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Infrared and Raman Spectra of Inert Solutions of Diatomic Molecules. II. Stochastic Theory of Band Moments

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The spectral moments of ir and Raman bands of diatomic molecules in inert solutions are calculated by the help of recent stochastic theories of ir- and Raman-band profiles. Both vibrational and rotational motions are considered. It is found that for ir and rotational Raman bands, the stochastic theories produce expressions for the band moments which closely parallel the corresponding thermodynamic expressions. New expressions are proposed for the moments of isotropic and of vibrational-rotational anisotropic Raman bands.

I. INTRODUCTION

Spectral moments $(\omega_n)_\omega$, of ir and rotational Raman (R) bands of liquids formed by linear molecules have been calculated, for low n, by the help of full thermodynamic theories implying the totality of $3N$ degrees of freedom of the liquid state.[1-4] The purpose of this communication is to show that, using widely different mathematical techniques, the stochastic theories[5,6] produce expressions for $(\omega_n)_\omega$, which closely parallel the corresponding thermodynamic expressions. The simplicity of the procedure makes it easy to determine the spectral moments of isotropic and of vibrational-rotational anisotropic R bands which have not yet been calculated in any other way.

II. THEORY

The system being investigated is formed by an active molecule and a large number of nonactive solvent molecules. The following four basic hypotheses are introduced: (a) The active molecule executes anharmonic vibrations modulated by a stochastic potential $V_s(r, t)$ because of the solvent. (b) The active molecule executes stochastic reorientations describable by means of the variable $\theta(t)$; this variable represents the angle between two successive directions $\vec{u}(0)$, $\vec{u}(t)$ of the molecular axis. (c) The correlation between vibrations and rotations is taken to be small and is neglected. (d) The vibrations are describable by the help of

quantum mechanics; the rotations are describable by means of classical mechanics. The conditions of validity of semiclassical theories have been discussed, e. g., in the Ref. 7.

The spectral moments $(\omega_n)_\omega$, and the correlation function $G(t)$ of the band under study are simply related. Putting

$$\omega^n e^{i\omega t} = (-i)^n \frac{d^n}{dt^n} (e^{i\omega t})$$

and integrating by parts gives

$$(\omega_n)_0 \equiv \frac{\int I(\omega) \omega^n d\omega}{\int I(\omega) d\omega} = \frac{\int d\omega\, \omega^n [\int_{-\infty}^{\infty} G(t) e^{i\omega t} dt]}{\int d\omega [\int_{-\infty}^{\infty} G(t) e^{i\omega t} dt]}$$

$$= i^n \frac{G^{(n)}(0)}{G(0)} , \tag{1a}$$

$$(\omega_n)_{\omega'} \equiv \frac{\int I(\omega)(\omega - \omega')^n d\omega}{\int I(\omega) d\omega}$$

$$= \sum_{p=0}^{n} (-1)^p C_n^p (\omega_{n-p})_0 \omega'^p , \tag{1b}$$

where $I(\omega)$ is the band intensity at the frequency ω and C_n^p are the binomial coefficients. Thus calculating band moments essentially reduces to the differentiation of correlation functions.[8,4,6] The results are most simply expressible by introducing unique symbol γ to designate either M, α, or β. where M is the length of the dipole moment vector $\vec{M}$ of the active molecule, α its mean polarizability, and β its magnitude of anisotropy. The calculation is indicated in Secs. III–V.

III. INFRARED SPECTRA

The ir transitions are electric dipole transitions. The absorption intensity $I(\omega)$ expected at the frequency ω of an ir absorption spectrum is thus given by the fluctuation-dissipation theorem in the following way[5]:

$$I(\omega) \sim \int_{-\infty}^{\infty} \langle \mathrm{Tr}\rho_0 \vec{M}^H(t)\vec{M}^H(0) \rangle e^{i\omega t} dt$$

$$= \int_{-\infty}^{\infty} \langle \mathrm{Tr}\rho_0 M^H(t) M^H(0) \rangle \langle \vec{u}(t)\vec{u}(0) \rangle e^{i\omega t} dt$$

$$= \int_{-\infty}^{\infty} G(t) e^{i\omega t} dt . \qquad (2)$$

In this formula $\vec{M}^H(t)$ represents the Heisenberg operator for $\vec{M}$; $\langle \rangle$ indicates the averaging over the ensemble of the stochastic processes $V_s(r, t)$, $\vec{u}(t)$; and ρ_0 is the vibrational density matrix. $G(t)$ appears as a product of two factors easily identifiable as vibrational and rotational correlation functions. Thus the spectral moments $(\omega_n)_{\omega'}$ appear as combinations of pure vibrational and of pure rotational spectral moments $(\omega_n)_{\omega'}^V$, $(\omega_n)_0^R$. The former are the moments that an ir band would have if the vibrational relaxation mechanisms were only present, and the latter are those that an ir band would have if the rotational relaxation mechanisms were operating alone. It is convenient, in what follows, to treat $(\omega_n)_{\omega'}^V$, $(\omega_n)_0^R$ separately from each other.

The purely vibrational spectral moments $(\omega_n)_{\omega'}^V$ are calculable by applying Eqs. (1a) and (1b) with the vibrational correlation function $\langle \mathrm{Tr}\rho_0 M^H(t)M^H(0) \rangle$. For the calculation of this function, see Ref. 5. Knowing $\langle \mathrm{Tr}\rho_0 M^H(t)M^H(0) \rangle$, assuming the stochastic function $V_s(r, t)$ to be stationary, and taking γ, $\gamma^H(t)$ to represent M, $M^H(t)$ gives

$$\langle \mathrm{Tr}\rho_0 \gamma^H(t)\gamma^H(0) \rangle = \left\langle |\langle 0|\gamma^H(0)|\alpha \rangle|^2 e^{-i\omega_0 t} \exp\left(-\frac{i}{\hbar}\int_0^t [\langle \alpha| V_s(r, t)|\alpha \rangle - \langle 0| V_s(r, t)|0 \rangle]dt\right) \right\rangle, \qquad (3)$$

$$\hbar(\omega_1)_0^V = \hbar\omega_0 + \langle \Delta V \rangle_\gamma \to \Delta\omega = \frac{1}{\hbar}\langle \Delta V \rangle_\gamma , \qquad (4a)$$

$$\hbar^2(\omega_2)_{\omega_0 + \Delta\omega}^V = [\langle(\Delta V)^2 \rangle_\gamma - \langle \Delta V \rangle_\gamma^2] , \qquad (4b)$$

$$\hbar^3(\omega_3)_{\omega_0 + \Delta\omega}^V = [\langle(\Delta V)^3 \rangle_\gamma - 3\langle(\Delta V)^2 \rangle_\gamma \langle \Delta V \rangle_\gamma + 2\langle \Delta V \rangle_\gamma^3] , \qquad (4c)$$

$$\hbar^4(\omega_4)_{\omega_0 + \Delta\omega}^V = [\langle(\Delta V)^4 \rangle_\gamma - 4\langle(\Delta V)^3 \rangle_\gamma \langle \Delta V \rangle_\gamma + 6\langle(\Delta V)^2 \rangle_\gamma \langle \Delta V \rangle_\gamma^2 - 3\langle \Delta V \rangle_\gamma^4] + \left\langle \left(\frac{\partial \Delta V}{\partial t}\right)^2 \right\rangle_\gamma , \qquad (4d)$$

$$\langle(\Delta V)^n \rangle_\gamma = \frac{\langle|\langle 0|\gamma^H(0)|\alpha \rangle|^2 [\langle \alpha| V_s(r, 0)|\alpha \rangle - \langle 0| V_s(r, 0)|0 \rangle]^n \rangle}{\langle|\langle 0|\gamma^H(0)|\alpha \rangle|^2 \rangle} , \qquad (5a)$$

$$\left\langle \left(\frac{\partial \Delta V}{\partial t}\right)^n \right\rangle_\gamma = \frac{\langle|\langle 0|\gamma^H(0)|\alpha \rangle|^2 \{(\partial/\partial t)[\langle \alpha| V_s(r, t)|\alpha \rangle - \langle 0| V_s(r, t)|0 \rangle]\}_{t=0}^n \rangle}{\langle|\langle 0|\gamma^H(0)|\alpha \rangle|^2 \rangle} . \qquad (5b)$$

Here, 0, α are vibrational quantum numbers and ω_0 represents the nonperturbed frequency of the $0 \to \alpha$ transition. A considerable simplification results by supposing M and $V_s(r, 0)$ statistically independent. In that case,

$$\langle(\Delta V)^n \rangle_M \to \langle[\langle \alpha| V_s(r, 0)|\alpha \rangle - \langle 0| V_s(r, 0)|0 \rangle]^n \rangle ,$$

i.e., the spectral moments $(\omega_n)_{\omega'}^V$ simply reflect the static distribution of the vapor-solution vibrational energy shifts.

The purely rotational classical spectral moments $(\omega_n)_0^R$ can be determined by applying Eq. (1a) with the classical rotational correlation function $\langle \vec{u}(t)\vec{u}(0) \rangle$. For the calculation of this function, see Ref. 5. The corresponding semiclassical expressions are obtainable by expanding $f(t) = \langle \vec{u}(t)\vec{u}(0) \rangle$ into the Taylor series around the point $t = 0$; using in $f^{(2n)}(0) = (\omega_{2n})_0^R/i^{2n}$ the classical value for $(\omega_{2n})_0^R$, and building into this series the Schofield substitution[9] $t \to t + i\hbar/2KT$. The results are

$$\langle \vec{u}(t)\vec{u}(0) \rangle = \langle \mathrm{Re} \exp[-i\int_0^t \omega(t) dt] \rangle , \qquad (6)$$

$$(\omega_1)_0^R = \hbar/I , \qquad (7a)$$

$$(\omega_2)_0^R = 2KT/I , \qquad (7b)$$

$$(\omega_3)_0^R = \frac{4\hbar KT}{I^2} + \frac{\hbar}{2KT}\left\langle \left(\frac{\partial \omega}{\partial t}\right)^2 \right\rangle, \qquad (7c)$$

$$(\omega_4)_0^R = \frac{8K^2 T^2}{I^2} + \left\langle \left(\frac{\partial \omega}{\partial t}\right)^2 \right\rangle . \qquad (7d)$$

Expressions (7a)–(7d) are correct up to the terms linear in $\hbar$.

Complete expressions for the vibrational-rotational spectral moments $(\omega_n)_{\omega'}$ are easily expressible in terms of $(\omega_n)_\omega^V$, $(\omega_n)_0^R$. It is sufficient to derive the product correlation function $G(t)$ of Eq. (2) and to use (4), (5), and (7) with $\gamma = M$. The results are

$$(\omega_1)_0 = (\omega_1)_0^V + (\omega_1)_0^R , \qquad (8a)$$

$$(\omega_2)_{\omega_0+\Delta\omega} = (\omega_2)^V_{\omega_0+\Delta\omega} + (\omega_2)^R_0 , \tag{8b}$$

$$(\omega_3)_{\omega_0+\Delta\omega} = (\omega_3)^V_{\omega_0+\Delta\omega} + (\omega_3)^R_0 + 3(\omega_1)^R(\omega_2)^V_{\omega_0+\Delta\omega} , \tag{8c}$$

$$(\omega_4)_{\omega_0+\Delta\omega} = (\omega_4)^V_{\omega_0+\Delta\omega} + (\omega_4)^R_0 + 4(\omega_1)^R_0(\omega_3)^V_{\omega_0+\Delta\omega}$$
$$+ 6(\omega_2)^R_0(\omega_2)^V_{\omega_0+\Delta\omega} . \tag{8d}$$

All these moments, except the first, refer to the shifted vibrational frequency

$$\omega = \omega_0 + \Delta\omega = \omega_0 + (1/\hbar)\langle\Delta V\rangle_M .$$

IV. RAMAN SPECTRA

A Raman spectrum can conveniently be considered as a superposition of two independent spectra: an isotropic spectrum and an anisotropic spectrum. They both result from modulation of the polarizability tensor $\overleftrightarrow{\alpha}^H(t)$ of the active molecule by molecular motions in the liquid state. The isotropic spectra are produced by the scattering through the trace of $\overleftrightarrow{\alpha}^H(t)$ (trace scattering); thus the profiles are determined by vibrational relaxation processes alone. The anisotropic spectra are associated with the anisotropic part $\overleftrightarrow{\beta}(t)$ of $\overleftrightarrow{\alpha}^H(t)$; here, vibrational and rotational relaxation mechanisms are both operating. Experimentally, $I_i(\omega)$, $I_a(\omega)$ are deducible from the intensities $I_\parallel(\omega)$, $I_\perp(\omega)$ measured at the 90° observation for VV and VH scattering geometries; compare with Table I and Ref. 6

$$I_\parallel(\omega) = A_\parallel I_i(\omega) + B_\parallel I_a(\omega) \rightarrow I_i(\omega) = C_i I_\parallel(\omega) + D_i I_\perp(\omega) , \tag{9}$$

$$I_\perp(\omega) = A_\perp I_i(\omega) + B_\perp I_a(\omega) \rightarrow I_a(\omega) = C_a I_\parallel(\omega) + D_a I_\perp(\omega) . \tag{10}$$

One concludes that, starting from measured values of $I_\parallel(\omega)$, $I_\perp(\omega)$, it is possible to disentangle the vibrational and rotational relaxation effects. This important possibility does not exist in ir spectroscopy.

Isotropic spectra result from the orientation-independent trace scattering. The key quantity is, here, the mean polarizability $\alpha = \frac{1}{3}\text{Tr}\,\overleftrightarrow{\alpha}$. Thus designating by $\alpha^H(t)$, the Heisenberg operator for α, the intensity $I(\omega)$ of the Stokes component of an isotropic spectrum is given by the fluctuation-dissipation theorem in the following way[6]:

$$I_i(\omega) \sim \int_{-\infty}^{\infty} \langle\text{Tr}\rho_0\,\alpha^H(t)\alpha^H(0)\rangle e^{i\omega t}\,dt = \int_{-\infty}^{\infty} G_i(t)e^{i\omega t}\,dt . \tag{11}$$

The moments $(\omega_n)_{\omega'}$ of an isotropic spectrum are closely related to the purely vibrational ir spectral moments $(\omega_n)^V_{\omega'}$ and can be calculated much in the same way, compare with Ref 6. It turns out that the formulas (3)–(5) remain applicable to an isotropic spectrum with $\gamma = \alpha$. This is a consequence of the fact that the same mechanism of vibrational modulation is operating in both cases. One should not conclude, however, that purely vibrational ir moments $(\omega_n)^V_{\omega'}$ necessarily coincide with those of an isotropic spectrum. This will happen only

TABLE I. The coefficients of the transformations [Eqs. (9) and (10)] indicate how, at the 90° observation, the isotropic and the anisotropic Raman components $I_i(\omega)$, $I_a(\omega)$ can be separated from each other experimentally. This makes a separate study of vibrational and rotational relaxation effects possible, since $I_i(\omega)$ only depends on vibrational relaxation mechanisms.

Polarized	$A_\parallel$	1	$B_\parallel$	$\frac{4}{45}$	C_i	1	D_i	$-\frac{4}{3}$
light	$A_\perp$	0	$B_\perp$	$\frac{1}{15}$	C_a	0	D_a	15
Natural	$A_\parallel$	$\frac{1}{2}$	$B_\parallel$	$\frac{7}{90}$	C_i	2	D_i	$-\frac{7}{3}$
light	$A_\perp$	0	$B_\perp$	$\frac{1}{15}$	C_a	0	D_a	15

if α, M, and $V_S(r, 0)$ are statistically independent; if not, $\langle(\Delta V)^n\rangle_\alpha \neq \langle(\Delta V)^n\rangle_M$, and the moments may differ to a certain extent.

Anisotropic spectra are produced by the scattering through the anisotropic part $\overleftrightarrow{\beta}$ of $\overleftrightarrow{\alpha}$. Considering the cylindrical symmetry of a diatomic molecule, the isotropy of a normal liquid, and applying the fluctuation-dissipation theorem leads to the following formula for the Stokes component of an anisotropic spectrum[6]:

$$I_a(\omega) \sim \int_{-\infty}^{\infty} \langle\text{Tr}\rho_0(\vec{\epsilon}^I \cdot \overleftrightarrow{\beta}^H(t) \cdot \vec{\epsilon}^S)(\vec{\epsilon}^I \cdot \overleftrightarrow{\beta}^H(0) \cdot \vec{\epsilon}^S)\rangle e^{i\omega t}\,dt$$
$$= \int_{-\infty}^{\infty} \langle\text{Tr}\rho_0\,\beta^H(t)\beta^H(0)\rangle\langle\frac{3}{2}\{[\vec{u}(t)\vec{u}(0)]^2 - \frac{1}{3}\}\rangle e^{i\omega t}\,dt$$
$$= \int_{-\infty}^{\infty} G_a(t)e^{i\omega t}\,dt . \tag{12}$$

In this formula $\overleftrightarrow{\beta}^H(t)$ is the Heisenberg operator associated with $\overleftrightarrow{\beta}$ and $\beta^H(t)$ is that associated with the magnitude of anisotropy β, $\vec{\epsilon}^I$ and $\vec{\epsilon}^S$ indicate the directions of the vectors $\vec{E}^I$, $\vec{E}^S$ of the incident and scattered radiation; all other symbols have their usual meaning. $G_a(t)$ once again appears as a product of a vibrational and of a rotational factor: Both vibrational and rotational motions modulate an anisotropic spectrum. It is thus convenient, as before, to define pure vibrational and pure rotational spectral moments $(\omega_n)^V_{\omega'}$, $(\omega_n)^R_0$ associated with these two factors. $(\omega_n)^V_{\omega'}$, $(\omega_n)^R_0$ are treated separately.

Not very much is to be said about the calculation of the purely vibrational spectral moments $(\omega_n)^V_{\omega'}$. The discussion parallels word by word that given in Sec. III (compare with the Ref. 6). The results are once again expressible by means of Eqs. (3)–(5) with $\gamma = \beta$. If α, β, M, and $V_S(r, 0)$ are statistically independent, the vibrational spectral moments in ir and in anisotropic spectra coincide with the moments in an isotropic spectrum. Purely rotational Raman spectral moments $(\omega_n)^R_0$ are obtainable by manipulating the function

$$g(t) = \langle\frac{3}{2}\{[\vec{u}(t)\vec{u}(0)]^2 - \frac{1}{3}\}\rangle$$

in a way similar to that described in Sec. III. The moments $(\omega_n)^R_0$ correct up to the terms of the first

order in $\hbar$ are

$$\left\langle \tfrac{3}{2} \{ [\ddot{u}(t)\ddot{u}(0)]^2 - \tfrac{1}{3} \} \right\rangle = \tfrac{3}{4} \left\langle \text{Re} \exp \left[-2i \int_0^t \omega(t) \, dt \right] \right\rangle + \tfrac{1}{4} \; , \tag{13}$$

$$(\omega_1)_0^R = 3\hbar/I \; , \tag{14a}$$

$$(\omega_2)_0^R = 6KT/I \; , \tag{14b}$$

$$(\omega_3)_0^R = \frac{48\hbar KT}{I^2} + \frac{3\hbar}{2KT} \left\langle \left(\frac{\partial \omega}{\partial t} \right)^2 \right\rangle , \tag{14c}$$

$$(\omega_4)_0^R = \frac{96 K^2 T^2}{I^2} + 3 \left\langle \left(\frac{\partial \omega}{\partial t} \right)^2 \right\rangle . \tag{14d}$$

Complete expressions for the vibrational-rotational moments of an anisotropic spectrum are given by Eqs. (8a)–(8d), where $(\omega_n)_{\omega'}^V$, $(\omega_n)_0^R$ satisfy to Eqs. (3)–(5) and (14) with $\gamma = \beta$. In principle, all moments of an anisotropic spectrum differ from the corresponding moments of an ir spectrum; the rotational contributions $(\omega_n)_0^R$ are not equal in the two cases. This difference is less pronounced, however, if the vibrational relaxation processes strongly predominate over the rotational relaxation processes.

According to Eqs. (9), the total intensity $I(\omega)$ of a Raman spectrum is a weighted sum, with coefficients $A_\perp$, $B_\perp$, $A_{\parallel}$, $B_{\parallel}$, of the intensities $I_i(\omega)$, $I_a(\omega)$ associated with the isotropic and anisotropic spectra. Thus the correlation function $G(t)$ can be written

$$G(t) = A_{\parallel} G_i(t) + B_{\parallel} G_a(t) \quad \text{(VV geometry)}, \tag{15a}$$

$$G(t) = A_\perp G_i(t) + B_\perp G_a(t) \quad \text{(VH geometry)}. \tag{15b}$$

The spectral moments $(\omega_n)_{\omega'}$ of a Raman spectrum can be easily calculated by the help of Eqs. (1), (4), (14), and (15). There is no obvious way, however, in interpreting the results obtained in this manner. In general, the moments can not be written as simple linear combinations of the corresponding moments of isotropic and anisotropic spectra. The situation is simpler, however, in the important case where α, β, and $V_S(r, 0)$ can be considered to be statistically independent. If so, $(\omega_n)_{\omega'}^R$, $(\omega_n)_{\omega'}^i$, $(\omega_n)_{\omega'}^a$ depend linearly on each other:

$$(\omega_n)_{\omega'}^R = \frac{A}{A + h(\rho)B} \, (\omega_n)_{\omega'}^i + \frac{h(\rho)B}{A + h(\rho)B} \, (\omega_n)_{\omega'}^a . \tag{16}$$

In this formula ρ is the depolarization factor, $h(\rho) = 45\rho/3 - 4\rho$ for a linearly polarized incident light, and $h(\rho) = 45\rho/6 - 7\rho$ for a nonpolarized natural light. A represents either $A_\perp$ or $A_{\parallel}$; B represents either $B_\perp$ or $B_{\parallel}$. All limiting cases are correctly reproduced by this equation. If the band is totally polarized, $\rho = h(\rho) = 0$ and $(\omega_n)_{\omega'}^R = (\omega_n)_{\omega'}^i$; if the band is strongly depolarized, $\rho \to \tfrac{3}{4}$ (or $\tfrac{6}{7}$), $h(\rho) \to \infty$, and $(\omega_n)_{\omega'}^R \to (\omega_n)_{\omega'}^a$.

V. DISCUSSION

The following conclusions can be reached by comparing stochastic and full thermodynamic

formulas for $(\omega_n)_{\omega'}^V$. If the vibrational modulation is slow $\omega_v \tau_v \gg 1$,[5] the time dependence in $V_S(r, t)$ can be suppressed and $\langle (\partial \Delta V/\partial t) \rangle_\gamma \to 0$. In that case the stochastic expressions (3)–(5) for the vibrational spectral moments coincide in their essential factures with the corresponding thermodynamic expressions; the average over the stochastic process $V_S(r, 0)$ is replaced by the quantum-mechanical average over the external states. If the vibrational modulation is moderately fast, the time dependence in $V_S(r, t)$ can no more be completely neglected and new terms appear. It is remarkable, that the fourth-order vibrational moment is the first one to be affected by this process. The dynamic effects are obviously inefficient over a very short time interval. It is concluded that the Born–Oppenheimer approximation used in the full thermodynamic theory and the slow modulation condition $\omega_v \tau_v \gg 1$ applied in the stochastic theory play an essentially equivalent role in the present context. The term $\langle (\partial \Delta V/\partial t)^2 \rangle_\gamma$ illustrates the effect of constraints built into the thermodynamic theory if the Born–Oppenheimer approximation is used.

The rotational moments $(\omega_n)_0^R$ given by the two theories under discussion agree in terms of the zero and of the first order in $\hbar$. The following formulas are used in this identification[3]:

$$\left\langle \left(\frac{\partial \omega}{\partial t} \right)^2 \right\rangle = \frac{1}{I^2} \left\langle \left(\frac{\partial V_S}{\partial \theta} \right)^2 + \frac{1}{\sin^2\theta} \left(\frac{\partial V_S}{\partial \varphi} \right)^2 \right\rangle , \tag{17a}$$

$$= \frac{KT}{I^2} \left\langle \frac{\partial^2 V_S}{\partial \theta^2} + \cot\theta \left(\frac{\partial V_S}{\partial \theta} \right) \right.$$

$$\left. + \frac{1}{\sin^2\theta} \frac{\partial^2 V_S}{\partial \varphi^2} \right\rangle . \tag{17b}$$

The proof is similar to that given in the Ref. 10. If $V_S = 0$, the intermolecular torques are absent, $\langle (\partial \omega/\partial t)^2 \rangle = 0$ and the rotational frequency ω remains constant. According to the classical mechanics the moments higher or equal to $(\omega_4)_0^R$ are affected by intermolecular dynamic effects; this statement applies to $(\omega_3)_0^R$ if the rotation is semiclassical.

Some secondary terms entering into the thermodynamic expression for the rotational-vibrational moment $(\omega_4)_{\omega'}$ are missing in the corresponding stochastic formula. This is a consequence of the fact that, in the present theory, $V_S(r, t)$ is a classical stochastic process and vibrations and rotations are taken to be uncorrelated. For example, the term $\langle \Delta V M_0(3) \rangle - \langle \Delta V \rangle \langle M_0(3) \rangle$ [Eq. (39b) of Ref. 3] vanishes if ΔV and $M_0(3)$ are independent processes. These terms are small, however, and it can safely be concluded that the results of both theories closely parallel each other in a majority of cases of practical interest.

In the case of purely rotational R spectra, the only case where the full thermodynamic calculations have been made, stochastic and thermodynamic

formulas coincide in term up to the first order in
$\hbar$. Formulas (17a) and (17b) are once again used
in this identification.

The spectral moments of the isotropic R and of
the vibrational-rotational anisotropic R spectra
are similar in many respects, to the corresponding
ir spectra. It must be stressed, however, that
the vibrational moments extracted from these three
sorts of spectra are not necessarily identical.
This only happens if M, α, β, and $V_S(r, t)$ are

statistically independent. If they are not, definite
although probably small differences exist.

A last comment may be of interest. Stochastic
theories are often useful in describing irreversible
processes, but they generally need justification in
terms of intrinsically more complete thermody-
namic theories.[11] It is therefore satisfactory that
the spectral moments, when available, are found
to be basically equivalent in the two theories under
study.

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Reanalysis of the Hyperfine Structure of the $4f^6 6s^2\ {}^7F$ Multiplet in ^{147,149}Sm, Including Measurements for the ${}^7F_6$ State*

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The hyperfine structure (hfs) of the $J=6$ member of the $4f^6 6s^2\ {}^7F$ ground multiplet of ^{147,149}Sm
has been measured by the atomic-beam magnetic-resonance technique, and that of the J
$=1-5$ states has been remeasured. The magnetic-dipole and electric-quadrupole hyperfine-
interaction constants obtained, after correction for second-order hfs, are found to be consis-
tent to a very high order with the three-parameter formulation of the Sandars—Beck effective-
operator theory of hfs and with the Conway-Wybourne eigenvectors for the $J=1-6\ {}^7F$ states
of Sm. The earlier apparent failure of these eigenvectors to be consistent with the magnetic
dipole hfs of the ${}^7F$ states with $J=1-5$ is now resolved.

I. INTRODUCTION

The hyperfine structure (hfs) of the $4f^6 6s^2\ {}^7F$
ground term of the samarium atom has been in-
vestigated in detail by Woodgate[1] and by Robertson,
Waddington, and Summers-Gill[2] with the atomic-
beam magnetic resonance technique. The multi-
plet comprises seven states with J values of
$0, 1, \ldots, 6$. The ${}^7F_0$ level lies lowest and is the
atomic ground state; the excitation energy of the
others increases with J, and the highest level
$(J=6)$ lies at 4021 cm^{-1}.[3]

Because samarium is relatively volatile,[4] the
highest usable temperature for an atomic beam
from a normal oven is low, only about 850 °C. At
this temperature, the Boltzmann factors for the
states with $J=4$, 5, and 6 are extremely small,
and the very small population of individual mag-
netic sublevels of these states makes observation

of transitions between them very difficult. In
1961, Pichanick and Woodgate[5] measured the elec-
tron g factor g_J for all six $J \neq 0$ states by observing
transitions in the abundant even-even isotopes
(which have no hfs), and in 1966 Woodgate[1] was
able to measure the hfs of ^{147,149}Sm in the states
with $J=1$, 2, 3, and 4. Robertson *et al.*[2] in 1968
had sufficient sensitivity to extend the hfs work to
the $J=5$ level but were unable to make the corre-
sponding measurements for the final state, ${}^7F_6$.

The ${}^7F$ multiplet of Sm I has been studied theoret-
ically by Judd and Lindgren[6] and by Conway and
Wybourne.[7] Both studies obtained eigenvectors
for each of the states in terms of the appropriate
Russell–Saunders basis states. In addition to
yielding excellent fits to the known excitation en-
ergies, the eigenvectors (particularly the more
recent ones of Conway and Wybourne) were re-
markably consistent with the g_J values measured