[{}^E_{1/2}\|\hat{\mathbf{I}}^E_I\|^{\Gamma_I}_I]=2i(\delta_{\Gamma_JA_1}+\delta_{\Gamma_JE}).$$

Note that according to (9), $\hat{\mathbf{I}}^{A_10}=\hat{\mathbf{I}}/\sqrt{3}$, while the rotational angular momentum is $\hat{\mathbf{J}}^{A_10}=\hat{\mathbf{J}}$.

$$[{}^E_{1/2}\|[\mathbf{I}^{\Gamma_1}_1\otimes\mathbf{I}^{\Gamma_2}_1]^E_2\|^{A_1}_{3/2}=-\sqrt{\frac{5}{2\cdot3}}\{\delta_{\Gamma_1A_1}\delta_{\Gamma_2E}+\delta_{\Gamma_1E}\delta_{\Gamma_2A_1}+2\delta_{\Gamma_1E}\delta_{\Gamma_2E}\},$$

$$[{}^{A_1}_{3/2}\|[\hat{\mathbf{I}}^\Gamma_1\otimes\hat{\mathbf{I}}^\Gamma_1]^{A_1}_2\|{}^{A_1}_{3/2}]=\sqrt{\frac{5}{3}}(\delta_{\Gamma E}-\sqrt{2}\delta_{\Gamma A_1}),$$

$$[I^h\|\hat{I}^h_1\|I^h]=i\sqrt{I^h(I^h+1)[I^h]}|_{I^h=1/2}=i\sqrt{\frac{3}{2}},$$

$$[I^h\|[\hat{\mathbf{I}}^h_1\otimes\hat{\mathbf{I}}^h_1]_2\|I^h]=\frac{\sqrt{6}I^h(I^h+1)(2I^h+1)[1-4I^h(I^h+1)/3]}{[(2I^h-1)2I^h(2I^h+1)(2I^h+2)(2I^h+3)]^{1/2}}.$$

5.2. Auxiliary rotational matrix elements

The matrix elements for the D functions are

$${}_a\langle{}^{J'_{\nu'}}_{M'\underline{M}'}|D^{\kappa_\eta*}_{q\underline{q}}(C)|^{J_\nu}_{M\underline{M}}\rangle_a=(-i)^{\tau-\tau'}(-1)^{J'+\kappa+J}(-1)^{\alpha\underline{q}}\sqrt{\frac{[J]}{[J']}}\times\langle J'_{\nu'}M'|\kappa_\eta qJ_\nu M\rangle\langle J'_{\nu'}\underline{M}'|\kappa_\eta\bar{\underline{q}}J_\nu\underline{M}\rangle. \tag{43}$$

The D functions relate irreducible tensors in spatially fixed ($\mathbf{u}_j$) and molecule-fixed ($\mathbf{u}^C_{\underline{i}}$) coordinate systems:

$$M_{\kappa_\eta q}(C)=\sum_{\underline{q}}D^{\kappa_\eta*}_{q\underline{q}}(C)M_{\kappa_\eta\dot{\underline{q}}}.$$

Here $C_{j\underline{i}}=(\mathbf{u}_j\cdot\mathbf{u}^C_{\underline{i}})$, with $C\in O_3$.

The matrix elements for rotational angular momentum are

$$[(K_0)^{\Gamma_J}_{J_p}\|_a\mathbf{J}^{A_1}_{1_+}\|(K_0)^{\Gamma_J}_{J_p}]_a=\sqrt{[\Gamma_J]}[J\|_a\mathbf{J}_1\|J]_a,$$

$$[J\|_a\mathbf{J}_1\|J]_a=i\sqrt{J(J+1)[J]},\quad [J]\equiv2J+1.$$

5.3. Diagonal matrix elements $\langle J_pK_r|\hat{H}_+|J_pK_r\rangle$

$$[(K_r)^{\Gamma_J}_{J_p}\|\tilde{\mathbf{M}}^\lambda_{(11)\kappa}\|(K_r)^{\Gamma_J}_{J_p}]=\delta_{\lambda A_1}(\delta_{\kappa0}+\delta_{\kappa2})\sqrt{[\Gamma_J][J]}\tilde{M}^{A_10}_{(11)\kappa\underline{0}}\langle J_pK|\kappa_+0J_pK+\delta_{\lambda E}\delta_{\kappa2}\delta_{\Gamma_JE}\delta_{K1}\sqrt{2[J]}p(-1)^{J+1}\times\tilde{M}^{E1}_{(11)2\underline{2}}\langle J_p1|2_+2J_p\bar{1}\rangle. \tag{44}$$

Here

$$\langle J1|22J\bar{1}\rangle=\sqrt{\frac{3J(J+1)}{2(2J-1)(2J+3)}},$$

$$\langle JK|20JK\rangle=\left(\frac{3K^2}{J(J+1)}-1\right)\sqrt{\frac{J(J+1)}{(2J-1)(2J+3)}}.$$

The discussion of diagonal matrix elements has been organized in accordance with the foregoing description of the

hyperfine interaction Hamiltonian. Besides the reduced matrix elements, an equivalent operator form comes into play.

5.3.1. Spin–rotation matrix elements

Off-axis spins:

$$[(K_p)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI)F_I}\|\hat{\bar{H}}_{sr}\|\,(K_p)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI)F_I}]$$

$$=\sqrt{[F_I]}(-1)^{J+I+F_I}\begin{Bmatrix} J & I & F_I\\ I & J & 1\end{Bmatrix}(-1)^1\sqrt{J(J+1)}[J]$$

$$\times\Bigg\{(\sqrt{5}\,\delta_{I,3/2}+\delta_{I,1/2})\Bigg(\tilde{M}^{A_1 0}_{(11)0\underline{0}}\begin{Bmatrix}0 & 1 & 1\\ J & J & J\end{Bmatrix}$$

$$+\tilde{M}^{A_1 0}_{(11)2\underline{0}}\Bigg)\begin{Bmatrix}2 & 1 & 1\\ J & J & J\end{Bmatrix}\langle J_pK|2_+0J_pK\rangle\Bigg)+\delta_{I,1/2}\delta_{K,1}p$$

$$\times(-1)^J\sqrt{2}\tilde{M}^{E1}_{(11)22}\begin{Bmatrix}2 & 1 & 1\\ J & J & J\end{Bmatrix}\langle J_p1|2_+2J_p\bar{1}\rangle\Bigg\}\,, \quad (45)$$

$$\langle\hat{\bar{H}}_{sr}\rangle^I_{J_pK}=[\hat{\mathbf{J}}_1\otimes\hat{\mathbf{I}}_1]_0\Bigg\{\langle M_{00}\rangle^I_J\langle M_{20}\rangle^I_J\Bigg(\frac{3K^2}{J(J+1)}-1\Bigg)$$

$$+\delta_{K,1}p(-1)^J\langle M_{22}\rangle^{1/2}_J\Bigg\}\,. \quad (46)$$

On-axis spins:

$$\langle\hat{\bar{H}}^h_{sr}\rangle^I_{J_pK}=[\hat{\mathbf{J}}_1\otimes\hat{\mathbf{I}}^h_1]_0\Bigg\{\langle M^h_{00}\rangle^I_J+\langle M^h_{20}\rangle^I_J\Bigg(\frac{3K^2}{J(J+1)}-1\Bigg)\Bigg\}. \quad (47)$$

5.3.2. Spin–spin matrix elements

Interaction of on- and off-axis spins:

$$[(K_r)^{(\Gamma_J\Gamma_I)A_2}_{((J_pI)F^I_JI^h)F^h}\|\hat{H}^h_{ss}\|(K_r)^{(\Gamma_J\Gamma_I)A_2}_{((J_pI)F_II^h)F^h}]$$

$$=\sqrt{I^h(I^h+1)[I^h][F^h]}$$

$$\times(-1)^{F'_I+I^hF^h}\begin{Bmatrix}F'_I & I^h & F^h\\ I^h & F_I & 1\end{Bmatrix}\sqrt{[F'_I][F_I]}$$

$$\times\begin{Bmatrix}J & I & F'_I\\ 2 & 1 & 1\\ J & I & F_I\end{Bmatrix}\sqrt{[J]}\{(\sqrt{5}_{I,3/2}+\delta_{I,1/2}/\sqrt{2})$$

$$\times\tilde{S}^{hA_1 0}_{(11)2\underline{0}}\langle J_pK|2_+0J_pK\rangle+\delta_{I,1/2}\delta_{K,1}\cdot p(-1)^J$$

$$\times\tilde{S}^{hE1}_{(11)2\underline{2}}\langle J_p1|2_+2J_p\bar{1}\rangle, \quad (48)$$

$$\langle\hat{H}^{hH}_{ss}\rangle^I_{J_pK}=[\hat{\mathbf{I}}_1\otimes\hat{\mathbf{I}}^h_1]_0\cdot\langle S^h_{00}\rangle^I_J+[[\hat{\mathbf{J}}_1\otimes\hat{\mathbf{J}}_1]_2\otimes\hat{\mathbf{I}}_1$$

$$\otimes\hat{\mathbf{I}}^h_1]_0\Bigg\{\langle S^h_{20}\rangle^I_J\Bigg(\frac{3K^2}{J(J+1)}-1\Bigg)$$

$$+\delta_{K,1}p(-1)^J\langle S^h_{22}\rangle^{1/2}_J\Bigg\}. \quad (49)$$

Interaction of off-axis spins with one another:

$$[(K_r)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI)F_I}\|\hat{H}_{ss}\|(K_r)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI)F_I}]$$

$$=\sqrt{\frac{[F_I]}{[2]}}(-1)^{J+I+F_I}\begin{Bmatrix}J & I & F_I\\ I & J & 2\end{Bmatrix}\sqrt{15[J]}$$

$$\times\tilde{S}^{(EE)A_1 0}_{(11)2\underline{0}}\langle J_pK|2_+0J_pK\rangle, \quad (50)$$

$$\langle\hat{H}_{ss}\rangle^I_{J_pK}=[\hat{\mathbf{I}}_1\otimes\hat{\mathbf{I}}_1]_0\langle S_{00}\rangle^I_J+[[\hat{\mathbf{J}}_1\otimes\hat{\mathbf{J}}_1]_2\otimes\hat{\mathbf{I}}_1\otimes\hat{\mathbf{I}}_1]_0$$

$$\times\langle S_{20}\rangle^{3/2}_J\Bigg(\frac{3K^2}{J(J+1)}-1\Bigg). \quad (51)$$

Interaction of on-axis spins with one another ($h_1\neq h_2$) and quadrupole interaction ($h_1=h_2$):

$$[(K_r)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI^h)F^h}\|\hat{H}^{hh}_{ss}\|(K_r)^{(\Gamma_J\Gamma_I)A_2}_{(J_pI^h)F^h}]$$

$$=\sqrt{\frac{[F^h]}{[2]}}(-1)^{J+I^h+F^h}\begin{Bmatrix}J & I^h & F^h\\ I^h & J & 2\end{Bmatrix}\sqrt{[J]}\tilde{S}^{(hh)}_{(11)2\underline{0}}$$

$$\times\langle J_pK|2_+0J_pK\rangle[I^h\|[\hat{I}^h_1\otimes\hat{I}^h_1]_2\|I^h], \quad (52)$$

$$\langle\hat{H}^{h_1h_2}_{ss}\rangle^I_{J_pK}=[\hat{\mathbf{I}}^{h_1}_1\otimes\hat{\mathbf{I}}^{h_2}_1]_0\langle S^{h_1h_2}_{00}\rangle_J+[[\hat{\mathbf{J}}_1\otimes\hat{\mathbf{J}}_1]_2\otimes\hat{\mathbf{I}}^{h_1}_1$$

$$\otimes\hat{\mathbf{I}}^{h_2}_1]_0\langle S^{h_1h_2}_{20}\rangle_J\Bigg(\frac{3K^2}{J(J+1)}-1\Bigg). \quad (53)$$

5.4. Off-diagonal matrix elements $\langle J'_pK'_r|\hat{H}_+|J_pK_0\rangle$

$$[(K'_r)^E_{J'_p}\|\tilde{\mathbf{M}}^E_{\kappa_+}\|(K_0)^{A_2}_{J_p}]_a$$

$$=(-1)^{\Delta J}i^{\Delta\tau}\sqrt{(1+\delta_{K,0})[J]}J'_pK'|\kappa_+\Delta KJ_pK\rangle$$

$$\times\Bigg\{\delta_{|\Delta K|,1}\cdot\Bigg(\delta_{\kappa,2}\tilde{M}^{E1}_{2\bar{1}}-\delta_{\kappa,1}\frac{\Delta K}{|\Delta K|}\tilde{M}^{E1}_{1\bar{1}}\Bigg)$$

$$+\delta_{|\Delta K|,2}\delta_{\kappa,2}\frac{\Delta K}{|\Delta K|}\tilde{M}^{E1}_{22}\Bigg\}\,. \quad (54)$$

Here $\tau=J+\nu$, $p=(-1)^\tau$, $\Delta\tau=\tau'-\tau$.

$$\Bigg[(K'_r)^E_{J'_p}\Bigg\|\sum_{\kappa=1,2}[\tilde{\mathbf{M}}^{E\otimes}_{\kappa\otimes}\mathbf{J}^{A_1}_1]^E_{1_+}\Bigg\|(K_0)^{A_2}_{J_p}\Bigg]$$

$$=-i^{\Delta\tau}\sqrt{3(1+\delta_{K,0})[J]}[J_p\|\mathbf{J}_{1+}\|J_p]\Bigg\{\delta_{|\Delta K|,1}$$

$$\times\Bigg[\tilde{M}^{E1}_{1\bar{1}}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 1\end{Bmatrix}\frac{\Delta K}{|\Delta K|}\langle J'_pK'|1_+\Delta KJ_pK\rangle$$

$$+\tilde{M}^{E1}_{2\bar{1}}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}\langle J'_pK'|2_+\Delta KJ_pK\rangle\Bigg]$$

$$+\delta_{|\Delta K|,2}\frac{\Delta K}{|\Delta K|}\tilde{M}^{E1}_{22}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}$$

$$\times\langle J'_pK'|2_+\Delta KJ_pK\rangle\Bigg\}\,. \quad (55)$$

This matrix element can alternatively be written

$$[(K_r')^{E}_{J_p'}\|[\tilde{\mathbf{R}}^{E}_{2}\otimes\Omega^{A_1}_{1}]^{E}_{1_+}\|(K_0)^{A_2}_{J_p}]$$

$$=-i^{\Delta\tau}\sqrt{3(1+\delta_{K,0})[J]}$$

$$\times[J_p]\|\mathbf{J}_{1+}\|J_p]\left\{\delta_{|\Delta K|,1}\tilde{R}^{E1}_{21}\left[\tilde{B}_{\perp}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}\right.\right.$$

$$\times\langle J_p'K'|2_+\Delta KJ_pK\rangle$$

$$\left.+\frac{K\cdot(\tilde{B}_z-\tilde{B}_{\perp})}{\sqrt{J(J+1)[J]}}\frac{(-1)^{1+\Delta J}}{\sqrt{10}}\langle J_p'K'|1_+\Delta KJ_pK\rangle\right]$$

$$+\delta_{|\Delta K|,2}\frac{\Delta K}{|\Delta K|}\tilde{R}^{E1}_{22}\tilde{B}_{\perp}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}$$

$$\left.\times\langle J_p'K'|2_+\Delta KJ_pK\rangle\right\}. \tag{56}$$

Here

$$[(K_0')^{A_2}_{J_p'}\|\hat{\Omega}^{A_1}_{1_+}\|(K_0)^{A_2}_{J_p}]$$

$$=\delta_{K_0',K_0}\cdot i^{\tau-\tau'}(-1)^{\Delta J}[J_p\|\hat{\mathbf{J}}_1\|J_p]$$

$$\times\left\{\tilde{B}_{\perp}\delta_{J'J}-\frac{K\cdot(\tilde{B}_z-\tilde{B}_{\perp})}{\sqrt{J(J+1)}}\langle J_p'K|1_+0J_pK\rangle\right\}, \tag{57}$$

and we also make use of the fact that

$$\sum_{J''}\sqrt{[J'']}\begin{Bmatrix}J' & 2 & J''\\ 1 & J & 1\end{Bmatrix}\langle J'K'|2\Delta KJ''K\rangle\langle J''K|10JK\rangle$$

$$=(-1)^{\Delta K+\Delta J+1}\langle J'K'|1\Delta KJK\rangle/\sqrt{10}. \tag{58}$$

6. SPECTROSCOPY

The field spectrum, discounting hyperfine interactions, can be constructed in the same way as the frequency spectrum for both linear and nonlinear absorption of light.[20] When linearly polarized radiation propagates in the direction of the swept magnetic field, the field structure of the nonlinear optical resonance corresponds to the frequency structure of the resonant interaction between the orthogonal circularly polarized components of that same radiation in a coordinate system that tracks the precession of the molecule's magnetic moment. One consequence of this analogy is, for example, that the frequency and field resonances display the same collisional structure. For circularly polarized radiation nad the same field geometry, only the Doppler structure of the field spectrum is preserved.

The experimental results reported in Refs. 21 and 22 were obtained under conditions in which hyperfine interactions could not be neglected, inasmuch as in the absence of collisions they affect the structure of the field spectrum much more significantly than that of the frequency spectrum. An analysis of the situation[1,2] shows that for linearly polarized light, the hyperfine structure of the field spectrum is related to the crossing of magnetic sublevels with $\Delta M_F = \pm 2$ in zero field and as the field builds up. The difference between the field spectra and the frequency spectra in this case is due mainly to the nonlinear magnetic field dependence of the splitting of M levels, rather than the field dependence of the absorption probability. For a circularly polarized light wave, it is precisely the field dependence of the absorption probability amplitudes in hyperfine transitions that leads to the onset of resonance. The contributors are magnetic sublevels with $\Delta M_F=0$ that undergo anticrossing in an external field. This resonance owes its very existence entirely to hyperfine interactions. Whereas hyperfine interactions can couple the spin and rotational angular momentum vectors, a field interaction that is turned on gradually can disrupt it. This then makes it feasible to carry out spectroscopy of the disruption of hyperfine coupling by an external field.

The interaction between light and a medium in the presence of hyperfine interactions can be described in terms of transition probability amplitudes in four-level subsystems. Popov[20] has described a similar situation in a discussion of polarization-based methods of nonlinear two-level spectroscopy neglecting hyperfine interactions. Thus, consideration of other than the degenerate case in the parameters of the medium or the radiation makes it necessary to distinguish among interactions of light with two-, three-, and four-level subsystems. One outstanding feature of field structures associated with hyperfine interactions is that they show up solely in the imaginary part of the susceptibility, which suggests that the given situation lacks any field analogs of the dispersion relations considered in Ref. 23. As a result, similar structures are usually observed via field-spectroscopy methods for studying saturation.

In going from frequency spectroscopy to field spectroscopy, we are still left with the problem of discriminating among the various hyperfine contributions to the nonlinear optical resonance amplitude, which corresponds to crossings and anticrossings in zero field.[24] We shall assume that this problem can be resolved through additional measurements of the relative amplitude of field resonances in various already identified $\binom{J'K'}{JK}$ fine-structure components of molecular infrared spectra.

We now continue our analysis of field spectra, examining external fields oriented perpendicular to the light-travel direction, in which both the magnetic field $\mathbf{B}^0$ and the electric field $\mathbf{E}^0$ can be swept. We restrict our attention to the resonance associated with the anticrossing components of the hyperfine structure, which arises when the field parallel to the linear polarization vector of the light is the one being swept.

The Hamiltonian has the structure

$$\hat{H}(\mathbf{r},t)=\hat{H}^0+\hat{H}^1+\hat{V}(\mathbf{r},t). \tag{59}$$

The zeroth approximation corresponds to a two-level system whose levels are degenerate in the projection M_J of the rotational angular momentum in the direction of the constant field (the quantization axis $\mathbf{u}_z$ is chosen to point along the field), as well as in the parity p:

$$\hat{H}^0|(\alpha)J_pM_J\rangle=\omega_{\alpha}|(\alpha)J_pM_J\rangle,\quad \alpha=m,n.$$

The frequency difference $\omega_{mn}=\omega_m-\omega_n$ lies in the optical range. The degeneracy is lifted by taking

$$\hat{H}^1=\hat{H}^1_{\text{in}}+\hat{H}^1_{\text{out}},$$

which incorporates the internal (hyperfine) and external (field) interactions. Thus, with no external fields, we would have

$$(\hat{H}^0+\hat{H}^1_{\text{in}})|(\alpha_p)FM_F\rangle=(\omega_\alpha+h^{\alpha_p}_F)|(\alpha_p)FM_F\rangle,$$

$$M_F=M_J+M_I,$$

where F is the total angular momentum. Including a constant field,

$$(\hat{H}^0+\hat{H}^1)|(\alpha_p)\tilde{F}M_F\rangle=(\omega_\alpha+\hat{h}^\alpha_{\tilde{F}M_F}|(\alpha_p)\tilde{F}M_F\rangle, \quad (60)$$

where we will call $\tilde{F}$ the quasimomentum, since F is in fact not conserved. If we are dealing with an electric field, then $\hat{h}^\alpha_{\tilde{F}M_F}$ is an operator that is not diagonal in p.

The last term takes into account the electric dipole interaction with the light:

$$\hat{V}(\mathbf{r},t)=-\hat{\mathbf{d}}\cdot\mathbf{E}(\mathbf{r},t)/\hbar, \quad (61)$$

$$\hat{\mathbf{d}}_{mn}=\langle m|\hat{\mathbf{d}}|n\rangle=d_{mn}\cdot\hat{\mathbf{T}}^{mn}={}_sd_{mn}\sum_q {}_s\hat{T}^{mn}_{1q}\cdot\mathbf{u}_q,$$

$${}_sd_{nm}=(-1)^{\Delta J}\cdot{}_sd^*_{mn}.$$

Here we have used the standard tensor operators

$${}_s\hat{T}^{mn}_{\kappa q}\equiv{}_s\hat{T}^{J_mJ_n}_{\kappa q}=\sum_{M'M}(-1)^{J_n-M}\times\langle J_mM'J_n\bar{M}|\kappa q\rangle|(m)J_mM'\rangle\langle(n)J_nM|,$$

$$\text{Tr}_{J_n}(\hat{T}^{mn\dagger}_{1q'}\hat{T}^{mn}_{1q})=\delta_{q'q},$$

$$[(m)J_m\|{}_s\hat{\mathbf{T}}^{mn}_\kappa\|(n)J_n]=(-1)^{-J_m+\kappa+J_n}\cdot\sqrt{[\kappa]}, \quad (62)$$

$$T^{mn}_q(M)=\langle M+q|\hat{T}^{mn}_{1q}|M\rangle=\sqrt{\frac{[1]}{[J_m]}}\langle J_mM+q|J_nM1q\rangle.$$

These are related to the components in the alternative basis (for entire representations):

$${}_aT^{mn}_{\kappa q}=(-i)^{J_m+\kappa+J_n}\cdot{}_sT^{mn}_{\kappa q}.$$

The electric component of the traveling light wave is

$$\mathbf{E}(\mathbf{r},t)=\text{Re}(\mathbf{E}^{(\omega)}\exp[-i(\omega t-\mathbf{kr})]), \quad \mathbf{E}^{(\omega)}\perp\mathbf{k}\ \ (k=\omega/c),$$

$$\mathbf{E}^{(\omega)}=\sum_q E_q\mathbf{u}_q=E^{(\omega)}\mathbf{e}, \quad \Omega=\omega-\omega_{mn}\ll\omega_{mn}, \quad (63)$$

where $\mathbf{e}$ is the unit polarization vector of the light.

We make use of the equation for the density matrix with relaxation $\hat{R}$ and pump $\hat{Q}$:

$$(\partial_t)+\mathbf{v}\nabla_r)\hat{\rho}(\mathbf{v},\mathbf{r},t)=-i[\hat{H}(\mathbf{r},t),\hat{\rho}(\mathbf{v},\mathbf{r},t)]+\hat{R}(\mathbf{v},\mathbf{r},t)+\hat{Q}(\mathbf{v},\mathbf{r},t),$$

where

$$\hat{\rho}=\begin{pmatrix}\hat{\rho}_m & \hat{\rho}_{mn}\\ \hat{\rho}^\dagger_{mn} & \hat{\rho}_n\end{pmatrix}, \quad \hat{H}=\begin{pmatrix}\omega_m+\hat{h}^m & \hat{V}_{mn}\\ \hat{V}^\dagger_{mn} & \omega_n+\hat{h}^n\end{pmatrix},$$

$$\hat{h}^j=\hat{H}^{(1)j}=\langle j|\hat{H}^{(1)}|j\rangle,$$

$$\hat{R}_{ij}=[\Gamma_j\delta_{ij}+\Gamma(1-\delta_{ij})]\hat{\rho}_{ij}, \quad \hat{Q}_{ij}(v)=W(v)\delta_{ij}Q_j\hat{1}_j,$$

$$W(v)=\frac{1}{\sqrt{\pi}\tilde{v}}\exp[(-v/\tilde{v})^2], \quad \int_{-\infty}^{\infty}dv\,W(v)=1.$$

The molecules have a Maxwellian velocity distribution, and $k\tilde{v}\gg\Gamma$. We assume that the gas medium in question is inherently isotropic, and that any anisotropy is due to nonlinear interactions with the laser light.

The equation in the interaction picture,

$$(\partial_t+\mathbf{v}\nabla_\mathbf{r})\hat{\rho}'(\mathbf{v},\mathbf{r},t)=-i[\hat{V}'(\mathbf{r},t),\hat{\rho}'(\mathbf{v},\mathbf{r},t)]+\hat{R}'(\mathbf{v},\mathbf{r},t)+\hat{Q}'(\mathbf{v},\mathbf{r},t), \quad (64)$$

where

$$\hat{\rho}'(t)=\exp[it(\hat{H}^{(0)}+\hat{H}^{(1)})\hat{\rho}\ \exp[-it(\hat{H}^{(0)}+\hat{H}^{(1)})],$$

can be solved approximately by iterating on

$$\hat{V}'(t)=\begin{pmatrix}0 & \hat{\tilde{V}}_{mn}(t)\exp[-i(\Omega t+\mathbf{kr})]\\ \hat{V}^\dagger_{mn}(t)\exp[i(\Omega t+\mathbf{kr})] & 0\end{pmatrix}. \quad (65)$$

Here

$$\hat{\tilde{V}}_{mn}(t)=\exp(it\hat{H}^{(1)})\hat{\tilde{V}}_{mn}\exp(-it\hat{H}^{(1)})=-\frac{d_{mn}}{2\hbar}(\hat{\mathbf{T}}^{mn}(t)\mathbf{E}^{(\omega)}),$$

$$\hat{\tilde{V}}_{mn}=-\frac{d_{mn}}{2\hbar}(\hat{\mathbf{T}}^{mn}\mathbf{E}^{(\omega)}),$$

$$\hat{\mathbf{T}}(t)=\exp(it\hat{H}^{(1)})\hat{\mathbf{T}}\exp(-it\hat{H}^{(1)}).$$

We seek a solution in the operator form

$$\hat{\rho}'(t)=\begin{pmatrix}\hat{\rho}'_m(t) & \hat{\tilde{\rho}}_{mn}(t)\exp[-i(\Omega t-\mathbf{kr})]\\ \hat{\tilde{\rho}}^\dagger_{mn}(t)\exp[i(\Omega t-\mathbf{kr})] & \hat{\rho}'_n(t)\end{pmatrix}.$$

We ultimately obtain the polarization of the medium at the frequency of the light:

$$\mathbf{P}(\mathbf{r},t)=\text{Re}(\mathbf{P}^{(\omega)}\exp[-i(\omega t-\mathbf{kr})]),$$

$$\mathbf{P}^{(\omega)}=2\ \text{Tr}_n(\hat{\mathbf{d}}^\dagger_{mn}\langle\hat{\rho}_{mn}\rangle_v)=\sum_q P^{(\omega)}_q\mathbf{u}_q, \quad (67)$$

where the contravariant components take the form

$$P_q^{(\omega)}=2\ \mathrm{Tr}_n(\hat{d}_{iq}^{mn\dagger}\langle\hat{\rho}_{mn}\rangle_v)$$
$$=i\tilde{\chi}_\omega E^{(\omega)}[X^{(1)}_{qq_1}e_{q_1}-2|G^{(\omega)}|^2X^{(3)}_{qq_1q_2q_3}e_{q_1}e^*_{q_2}e_{q3}]. \tag{68}$$

Here

$$G^{(\omega)}=\frac{d_{mn}E^{(\omega)}}{2\hbar},\quad \tilde{\chi}_\omega=\frac{N_{nm}|d_{mn}|^2}{\hbar}\cdot\frac{\sqrt{\pi}}{k\tilde{v}},$$

$$N_{nm}=\frac{N_n}{[n]}-\frac{N_m}{[m]},\quad \frac{N_j}{[j]}=\frac{Q_j}{\Gamma_j},$$

$$[j]=\mathrm{Tr}_j\hat{1}_j=2[I][J_j].$$

In (68),

$$X^{(1)}_{qq1}=\frac{k\tilde{v}}{\sqrt{\pi}}\int_0^\infty d\tau\ \exp\left[-\left(\frac{k\tilde{v}\tau}{2}\right)^2+i(\Omega+i0)\tau\right]$$
$$\times\mathrm{Tr}_n(\hat{T}^{mn\dagger}_{1q}\ \exp[-ih^m\tau]\hat{T}^{mn}_{1q1}\ \exp[ih^n\tau])$$
$$=\delta_{qq_1}\cdot 2[I]\cdot w\ (\Omega_q+i0)k\tilde{v}),\quad \Omega_q=\Omega+\Delta_j\cdot q. \tag{69}$$

The last expression results when we have $k\tilde{v}\gg\langle\hat{h}^j_{in}\rangle$ and the normal Zeeman effect ($\Delta^m_J=\Delta^n_J$).The linear response (susceptibility) of the medium has been reduced to $w(\xi\pm i0)$—the probability integral of a complex argument.[20] In general, the argument contains a linear combination of frequency and field terms, but in the present (transverse) field geometry, $q=0$.

All of the field structures of interest here are confined to the nonlinear supplementary term, which after velocity averaging looks like

$$X^{(3)}_{q_1q_2q_3q_4}=\exp\left[-\left(\frac{\Omega}{k\tilde{v}}\right)^2\right]\int_0^\infty d\tau\ \exp[-2\Gamma\tau]\int_0^\infty d\tau_1$$
$$\times[\exp[-\Gamma_m\tau_1]X^{(3)}_{q_1q_2q_3q_4}(\tau+\tau_1|\tau\rangle$$
$$+\exp[-\Gamma_n\tau_1]X^{(3)}_{q_1q_2q_3q_4}(\tau|\tau+\tau_1)], \tag{70}$$

or, if $2\Gamma=\Gamma_m+\Gamma_n$,

$$X^{(e)}_{q_1q_2q_3q_4}=\exp\left[-\left(\frac{\Omega}{k\tilde{v}}\right)^2\right]\int_0^\infty d\tau'$$
$$\times\exp[-\Gamma_m\tau']\int_0^\infty d\tau$$
$$\times\exp[-\Gamma_n\tau]X^{(3)}_{q_1q_2q_3q_4}(\tau'|\tau), \tag{71}$$

where

$$X^{(3)}_{q_1q_2q_3q_4}(\tau'|\tau)=\mathrm{Tr}_n(\hat{T}^{mn\dagger}_{1q_1}\ \exp[-ih^m\tau']\hat{T}^{mn}_{1q_2}$$
$$\times\exp[-ih^n\tau]\hat{T}^{mn\dagger}_{1q_3}\ \exp[ih^m\tau']\hat{T}^{mn}_{1q_4}$$
$$\times\exp[ih^n\tau]). \tag{72}$$

Proceeding further, we can individually consider two types of doubling:

1) $K=1$—hyperfine doubling [see (46) and (49)],

$$\hat{H}^{(1)j}_{\mathrm{in}}=\hat{h}^j_{hf}=-(\alpha^j_0\hat{1}_2+\alpha^j_z\hat{\sigma}_z)\hat{\mathbf{J}}^j\cdot\hat{\mathbf{I}},\quad j\in(m,n), \tag{73}$$

2) $K=3$—K doubling due to centrifugal distortion [see (91)],

$$\hat{H}^{(1)j}_{\mathrm{in}}=\hat{h}^j_{\mathrm{split}}=-\eta^j_z\hat{\sigma}_z. \tag{74}$$

Here the Pauli spin matrices $\hat{\sigma}$ are evaluated in states j_p of opposite parity, $p=\pm1$:

$$\hat{\sigma}_z|p\rangle=p|p\rangle.$$

The field interaction is evaluated in these same states:

$$\hat{H}^{(1)j}_{\mathrm{out}}=\hat{H}^j_E+\hat{H}^j_B=\frac{d^j}{\hbar}\hat{\mathbf{J}}^j\cdot\mathbf{E}^{(0)}\hat{\sigma}_x-\left(\frac{\mu^j_J}{\hbar}\hat{\mathbf{J}}^j+\frac{\mu_I}{\hbar}\hat{\mathbf{I}}\right)\cdot\mathbf{B}^{(0)}\hat{1}_2$$
$$=\mathbf{G}^{j(0)}\cdot\mathbf{J}\hat{\sigma}_x-(\Delta^j_J\cdot\hat{\mathbf{J}}+\Delta_I\cdot\hat{\mathbf{I}})1_2, \tag{75}$$

where the electric and magnetic dipole moments correspond to J_pK levels

$$d^j=d_{JK}=\frac{d_zK}{J(J+1)},$$

$$\mu^j_J=\mu^{(r)}_{JK}=\mu^{(r)}_{\perp}+(\mu^{(r)}_z-\mu^{(r)}_{\perp})\frac{K^2}{J(J+1)}.$$

The light couples pairs of levels (m_+,n_-) and (m_-,n_+):

$$\hat{V}_{mn}=-\frac{\hat{\mathbf{d}}_{m^+,n^-}\mathbf{E}^{(\omega)}}{2\hbar}\hat{\sigma}_x. \tag{76}$$

Let us start with the first case, and so as to carry the calculation through to the end analytically, let us assume that $J\gg I$. The matrix elements of interactions with the orbital angular momentum simplify in the split basis $|J_p,M_F-M_I\rangle\otimes|IM_I\rangle$:

$$\hat{J}_z=M\cdot\hat{1}_I-\hat{I}_z,\quad M\equiv M_F,$$
$$(\hat{\mathbf{J}}\cdot\hat{\mathbf{I}})_M\simeq M\cdot\hat{I}_z+\sqrt{J(J+1)-M^2}\cdot\hat{I}_x, \tag{77}$$
$$\hat{T}^{mn}_{1q}(M)\simeq T^{mn}_{1q}(M)\cdot\hat{1}_I-\partial_MT^{mn}_{1q}(M)\cdot\hat{I}_z$$
$$+\frac{\partial^2_MT^{mn}_{1q}(M)}{2}\cdot\hat{I}^2_z. \tag{78}$$

Here

$$T^{mn}_q(M)=\langle M+q|\hat{T}^{mn}_{1q}|M\rangle\simeq\sqrt{\frac{[1]}{[J_m]}}\cdot d^1_{q\Delta J}(\theta), \tag{79}$$

$$\Delta J=J_m-J_n,\quad \cos\theta=M/\sqrt{J_n(J_n+1)}. \tag{80}$$

We next consider the situation in which we have a swept magnetic field aligned with the linear polarization vector of the light, $\mathbf{B}^{(0)}\|\mathbf{E}^{(\omega)}\perp\mathbf{k}$. We have

$$\hat{H}^{(1)j}(M)=\hat{h}^j(M)+\Delta^j_JM\cdot\hat{1}_2,$$
$$-\hat{h}^j(M)=(\alpha^j_0\hat{1}_2+a^j_z\hat{\sigma}_z)(\hat{\mathbf{J}}^j\cdot\hat{\mathbf{I}})_M+\delta^j_z\cdot\hat{I}_z\cdot\hat{1}_2,$$
$$\delta^j_z=\Delta_I-\Delta^j_J. \tag{81}$$

To facilitate the calculation, set

$$\hat{h}' \equiv \omega' \hat{\mathbf{I}} = \hat{h}^{m(+)}(M),$$

$$\hat{h} \equiv \hat{\sigma}_x \hat{h}^n(M) \hat{\sigma}_x = \omega \hat{\mathbf{I}} = \hat{h}^{n(-)}(M),$$

where

$$\hat{h}^{j(\pm)}(M) = (\hat{\omega}^j \pm \Delta\hat{\omega}^j) \cdot \hat{\mathbf{I}} = -(a_0^j \pm a_z^j \hat{\sigma}_z)(\hat{\mathbf{J}}^j \cdot \hat{\mathbf{I}})_M - \delta_z^j \cdot \hat{I}_z \cdot \hat{1}_2. \quad (82)$$

Everything reduces to the calculation of a single component when all $q_i = 0$:

$$X_{0000}^{(3)}(\tau'|\tau) = \sum_M \mathrm{Tr}_{I_p}(\hat{T}_{10}^{\dagger} \exp(-i\tau'\hat{h}')\hat{T}_{10} \times \exp(-i\tau\hat{h})\hat{T}_{10}^{\dagger} \exp(i\tau'\hat{h}')\hat{T}_{10} \exp(i\tau\hat{h})). \quad (83)$$

For the calculation we have used the relation[10]

$$\mathrm{Tr}_I[(\mathbf{m}\hat{\mathbf{I}})\exp(-i\psi\mathbf{n}\hat{\mathbf{I}})(\mathbf{m}\hat{\mathbf{I}})\exp(i\psi\mathbf{n}\hat{\mathbf{I}}] = [(\mathbf{mn})^2 + [\mathbf{m}]^2 \cos\psi]\mathrm{Tr}_I \hat{I}_z^2,$$

where $\mathrm{Tr}_I \hat{I}_z^2 = I(I+1)[I]/3$, $\mathbf{n} = \omega/\omega$, $\psi = \omega\tau$.

A rotation of β about the $\mathbf{u}_y$ axis will diagonalize $\hat{h}$:

$$\exp[-i\beta\hat{I}_y](\omega_x\hat{I}_x + \omega_z\hat{I}_z)\exp[i\beta\hat{I}_y] = \omega\hat{I}_z,$$

$$\sin\beta = -n_x, \quad \cos\beta = n_z, \quad \omega = \sqrt{\omega_x^2 + \omega_z^2}.$$

Since $\Delta\beta = \beta' - \beta \ll 1$, we can assume that

$$\Delta\beta \simeq \sin\Delta\beta = [\mathbf{n}'\mathbf{n}]_y = n_z' n_x - n_z n_x', \quad n_y' = n_y = 0.$$

For example, when $J_m = J_n$ (the Q-branch) and $\omega_k^{(\pm)} = \omega_k \pm \Delta\omega_k$, we have from (82) that

$$\Delta\beta \simeq \frac{2}{\omega^{(+)}\omega^{(-)}}(\omega_x\Delta\omega_z - \omega_z\Delta\omega_x) = \frac{a_z p}{a_0}\frac{2\delta_z\omega_x}{\omega^2},$$

$$\max_{\delta_z} \Delta\beta = \Delta\beta|_{\delta_z = a_0\sqrt{J(J+1)}} = -\frac{a_z p}{a_0}\sqrt{\frac{\sqrt{J(J+1)} - M}{\sqrt{J(J+1)} + M}}.$$

The result of the calculation is then

$$X_{0000}^{(3)}(\tau'|\tau) = 2\sum_M |T|^4 \mathrm{Tr}_I \left\{ \hat{1}_I + \hat{I}_z^2 \left[2\frac{\partial_M^2 T}{T} + 6\left(\frac{\partial_M T}{T}\right)^2 - 8\left([\mathbf{n}'\mathbf{n}]_y^2 \sin^2\frac{\omega\tau'}{2}\sin^2\frac{\omega\tau}{2} + \left(\frac{\partial_M T}{T}\right)^2 \cdot n_x^2\left(1 - \cos^2\frac{\omega\tau'}{2}\cdot\cos^2\frac{\omega\tau}{2}\right)\right)\right]\right\}, \quad (84)$$

where

$$T \equiv T_{10}^{JJ}(M) = \sqrt{\frac{3}{J(J+1)[J]}} \cdot M, \quad \sum_M |T|^2 = 1$$

and

$$\omega = (\omega_x, 0, \omega_z) = -(a_0\sqrt{J(J+1) - M^2}, 0, a_0 M + \delta_z).$$

The first two terms in square brackets in the resulting expression are independent of the field and will not be considered any further. The next two negative terms have exactly the same form as in the transverse-field geometry of Ref. 2. The temporal averaging integral reduces to two expressions:

$$\int_0^\infty d\rho \exp[-\Gamma\tau]\begin{pmatrix}\cos\\ \sin\end{pmatrix}^2 \frac{\omega\tau}{2} = \frac{1}{2\Gamma}\left(1 \pm \mathscr{L}'\left(\frac{\omega}{\Gamma}\right)\right).$$

Here the cosine and sine functions on the left-hand side correspond to the plus and minus signs, respectively. The Lorentz function $\mathscr{L}(x) = \mathscr{L}'(x) + i\mathscr{L}''(x) = 1/(1-ix)$.

When levels m and n have the same characteristics, we finally obtain

$$X_{0000}^{(3)} = \exp\left[-\left(\frac{\Omega}{k\bar{v}}\right)^2\right]\frac{2[I]}{\Gamma^2}\sum_M |T|^4 \left\{1 - \frac{8}{3}I(I+1) \times \left(\frac{\omega_x}{\Gamma}\right)^2\left[\left(\frac{a_z}{a_0}\right)^2\left(\frac{\delta_z}{\Gamma}\mathscr{L}'\left(\frac{\omega}{\Gamma}\right)\right)^2 + \left(\frac{\partial_M T}{T}\right)^2 \times \frac{3}{4}\mathscr{L}'\left(\frac{\omega}{\Gamma}\right)\left(1 + \frac{1}{3}\mathscr{L}'\left(\frac{\omega}{\Gamma}\right)\right)\right]\right\}. \quad (85)$$

The first term in square brackets accounts for the symmetry of the double-peaked structure responsible for hyperfine doubling. The second resonance structure—a linear combination of the Lorentz function and its square—corresponds to the scalar part of the hyperfine interaction, and is independent of the field geometry. We can say that for $J \gg 1$, the second term is small compared to the first.

Consider now the second case when $k\bar{v} \gg \langle \hat{H}_{\mathrm{split}} \rangle \gg \langle \hat{H}_{hf} \rangle$. It is necessary to use the electric field instead of the magnetic field, and to orient it in the direction of the linear polarization vector of the light: $(\mathbf{E}^{(0)} \| \mathbf{E}^{(\omega)} \perp \mathbf{k})$:

$$-\hat{H}^{(1)j} = \eta^j \hat{\sigma} + G_z^{j(0)} \hat{J}_z \hat{\sigma}_x. \quad (86)$$

Here we assume an interaction that is even somewhat more general—violating parity conservation—than the one in (74): $\boldsymbol{\eta}^j = (\eta_{PT}^j, \eta_P^j, \eta_z^j)$. Once again we put

$$\hat{h}' = \omega' \cdot \hat{\sigma}/2 = \hat{h}^m(M) = -(G_z^{m(0)}M + \eta_x^m, \eta_y^m, \eta_z^m)\hat{\sigma},$$

and

$$\hat{h} = \omega \cdot \hat{\sigma}/2 = \hat{\sigma}_x \hat{h}^n(M)\hat{\sigma}_x = -(G_z^{n(0)}M + \eta_z^n, -\eta_y^n, -\eta_{z\_}^n)\hat{\sigma}.$$

Using

$$\mathrm{Tr}_p\left[\exp\left(-i\psi'\mathbf{n}'\frac{\hat{\sigma}}{2}\right) \times \exp\left(-i\psi\mathbf{n}\frac{\hat{\sigma}}{2}\right)\exp\left(i\psi'\mathbf{n}'\frac{\hat{\sigma}}{2}\right)\exp\left(i\psi\mathbf{n}\frac{\hat{\sigma}}{2}\right)\right] = 2\left[1 - 2(\mathbf{n}'\mathbf{n})^2 \sin^2\frac{\psi'}{2}\sin^2\frac{\psi}{2}\right]$$

and integrating over time in (83), we obtain

$$X_{0000}^{(3)}=\exp\left[-\left(\frac{\Omega}{k\bar{v}}\right)^2\frac{2[I]}{\Gamma'\Gamma}\sum_M|T|^4\right]\times\left[1-\frac{1}{2}\frac{[\boldsymbol{\omega}'\boldsymbol{\omega}]^2}{[(\Gamma')^2+(\omega')^2][\Gamma^2+\omega^2]}\right]. \quad (87)$$

Now, when levels m and n share the same characteristics,

$$X_{0000}^{(3)}=\exp\left[-\left(\frac{\Omega}{k\bar{v}}\right)^2\right]\frac{2[I]}{\Gamma^2}\sum_M|T|^4\times\left[1-\frac{1}{2}\left(\frac{2(G_z^{(0)}M+\eta_x)\sqrt{\eta_y^2+\eta_z^2}}{(\Gamma/2)^2+\eta_y^2+\eta_z^2+(G_z^{(0)}M+\eta_x)^2}\right)^2\right]. \quad (88)$$

In particular, for $\eta_x = \eta_y = 0$, we again obtain the typical double-peaked structure responsible for K doubling. The general case is a simple extension of the foregoing derivation.

7. CONVERSION

In considering spin conversion of a specific type (molecules with C_{3v} symmetry have only $A_1 \leftrightarrow E$), it is necessary to take account of quasidegeneracy of the vibration–rotation spectrum in cluster structures of the corresponding type ($A_2 + E$ in the present case), which shows up at sufficiently large J.[10,25] In the present work, cluster quasidegeneracy was only partially allowed for via centrifugal corrections responsible for a shift (convergence) in the A_2 and E rotational levels and (parity) splitting of the A_2 levels. This was deemed adequate at low enough temperatures, for which the population of high-J levels is small.

The evolution of both spin subsystems toward equilibrium can be described by a single exponential,

$$\frac{\rho_I(t)-\rho_I(\infty)}{\rho_I(0)-\rho_I(\infty)}=\exp[-\gamma_c t],\quad \rho_I(\infty)=\gamma_{I_1}N/\gamma_c,$$

where $I \neq I_1$,

$$\gamma_c=\sum_I\gamma_I=\gamma_{1\to 2}+\gamma_{2\to 1},\quad I\in(1/2,3/2). \quad (89)$$

The total population of spin states, $N=\Sigma_I\rho_I(t)$, is conserved. The expression for the conversion rate is similar to that employed in Ref. 4:

$$\gamma_c=\sum_{\substack{J_pK_r'\\J_pK_r=0}}\frac{2\Gamma[\mathscr{W}_B(J_p'K_r')+\mathscr{W}_B(J_pK_0)]}{\Gamma^2+(\omega_{J_pK_r'}-\omega_{J_pK_0})^2}\times\sum_{(a')(a)}|\langle(a')J_p'K'|\hat{H}_+^{\text{conv}}|(a)J_pK_0\rangle|^2. \quad (90)$$

Here $\Gamma=\Gamma_{J'K',JK}=(\Gamma_{J'K'}+\Gamma_{JK})/2$. Relaxation of possible disequilibrium spin modifications becomes possible by virtue of external perturbations that destabilize the system of rotational levels

$$|\alpha\rangle|(a)J_pK_r\rangle=|(a_p)JK_r\rangle.$$

The emptying of these levels is described by the constants Γ_{JK}.

For the rotational spectrum ω_{J_pK}, we must use an expression that takes account of fourth- and sixth-order centrifugal corrections:

$$\begin{aligned}\omega_{J_pK}&=\langle H_{02}^r+H_{04}^r+H_{06}^{\text{shift}}+H_{06}^{\text{split}}\rangle_{J_pK}\\&=B_\perp\mathbf{J}^2+(B_z-B_\perp)K^2-D_J\mathbf{J}^4-D_{JK}\mathbf{J}^2K^2-D_KK^4\\&\quad+F_J\mathbf{J}^6+F_{JK}\mathbf{J}^4K^2+F_{KJ}\mathbf{J}^2K^4+F_KK^6+\delta_{K,3}F_3^{\text{split}}\\&\quad\times p(-1)^J\cdot\mathbf{J}^2(\mathbf{J}^2-2)(\mathbf{J}^2-6),\quad \mathbf{J}^2\equiv J(J+1). \quad (91)\end{aligned}$$

The sixth-order correction allows for K doubling of levels with $M=\pm 3(K\equiv|M|)$. Levels for which $K = 3p/2$ is an integer when p is an integer are split, i.e., $K=3,6,9,...$ (Ref. 6).

Level populations are governed by the Boltzmann factors

$$\mathscr{W}_B(J_p'K_r')=\exp\left(-\frac{\hbar\omega_{J_p'K_r'}}{k_BT}\right)\Big/Q_{sr}^{(1/2)},$$

$$\mathscr{W}_B(J_pK_0)=\exp\left(-\frac{\hbar\omega_{J_pK_0}}{k_BT}\right)\Big/Q_{sr}^{(3/2)},$$

where the rotational partition functions incorporate the statistical weights of all of the nuclei:

$$Q_{sr}^{(1/2)}=\left(\prod^{h_1}[I^{h_1}]\right)[1/2]\sum_{J'}[J']\sum_{K_{r_3=1_3,2_3}'}2\times\exp\left(-\frac{\hbar\omega_{J_p'K_r'}}{k_BT}\right),$$

$$Q_{sr}^{(3/2)}=\left(\prod^{h_1}[I^{h_1}]\right)[3/2]\sum_{J}[J]\sum_{K_{r_3=0_3}}(2-\delta_{K,0})\times\exp\left(-\frac{\hbar\omega_{J_pK_0'}}{k_BT}\right).$$

In the present case, $Q_{sr}^{(1/2)} \simeq Q_{sr}^{(3/2)}$.

Making use of the previously calculated off-diagonal hyperfine interaction matrix elements, we obtain

$$\sum_{(a')(a)} |\langle (a')J'_pK'_r|\hat{H}_+^{\rm conv}|(a)J_pK_0\rangle|^2$$

$$=\left(\prod^{h_1}[I^{h_1}]\right)\left\{\sum_F |[(K'_r)^{(EE)A_2}_{(J'_pI')F}\|\hat{H}_{sr}\|(K_0)^{(A_2A_1)A_2}_{(J_pI)F}]|^2+\sum_F |[(K'_r)^{(EE)A_2}_{(J'_pI')F}\|\hat{H}_{ss}\|(K_0)^{(A_2A_1)A_2}_{(J_pI)F}]|^2\right.$$

$$\left.+\sum{}^h\frac{1}{[I^h]}\sum_{\binom{F'}{F}|F^h}|[(K'_r)^{(EE)A_2}_{((J'_pI')F'I^h)F^h}\|\hat{H}^h_{ss}\|(K_0)^{(A_2A_1)A_2}_{((J_pI)FI^h)F^h}]|^2\right\}$$

$$=\left(\prod^{h_1}[I^{h_1}]\right)\left\{\frac{1}{2^2\cdot 3^2}|[(K'_r)^E_{J'_p}\|[\tilde{\mathbf{R}}^E_{(11)2}\otimes\Omega^{A_1}_1]^E_{1_+}\|(K_0)^{A_2}_{J_p}]|^2|[^E_{1/2}\|\hat{\mathbf{I}}^E_1\|^{A_1}_{3/2}]|^2+\frac{1}{2^2\cdot 5^2}\left|\sum^{\Gamma_1\Gamma_2}[(K'_r)^E_{J'_p}\|\tilde{\mathbf{S}}^{(\Gamma_1\Gamma_2)E}_{(11)2_+}\|(K_0)^{A_2}_{J_p}]\right.\right.$$

$$\left.\left.\times[^{1/2}_E]\|[\hat{\mathbf{I}}^{\Gamma_1}_1\otimes\hat{\mathbf{I}}^{\Gamma_2}_1]^E_2\|^{A_1}_{3/2}]\right|^2+\sum^h\frac{|[I^h\|\hat{\mathbf{I}}^h_1\|I^h]|^2}{[I^h]\cdot 2^2\cdot 3^2\cdot 5}|[(K'_r)^E_{J'_p}\|\tilde{\mathbf{S}}^{(h)E}_{(11)2_+}\|(K_0)^{A_2}_{J_p}]|^2\cdot|[^E_{1/2}\|\hat{\mathbf{I}}^E_1\|^{A_1}_{3/2}]|^2\right\}$$

$$=\left(\prod^{h_1}[I^{h_1}]\right)[J](1+\delta_{K,0})\left\{\frac{J(J+1)[J]}{3}\left[\delta_{|\Delta K|,2}(\tilde{M}^{E1}_{(11)22})^2\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}^2\langle J'_pK'|2_+\Delta KJ_pK\rangle^2\right.\right.$$

$$+\delta_{|\Delta K|,1}\left(\tilde{M}^{E1}_{(11)11}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 1\end{Bmatrix}\frac{\Delta K}{|\Delta K|}\langle J'_pK'|1_+\Delta KJ_pK\rangle+\tilde{M}^{E1}_{(11)21}\begin{Bmatrix}J' & 1 & J\\ 1 & J & 2\end{Bmatrix}\langle J'_pK'|2_+\Delta KJ_pK\rangle\right)^2\Big]$$

$$+\frac{3}{2\cdot 5}\delta_{|\Delta K|,2}(\tilde{S}^{(A_1E)E1}_{(11)22})^2\langle J'_pK'|2_+\Delta KJ_pK\rangle^2+\sum^h\frac{|[I^h\|\hat{I}^h_1\|I^h]|^2}{3^2\cdot 5\cdot[I^h]}\langle J'_pK'|2_+\Delta KJ_pK\rangle^2$$

$$\left.\times[\delta_{|\Delta K|,1}(\tilde{S}^{(h)E1}_{(11)21})^2+\delta_{|\Delta K|,2}(\tilde{S}^{(h)E1}_{(11)22})^2]\right\}. \qquad (92)$$

Here $\Delta K=K'-K=|\Delta K|(-1)^{r+\Delta K}$.

Parity doubling of the K levels need only be taken into account for $K_0=3$. In all other cases one can sum over p, but since the range of p depends on whether K_0 is zero, it is convenient first to identify the corresponding term:

$$\sum_p(1+\delta_{K,0})\times\ldots=\sum_p[2\delta_{K,0}+(1-\delta_{K,0})]\times\ldots=2\times.$$

We obtain as a result the single common factor 2, since it still applies in summing the first term, and it now appears in the second.

In accordance with Eq. (92), Table II shows the distribution of hyperfine contributions to conversion transitions. Nonvanishing contributions are marked with a plus sign.

TABLE II. Hyperfine interaction contributions for conversion transitions.

$\|\Delta J\|$	$\|\Delta K\|$	$R^E_{\perp}$	$R^E_{\parallel}$	S_{HH}	S_{hH}
2	2	−	−	+	+
2	1	−	−	−	+
1	2	+	−	+	+
1	1	−	+	−	+

8. CONCLUSION

We have carried out a theoretical calculation of hyperfine interaction matrix elements both between spin modifications and for each individually. In contrast to the previous work of Chapovski,[4] the expression for spin-modification conversion contains two additional terms corresponding to the two hyperfine tensor spin–rotation constants, and it yields a complete description of conversion. The completeness of that description makes it possible to invert the problem when information about the tensor spin–rotation constants is lacking. The uniqueness of the information thus obtained is due to the fact that, as shown by an analysis of the matrix elements, spectroscopic measurements cannot provide information about all of the hyperfine constants, as one of the tensor constants drops out. We have examined an alternative approach to spectroscopic measurements of the remaining hyperfine constants—field spectroscopy of the disruption of spin–rotation coupling. Spectroscopy of the hyperfine interaction and the spin-modification conversion phenomenon complement one another. A description of conversion requires that one take account of the splitting of rotational A_2 levels, which can be determined from electric field spectra.

As a possible application of this approach, consider an example based on the isotopic pair $^{12}CH_3F$ and $^{13}CH_3F$. The first step is the experimental determination of K doubling via

the electric field spectrum. To judge by Ref. 4, this is necessary for $^{12}CH_3F$, and is not required in practice for $^{13}CH_3F$. Since the conversion rates are known for these isotopes, the next step would reduce to deriving and solving a system of two equations in the two unknowns $(R_{\perp}^{E})^2$ and $(R_{z}^{E})^2$, assuming both to be independent of the isotopic composition of the molecules. After calculating the tensor constants $|R_{\perp}^{E}|$, hyperfine doubling can be observed experimentally by means of the magnetic field spectrum to provide an independent check and improvement.

I thank A. E. Bakarev for the use of his personal computer in preparing this paper for publication.

This work was financially supported by the Russian Fund for Fundamental Research (Grant No. 93-02-15084).

APPENDIX A
WIGNER COEFFICIENTS FOR THE GROUPS C_{3v} AND C_i

To construct matrices for irreducible representations, it is convenient to consider active transformations of the contravariant components of a vector by elements of the group C_{3v},

$$S_g \underline{x}^{\sigma}=(\underline{x}^{\sigma})^g=\sum^{\sigma_1}\Delta^{\Gamma}_{\sigma\sigma_1}(g)\cdot\underline{x}^{q_1},$$

or transformations of the covariant basis vectors,

$$S_g \underline{\mathbf{u}}^{\dot\sigma}=(\underline{\mathbf{u}}^{\dot\sigma})^g=\sum^{\sigma_1}\underline{\mathbf{u}}^{\dot\sigma_1}\cdot\Delta^{\Gamma}_{\sigma_1\sigma}(g).$$

These induce transformations of the functions

$$\mathscr{U}_g\langle\underline{\mathbf{x}}|\Gamma\sigma\rangle=\langle S_g^{-1}\underline{\mathbf{x}}|\Gamma\sigma\rangle=\sum^{\sigma_1}\langle\underline{\mathbf{x}}|\Gamma\sigma_1\rangle\cdot\Delta^{\Gamma}_{\sigma_1\sigma}(g),$$

and corresponding transformations of the tensor operators

$$\mathscr{U}_g\hat{T}^{\Gamma\dot\sigma}\mathscr{U}_g^{-1}=(\hat{T}^{\Gamma\dot\sigma})^g=\sum^{\sigma_1}\hat{T}^{\Gamma\dot\sigma_1}\cdot\Delta^{\Gamma}_{\sigma_1\sigma}(g).$$

The E representation matrices for Cartesian (x,y) and spherical $(+,-)$ bases are given in Table I. We assume that $\varepsilon=\varepsilon_+=\bar{c}+is$.

The Wigner coefficients depend on the choice of irreducible representation matrices:

$$\langle\Gamma\sigma|\Gamma_1\sigma_1\Gamma_2\sigma_2\rangle=\sqrt{\frac{[\Gamma]}{[G]}}\frac{\Sigma_{g\in G}\Delta^{\Gamma*}_{\sigma\sigma'}(g)\Delta^{\Gamma_1}_{\sigma_1\sigma_1'}(g)\Delta^{\Gamma_2}_{\sigma_2\sigma_2'}(g)}{[\Sigma_{g\in G}\Delta^{\Gamma*}_{\sigma'\sigma'}(g)\Delta^{\Gamma_1}_{\sigma_1'\sigma_1'}(g)\Delta^{\Gamma_2}_{\sigma_2'\sigma_2'}(g)]^{1/2}}. \tag{A1}$$

We use the E representation matrices in the spherical basis:

$$\langle\Gamma\sigma|A_1 0\Gamma\sigma\rangle=\langle E\bar\sigma|E\sigma E\sigma\rangle=1,\quad \langle E\sigma|A_2 0E\sigma\rangle=\sigma. \tag{A2}$$

The rest of the coefficients can be obtained by using the analog of the symmetry relations for SO_3,[10] except that σ (the analog of m) need not enter into the phase factors.

The relationship with the 3Γ symbols takes the form

$$\langle\Gamma\sigma|\Gamma_1\sigma_1\Gamma_2\sigma_2\rangle=(-1)^{\Gamma_1+\Gamma_2}\sqrt{[\Gamma]}\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma\\ \sigma_1 & \sigma_2 & \bar\sigma\end{pmatrix}.$$

The Racah coefficients[13] do not depend on the choice of irreducible representation matrices:

$$\begin{Bmatrix}E & E & E\\ E & E & E\end{Bmatrix}=0,\quad \begin{Bmatrix}E & E & E\\ A_2 & E & E\end{Bmatrix}=\begin{Bmatrix}A_2 & E & E\\ A_2 & E & E\end{Bmatrix}=\frac{1}{2},$$

$$\begin{Bmatrix}\Gamma_1 & \Gamma_2 & \Gamma_3\\ A_1 & \Gamma_3 & \Gamma_2\end{Bmatrix}=\frac{(-1)^{\Gamma_1+\Gamma_2+\Gamma_3}}{\sqrt{[\Gamma_2][\Gamma_3]}}\cdot\Delta_{\Gamma_1\Gamma_2\Gamma_3}. \tag{A3}$$

The Wigner coefficients for C_i are $\langle\rho|\rho'\rho''\rangle=\delta_{\rho+\rho'+\rho'',g}$.

APPENDIX B
SPHERICAL COMPONENTS OF THE SECOND-RANK TENSOR FOR $SO_3\otimes S_3$

Consider the expansion of the two-sided tensor operator

$$\hat{\mathsf{T}}=\sum_{j_1j_2}^{(p_1p_2)}T^{p_1p_2}_{j_1j_2}\mathbf{u}^{p_1}_{j_1}\mathbf{u}^{p_2}_{j_2}=\sum_{\kappa q}^{(\Gamma_1\Gamma_2)\Gamma\sigma}\hat{T}^{(\Gamma_1\Gamma_2)\Gamma\dot\sigma}_{(11)\kappa\dot q}\mathbf{u}^{(\Gamma_1\Gamma_2)\Gamma\sigma}_{(11)\kappa q}.$$

The first sum (p_1p_2) is ordered in accordance with (10) and (23). Here we have used the two-sided contravariant spherical basis

$$\mathbf{u}^{(\Gamma_1\Gamma_2)\Gamma\sigma}_{(11)\kappa q}=\frac{1}{2}\sum_{q_1q_2}^{\sigma_1\sigma_2}\left\langle\begin{matrix}\Gamma\sigma\\ \kappa q\end{matrix}\middle|\begin{matrix}\Gamma_1\sigma_1\Gamma_2\sigma_2\\ 1q_1\ \ 1q_2\end{matrix}\right\rangle\mathbf{u}^{\Gamma_1\sigma_1}_{1q_1}\mathbf{u}^{\Gamma_2\sigma_2}_{1q_2}.$$

$$\mathbf{u}^{\Gamma\dot\sigma}_{1\dot q}=\sum_{j}^{p}\mathbf{u}^{p}_{j}U^{p\Gamma\dot\sigma}D_{j\dot q}.$$

The ${}^aU$ and ${}_aD$ matrices are defined in (9) and (5). The general form of component coupling in the various bases is

$$T^{(\Gamma_1\Gamma_2)\Gamma\dot\sigma}_{(11)\kappa\dot q}=\sum_{j_1j_2q_1q_2}^{p_1p_2\sigma_1\sigma_2}T^{p_1p_2}_{j_1j_2}U^{p_1\Gamma_1\dot\sigma_1}U^{p_2\Gamma_2\dot\sigma_2}\times D_{j_1\dot q_1}D_{j_2\dot q_2}\left\langle\begin{matrix}\Gamma\sigma\\ \kappa q\end{matrix}\middle|\begin{matrix}\Gamma_1\sigma_1\Gamma_2\sigma_2\\ 1q_1\ \ 1q_2\end{matrix}\right\rangle. \tag{B1}$$

Here p_1p_2 are independent, so we have provided the factor of 1/2. The individual components for SO_3 are[26]

$$T_{j_1j_2}\neq T_{j_2j_1},$$

$$\tilde{S}_{ij}=\frac{T_{ij}+T_{ji}}{2}-\langle\hat{T}\rangle\delta_{ij},\quad \langle\hat{T}\rangle=\frac{1}{3}\,\mathrm{Tr}(\hat{T}),$$

$$A_{ij}=\frac{T_{ij}-T_{ji}}{2}=A^{(k)}_{ij},$$

$${}_aT_{(11)0,0}=\frac{1}{\sqrt{3}}\sum_j T_{jj}=\sqrt{3}\langle\hat{T}\rangle,$$

$${}_aT_{(11)1,\dot 0}=(-i\sqrt{2})A^{z}_{xy},$$

$${}_aT_{(11)1,\sigma}=(-i\sqrt{2})\left(-\frac{\sigma}{\sqrt{2}}\right)(A^{x}_{yz}+i\sigma A^{y}_{zx}),$$

$$
{}_aT_{(11)2,\dot{0}}=\left(-\sqrt{\frac{3}{2}}\right)\bar{S}_{zz},
$$

$$
{}_aT_{(11)2,\sigma}=\left(-\sqrt{\frac{3}{2}}\right)\left(-\sigma\sqrt{\frac{2}{3}}\right)(\bar{S}_{xz}+i\sigma\bar{S}_{yz}),
$$

$$
{}_aT_{(11)2,2\sigma}=\left(-\sqrt{\frac{3}{2}}\right)\left(\frac{1}{\sqrt{6}}\right)(\bar{S}_{xx}-\bar{S}_{yy}+2i\sigma\bar{S}_{xy}); \quad \text{(B2)}
$$

$$
S^{p_1p_2}=S^{p_2p_1},
$$

$$
{}_aS^{(A_1A_1)A_1\dot{0}}=\frac{1}{3}\sum^{(p_1p_2)}S^{p_1p_2}=\frac{1}{3}\sum^{p_3}S^{p_3},
$$

$$
p_3\equiv(p_1p_2),
$$

$$
{}_aS^{(EE)A_10}=-\frac{1}{\sqrt{2}}\,{}_aS^{(A_1A_1)A_10}, \quad {}_aS^{(EE)A_20}=0,
$$

$$
{}_aS^{(A_1E)E\sigma}=\tfrac{1}{2}\,{}_aS^{(EE)E\sigma},
$$

$$
{}_aS^{(EE)E\sigma}=\tfrac{1}{3}(S^{(1)}_{23}+\varepsilon_\sigma\cdot S^{(2)}_{31}+\varepsilon_{\bar{\sigma}}\cdot S^{(3)}_{12}). \quad \text{(B3)}
$$

[1)]From this point on, an underscore denotes this coordinate system.
[2)]Here and in some instances further on, an overbar is used instead of a minus sign.
[3)]A covariant index is signified by a dot above a letter, a contravariant index by a dot below.
[4)]In the case of SO_3 we have $[\kappa]=2\kappa+1$.
[5)]Square brackets denote either the dimensionality of the representation Γ or the number of elements in the group G.

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Translated by Marc Damashek