Functional series in asymmetric-molecular-rotors theory.
I. Vectorial correlation functions and spectral densities for a free classical ensemble

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A new method is presented to calculate vectorial correlation functions for a system of free asymmetric-top molecules. The analytical expression of the rotation matrix of an asymmetric top is determined first by using a special set of functions. Next, this matrix is developed into a Fourier series. Final results, obtained after averaging over a canonical ensemble, appear in the form of rapidly converging series of integrals of free spherical-rotor correlation functions. This development contains no approximation and is well adapted to numerical treatment. It also represents a convenient starting point to develop rotational models for extended diffusion.

I. INTRODUCTION

Three types of methods were proposed to compute vectorial correlation functions of free asymmetric rotors and the corresponding infrared band profiles. In a first method,[1] analytical solutions of Euler's equations are employed to express the rotation matrix in terms of elliptic functions and integrals. Polynomial approximations then permit a direct calculation of the Boltzmann averages.[2] In a second method,[3] Euler's equations are solved numerically and give rotational trajectories. Time scaling property then permits the calculation of thermal averages. Finally, in a third method,[4] equations giving time derivatives of Euler's angles are solved numerically. Here again, the ensemble average is determined in a purely numerical way; this theory also provides rotational correlation times. In all these methods, the computational time is largely excessive; this is particularly true if the long-time behavior of correlation functions is desired or if nearly linear tops are considered.

In this paper, we present new analytical expressions for the correlation functions of free asymmetric rotors. The theory employs a factorization of the rotation matrix elements into products of two periodic functions. One period corresponds to the nutation and spin rotation of the asymmetric top under consideration, whereas the second period, incommensurable with the first, is associated with the precessional motion. Fourier transforming the rotation matrix then permits the correlation function to be presented in the form of an infinite series of spherical-top correlation functions. The theory developed here, leads to the following results. (i) Correlation functions are obtained with a gain of the order 10^3 in computer time as compared with other methods.[5] (ii) The computer time required to calculate $G(t)$ decreases with t; the opposite statement holds true in all previous work. (iii) Nearly linear tops are conveniently studied in the frame of the present theory; this was not easily done in precedent methods. (iv) Finally, this theory provides a convenient way to compute correlation functions of various extended diffusion models. The present analysis moreover permits

one to take account of the rotation-vibration couplings.

The outline of this paper is as follows. Section II contains a brief description of Euler's equations and their well-known solutions; it permits one to introduce the notations used in this article. This section is concluded by Fourier analyzing the rotation matrix. Section III treats the correlation functions of freely asymmetric tops comparing them with their symmetric-top limits. The last section contains an analysis of spectral densities. It is closed by a short discussion of extended diffusion models.

II. EQUATIONS OF MOTION
OF AN ASYMMETRIC TOP

A. Solutions of Euler equations

The system to be considered in this section is a freely rotating rigid body. To describe its motion, the rotating coordinate axes, $Oxyz$, are chosen as to coincide with the principal axes of the inertial ellipsoid $\overleftrightarrow{I}$; without loss of generality, one always takes $I_x \leq I_y \leq I_z$. Again, a space-fixed coordinate system, $OXYZ$, is defined such that the angular momentum, $\mathbf{J}(t)$, coincides with the Z axis. Then, the rotational motion is completely characterized by the initial values of the angular momentum $[J_X(0)=0$, $J_Y(0)=0$, $J_Z(0)=J_Z(t)]$ and the Euler equations in the body frame:

$$\dot{J}_x(t) = (I_z^{-1} - I_y^{-1})J_y(t)J_z(t) , \tag{1}$$

$$\dot{J}_y(t) = (I_x^{-1} - I_z^{-1})J_z(t)J_x(t) , \tag{2}$$

$$\dot{J}_z(t) = (I_y^{-1} - I_x^{-1})J_x(t)J_y(t) . \tag{3}$$

The solutions of these equations are well known for symmetric tops ($I_x = I_y$ or $I_y = I_z$); the rotational dynamics of asymmetric tops is much more complex. The angular momentum, $\mathbf{J}(t)$, can precess around the x or the z axis of the body-fixed frame.[6] More precisely, one always has an infinity of times t' such that $\mathbf{J}(t')$ is contained in the xz plane and $\dot{J}_y(t') > 0$. Let t_0 be one of these t' and θ the angle formed by $\mathbf{J}(t_0)$ and the z axis (Fig. 1). Moreover,
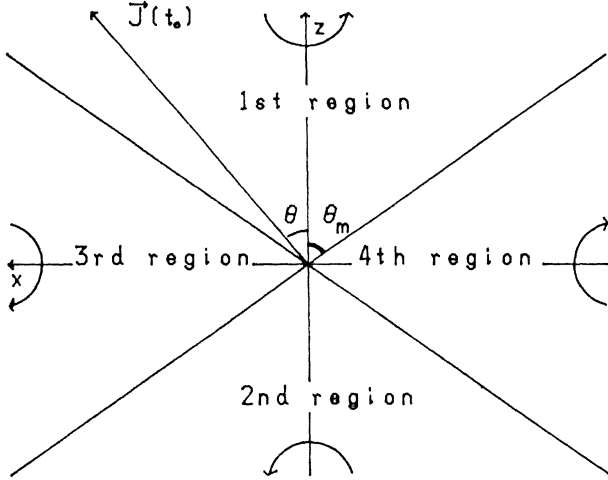
FIG. 1. Definition of the four regions; the x and z axes correspond, respectively, to the principal axes of the least and largest momentums of inertia. The y axis associate with the intermediate momentum of inertia is perpendicular to the plane. See the text for θ_m definition. The direction of the angular momentum precession is indicated by circular arrows.

$\cos\theta_m$ is chosen to be the positive root of the equation:

$$\cos^2\theta_m = I_z(I_x - I_y)/I_y(I_x - I_z) . \qquad (4)$$

Then the space $Oxyz$ can be divided in four regions. (i) In the first region, $\cos\theta_m < \cos\theta < 1$, the angular momentum precesses around the z axis and its component $J_z(t)$ is always positive. (ii) In the second region, $-1 < \cos\theta < -\cos\theta_m$, $\mathbf{J}(t)$ precesses around the z axis in the opposite sense as in the first region and its component $J_z(t)$ remains always negative. (iii) In the third region, $0 < \cos\theta < \cos\theta_m$, $\mathbf{J}(t)$ precesses around the x axis and its component $J_x(t)$ is always positive. (iv) Finally, in the fourth region, $-\cos\theta_m < \cos\theta < 0$, $\mathbf{J}(t)$ precesses around the x axis and its component $J_x(t)$ remains always negative.

In each of these regions, the solutions of Euler equations (1)—(3) can be expressed in terms of Jacobian doubly periodic functions[7] $\text{sn}(u,k)$, $\text{cn}(u,k)$, etc.; in what follows, the explicit reference to the modulus k will be omitted. In the first region, the solutions can be written in the form

$$J_x(t) = J \sin\theta \, \text{cn}(mt - \phi) , \qquad (5)$$

$$J_y(t) = J \sin\theta \, \text{dn}(ia)\text{sn}(mt - \phi) , \qquad (6)$$

$$J_z(t) = J \cos\theta \, \text{dn}(mt - \phi) , \qquad (7)$$

where ϕ designates mt_0. The modulus k, the quantities a and m are related by

$$k = \tan\theta/\tan\theta_m , \qquad (8)$$

$$\text{dn}(ia) = 1/\sin\theta_m , \qquad (9)$$

$$m = (I_x^{-1} - I_z^{-1})^{1/2}(I_y^{-1} - I_z^{-1})^{1/2} J \cos\theta . \qquad (10)$$

One can note that the initial value of the angular momentum, $\mathbf{J}(0)$, is completely determined by the variables J, θ,

and ϕ. One has, in the region considered above, $0 < J < \infty$, $0 < \theta < \theta_m$, and $0 < \phi < 4K$ where $4K$ is the real period of the sn or cn functions.

The analytical solutions of Euler equations in the three other regions are similar to that found for the first region. Their detailed expressions are given in Ref. 1 and are not reproduced here.

B. Rotation matrix

Once $J_x(t)$, $J_y(t)$, and $J_z(t)$ are known, one can determine the Eulerian angles $\alpha(t)$, $\beta(t)$, and $\gamma(t)$ relating the body-fixed frame $Oxyz$ to the space-fixed coordinate system $OXYZ$ (see Refs. 1 and 8). Next they are built into the Wigner rotation matrix $D^{(1)}$ $(\alpha(t),\beta(t),\gamma(t))$. After some calculations, the various elements of this matrix can be expressed by the help of the following set of functions:[9]

$$A_0(t) = \frac{H_1\Theta(\tau - ia)}{H_1(ia)\Theta(\tau)} e^{-i\lambda t} , \qquad (11)$$

$$A_1(t) = \frac{\Theta_1 H(\tau - ia)}{H_1(ia)\Theta(\tau)} e^{-i\lambda t} , \qquad (12)$$

$$A_2(t) = \frac{\Theta H_1(\tau - ia)}{H_1(ia)\Theta(\tau)} e^{-i\lambda t} , \qquad (13)$$

$$A_3(t) = \frac{-iH\Theta_1(\tau - ia)}{H_1(ia)\Theta(\tau)} e^{-i\lambda t} , \qquad (14)$$

$$B_0(t) = \frac{H_1(ia)\Theta(\tau)}{H_1(ia)\Theta(\tau)} = 1 , \qquad (15)$$

$$B_1(t) = \frac{\Theta_1(ia)H(\tau)}{H_1(ia)\Theta(\tau)} , \qquad (16)$$

$$B_2(t) = \frac{\Theta(ia)H_1(\tau)}{H_1(ia)\Theta(\tau)} , \qquad (17)$$

$$B_3(t) = \frac{-iH(ia)\Theta_1(\tau)}{H_1(ia)\Theta(\tau)} . \qquad (18)$$

In these equations $H(u)$, $H_1(u)$, $\Theta(u)$, and $\Theta_1(u)$ are the four Θ functions;[7] when there is no ambiguity, $H_1(0)$, $\Theta(0)$, and $\Theta_1(0)$ are simply written H_1, Θ, and Θ_1. The variable τ designates the combination mt-ϕ. Note that the $A_i(t)$ and $B_i(t)$ have similar denominators. The functions $B_i(t)$ may be deduced from the functions $A_i(t)$ by transferring, in the numerators, the quantity ia from the second to the first Θ function and by putting λ equal to zero. The frequency λ corresponds to one of the periods of the precessional motion and can be written as

$$\lambda = I_z^{-1}J + imH'(ia)/H(ia) . \qquad (19)$$

Here, $H'(u)$ designates the derivative of $H(u)$.

The nine elements of the Wigner matrix $D^{(1)}$ $(\alpha(t),\beta(t),\gamma(t))$ can be expressed as follows:

$$D^{(1)}_{1,\pm 1} = 2^{-1}[A_2(t) \pm iA_1(t)] , \qquad (20)$$

$$D^{(1)}_{0,\pm 1} = 2^{-1/2}[B_2(t) \pm iB_1(t)] , \qquad (21)$$

$$D^{(1)}_{1,0} = -2^{-1/2}A_0(t) , \qquad (22)$$

$$D^{(1)}_{0,0} = B_3(t) , \qquad (23)$$

$$D_{i,j}^{(1)} = (-1)^{i+j} D_{-i,-j}^{(1)*} . \qquad (24)$$

The rotational motion in the first region is completely determined by Eqs. (20)–(24). In particular, considering the expression of $D_{0,0}^{(1)}(t)$, one notices that the angular momentum precesses around the z axis. It forms with this axis a nutational angle $\beta(t)$. This nutation is periodic with a period equal to $2K/m$. When $\mathbf{J}(t)$ is in the xz plane, $\cos\beta(t)$ attains its maximum and is equal to $\cos\theta$; inversely, the minimum value of $\cos\beta(t)$ is reached when $\mathbf{J}(t)$ is in the yz plane. In addition, the time for a complete precessional revolution increases when the angle θ approaches θ_m. This last point plays a particular role in analyzing the long-time behavior of the correlation function. For a complete description of the free asymmetric-top motion, see for example Ref. 10.

C. Fourier series

It is convenient to perform a Fourier analysis of the rotation matrix or, equivalently, of the functions $A_i(t)$ and $B_i(t)$. Equations (11)–(14) show that $A_i(t)$'s factorize into two periodic functions. As mentioned earlier the period $4K/m$ is associated with the nutation and the spin rotation of the top under consideration; and the period $2\pi/\lambda$, generally incommensurable with $4K/m$, is related to the precessional motion. Using Hermite results[11] on the development of elliptic functions, one finds the following Fourier series:

$$A_0(t) = \frac{i\pi H_1 H(ia)}{KH'H_1(ia)} e^{-i\lambda t} \sum_{r,\epsilon} \epsilon (\Lambda_{r,\epsilon}^+)^{1/2} e^{ir\epsilon v} , \qquad (25)$$

$$A_1(t) = \frac{\pi\Theta_1\Theta(ia)}{iKH'H_1(ia)} e^{-i\lambda t} \sum_{s,\epsilon} \epsilon (\Lambda_{s,\epsilon}^+)^{1/2} e^{is\epsilon v} , \qquad (26)$$

$$A_2(t) = \frac{\pi\Theta\Theta_1(ia)}{KH'H_1(ia)} e^{-i\lambda t} \sum_{s,\epsilon} (\Lambda_{s,\epsilon}^-)^{1/2} e^{is\epsilon v} , \qquad (27)$$

$$A_3(t) = \frac{-i\pi H}{KH'} e^{-i\lambda t} \sum_{r,\epsilon} (\Lambda_{r,\epsilon}^-)^{1/2} e^{ir\epsilon v} . \qquad (28)$$

In these formulas, the index ϵ takes the value ± 1, the subscript s has odd ($s = 1,3,5,\ldots$), while the subscript r has even values ($r = 0,2,4,\ldots$). The variable v designates the quantity $\pi(mt - \phi)/2K$. It may be useful to remember that H' is equal to the square root of $2kk'K/\pi$.[7]

The convergence of the above Fourier series depends on the factors

$$(\Lambda_{n,p}^\pm)^{1/2} = \frac{2^{1/2}}{(1+\delta_{0,n})(1+p^2)^{1/2}} \frac{x_{np}}{1\pm(-1)^p x_{np}^2} . \qquad (29)$$

Here $x_{n,p}$ is the positive root of $x_{n,p}^2 = q^2 \exp(p\pi a/K)$. The so-called "nome q"[7] corresponds to the quantity $\exp(-\pi K'/K)$ where K' is the complete elliptic integral of the first kind depending on the modulus $k' = (1-k^2)^{1/2}$. The series given by Eqs. (25)–(28) are rapidly converging except if k is very close to unity, i.e., if θ is approaching θ_m. This convergence of the q series may be illustrated by considering that $q = 10^{-3}$ for $k^2 = 0.02$, $q = 10^{-2}$ for $k^2 = 0.15$, $q = 10^{-1}$ for $k^2 = 0.81$, and $q = 0.25$ for $k^2 = 0.99$. The use of the q series is a usual tool to compute elliptic functions or integrals.

III. ROTATIONAL CORRELATION FUNCTIONS

A. Thermal average

The basic object considered in this section is the orientational correlation function $G(t) = \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ where $\mathbf{u}(t)$ is a unit vector fixed in the molecule and rotating with it. The operation $\langle \ \rangle$ does not imply an average over the initial orientations. This is a consequence of the fact that (i) the scalar products like $\mathbf{u}(t) \cdot \mathbf{u}(0)$ are independent of the choice of coordinate system and (ii) all molecular orientations are equiprobable in the free space. Then, averaging over a canonical ensemble involves only a reduced probability density for the initial angular momentum. As mentioned in the preceding section, the dynamics of an asymmetric top depends on the region of the $Oxyz$ space in which the initial angular momentum is located. It is then convenient to evaluate the averages over these four regions separately. If $F(t)$ indicates $\mathbf{u}(t) \cdot \mathbf{u}(0)$, one has:

$$\langle F(t)\rangle = \langle F(t)\rangle_I + \langle F(t)\rangle_{II} + \langle F(t)\rangle_{III} + \langle F(t)\rangle_{IV} , \qquad (30)$$

$$\langle F(t)\rangle_I = Q \int_0^{\theta_m} \sin\theta \, d\theta \int_0^\infty dJ \, W(J,\theta) \int_0^{4K} d\phi \, F(t) , \qquad (31)$$

$$Q = (2\pi k_B T)^{-3/2} (I_z - I_x)^{1/2} (I_z - I_y)^{-1/2} I_x^{-1} I_z^{-1/2} , \qquad (32)$$

$$W(J,\theta) = J^2 \exp[-(\cos^2\theta/I_z + \sin^2\theta/I_x)J^2/2k_B T] . \qquad (33)$$

The average $\langle F(t)\rangle_{II}$ over the second region is obtained by changing the limits of integration over the variable θ: the limits 0 and θ_m are replaced by the limits $-\theta_m$ and π, respectively. Interchanging the role of x and z axes gives the expressions in the regions III and IV; compare with Refs. 1 and 8.

The next step consists of reducing the average over regions I and II to an average over the first region only. This result may be reached by considering that the second region is obtained from the first one by a reflection on the xy plane and that the precession in the second region has an opposite direction to that in the first region (see Fig. 1). Similar results appear when regions III and IV are considered. The vectorial correlation function $G(t)$, is then expressed as

$$G(t) = u_x^2 [\langle R_{1,1}(t) - R_{1,-1}(t)\rangle_I + \langle R_{0,0}(t)\rangle_{III}]$$

$$+ u_z^2 [\langle R_{00}(t)\rangle_I + \langle R_{1,1}(t) - R_{1,-1}(t)\rangle_{III}]$$

$$+ u_y^2 [\langle R_{1,1}(t) + R_{1,-1}(t)\rangle_{I+III}] . \qquad (34)$$

In this equation, the components $\{u_x(0), u_y(0), u_z(0)\}$ of the unit vector $\mathbf{u}(0)$ are simply designated by $\{u_x, u_y, u_z\}$ and the matrix $\overleftrightarrow{R}(t)$ represents twice the real part of the free rotator correlation matrix in the first region, such that

$$R_{k,l}(t) = 2 \, \text{Re} \left[\sum_{m=-1}^{+1} D_{m,k}^{(1)}(\alpha(t), \beta(t), \gamma(t)) \right.$$

$$\left. \times [D_{m,l}^{(1)}(\alpha(0), \beta(0), \gamma(0))]^* \right] . \quad (35)$$

B. Functional series for $G(t)$

The rotational correlation function $G(t)$ can be expanded into functional series of integrals of spherical-top correlation functions. This is the main point of this paper and can be proved as follows.

Infinite summations over two indices appear in the ex-

$$\langle R_{1,1}(t) - R_{1,-1}(t) \rangle_I = \sum_{s=1,3,5,\ldots} \sum_{\sigma=-1}^{+1} \int_0^{\theta_m} d\theta \, \sin\theta \, Q_x \Lambda_{s\sigma}^+ g(s,\sigma,t) , \quad (36)$$

$$\langle R_{1,1}(t) + R_{1,-1}(t) \rangle_I = \sum_{s=1,3,5,\ldots} \sum_{\sigma=-1}^{+1} \int_0^{\theta_m} d\theta \, \sin\theta \, Q_y \Lambda_{s\sigma}^- g(s,\sigma,t) , \quad (37)$$

$$\langle R_{0,0}(t) \rangle_I = \sum_{r=0,2,4,\ldots} \sum_{\sigma=-1}^{+1} \int_0^{\theta_m} d\theta \, \sin\theta \, Q_z (1+\delta_{r,0}) \Lambda_{r\sigma}^+ g(r,\sigma,t) , \quad (38)$$

$$g(n,p,t) \equiv (1-\mu t^2) \exp(-\mu t^2/2) , \quad (39)$$

$$\mu = \frac{k_B T (n\pi m/2KJ - p\lambda/J)^2}{\cos^2\theta/I_z + \sin^2\theta/I_x} . \quad (40)$$

The coefficients Q_x, Q_y, Q_z, and $\Lambda_{np}^\pm$ depend only on the variable θ; their expressions are developed in Eq. (29) and in the Appendix. Averages over the third region are deducible from the above equations by interchanging the role of I_x and I_z and by replacing θ_m by $\pi/2 - \theta_m$.

The time dependence of $G(t)$ is contained entirely in that of the elementary functions $g(n,p,t)$, defined by Eqs. (39) and (40). This important property deserves the following comments. (i) Any function $g(n,p,t)$ considered as a function of time, has the form of a correlation function of a free spherical-top rotor. After an initial decrease and a passage through a negative minimum, these functions increase monotonically to vanishing in the long-time limit. (ii) In the method developed in Ref. 1, one has to integrate numerically oscillatory functions over the variable J. The computational time thus increases rapidly when large values of t are considered. In the present theory, the monotonic and exponential behavior of the functions $g(n,p,t)$ offers a great advantage in this respect. (iii) The function $g(0,0,t)$ is independent of time. The long-time limit of $G(t)$ is consequently given by the term Λ_{00}^+ in Eq. (38). (iv) One may finally emphasize that the series described in Eqs. (36)—(38) do not result from a perturbation theory but represent an exact result.

C. The symmetric-top limit

The study of the above functional series in the symmetric-top limit merits attention. Consider for example the case $I_x = I_y < I_z$. The third region then vanishes. In the first region, the modulus k and the nome q are

pressions of the matrix elements $R_{kl}(t)$ when the Fourier series (20)—(28) are employed to express the Wigner matrix elements $D_{mn}^{(1)}$. However, the integration over the variable ϕ described in Eq. (31) reduces these double summations into single summations. The integration over the variable J is effectuated next; the results can be expressed in terms of elementary functions. Unfortunately the integration over the angle θ cannot be obtained in an analytical form; a similar observation has already been made in the much simpler case of the symmetric-top molecules (see below). The integrations over the angle θ then remain numerical. It results that the averages in the first region can be written as

equal to zero but $k^2/16q$ is equal to unity.[12] The limits of the coefficients $\Lambda_{n,p}^\pm$ are found by noticing that $\exp(\pm\pi a/2K)$ tends to $(1\pm\cos\theta)/\sin\theta$. The factor μ in Eq. (40) takes the value μ_s such that

$$\mu_s = \frac{k_B T [n(I_z - I_x)\cos\theta/I_x I_z - p/I_x]^2}{\cos^2\theta/I_z + \sin^2\theta/I_x} . \quad (41)$$

Collecting these results and noticing that in the infinite series [Eqs. (36)—(38)] only the terms with $s=1$ and $r=0$ survive, one finds the familiar formula of St. Pierre and Steele[13] which can be expressed as

$$G(t) = (u_x^2 + u_y^2) \int_0^{\pi/2} d\theta \, \sin\theta \, A_s \sum_{\sigma=-1}^{+1} d_{1,\sigma}^{(1)2}(\theta) g(1,\sigma,t)$$

$$+ u_z^2 \int_0^{\pi/2} d\theta \, \sin\theta \, A_s \sum_{\sigma=-1}^{+1} d_{0,\sigma}^{(1)2}(\theta) g(0,\sigma,t) . \quad (42)$$

In this equation, $d_{ij}^{(1)}(\theta)$ represents as usual the reduced rotation matrix element $D_{ij}^{(1)}(0,\theta,0)$. The normalization factor A_s is equal to

$$I_x^{-1} I_z^{-1/2} (\cos^2\theta/I_z + \sin^2\theta/I_x)^{-3/2}$$

and the long-time limit of $G(t)$ is given by the term in u_z^2 and $\sigma=0$.

In fact, considering the symmetric-top limits ($I_x = I_y$ or $I_y = I_z$) represents a suitable check of computer programs determining asymmetric-top correlation functions. The comparison of relation (42) with the series [Eqs. (36)—(38)] is also instructive. The structure of these expressions is basically similar but an infinite series appears
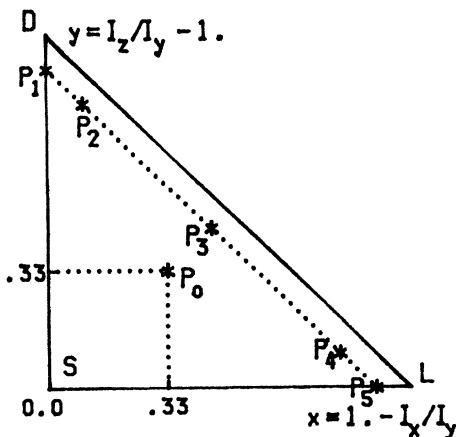
FIG. 2. Representation of molecular rotors in the plane $x = 1 - I_x/I_y$ and $y = I_z/I_y - 1$. All molecules can be represented by a point in or on the border of the triangle SLD. Spherical, linear, and planar symmetrical rotors correspond to the apexes S, L, and D, respectively. Oblate—and prolate—symmetric and planar asymmetric tops are associated with points on the segments DS, SL, and LD, respectively. P_0 is the median point. Spectral densities associated with the points P_1 to P_5 are presented in Figs. 4(a)—(e).

in the asymmetric-top case. The problem of the convergence is analyzed in the next section.

IV. RESULTS AND DISCUSSION

A. Preliminary remarks

In order to facilitate the subsequent discussion, it is convenient to first consider the following two points. (i) To classify the various molecular rotators, a diagram is constructed in a two-dimensional coordinate system. The abscissa and ordinate are chosen equal to $1 - I_x/I_y$ and $I_z/I_y - 1$, respectively (see Fig. 2). Then, all the existent molecular rotators are represented by a point into or on the border of a triangle SLD. In particular, spherical, linear, and symmetric planar tops are located on the apexes S, L, and D; the prolate and oblate symmetric tops are situated on the segments SL and SD; and all planar asymmetric tops are described by points on the segment LD. (ii) Rotational dynamics of molecules is analyzed by a number of experimental techniques,[14] for example, by infrared and Raman spectroscopies. It can be shown that the infrared absorption coefficient is proportional to the spectral density, $I(\omega)$, the Fourier transform of the vectorial correlation function, $G(t)$, described in the preceding section.[15] In view of possible spectroscopic applications, the subsequent discussion refers to $I(\omega)$ rather than to $G(t)$.

B. Convergence

In the triangle SLD, the median point, P_0, is the point corresponding to rotators of lowest symmetry. The convergence of the series is thus particularly uncertain at this point. In order to analyze it, we report in Figs. 3(a)—3(d)

the contributions of the successive terms of the series for a $G(t)$ with $u_x = 0$, $u_y = 1$, and $u_z = 0$. Figure 3(a) gives the exact profile; the contribution of the first term of the series [$s = 1$ in Eq. (37)] is represented in Fig. 3(b); the contributions of the second and third terms, $s = 3$ and 5, respectively, are reported in Figs. 3(c) and 3(d). One can see that the second and third terms differ from the first one by factors of the order 10^{-2} and 10^{-4}. Thus, the first term gives ninety-nine percent of the spectral density. This remarkable result is the consequence of the very
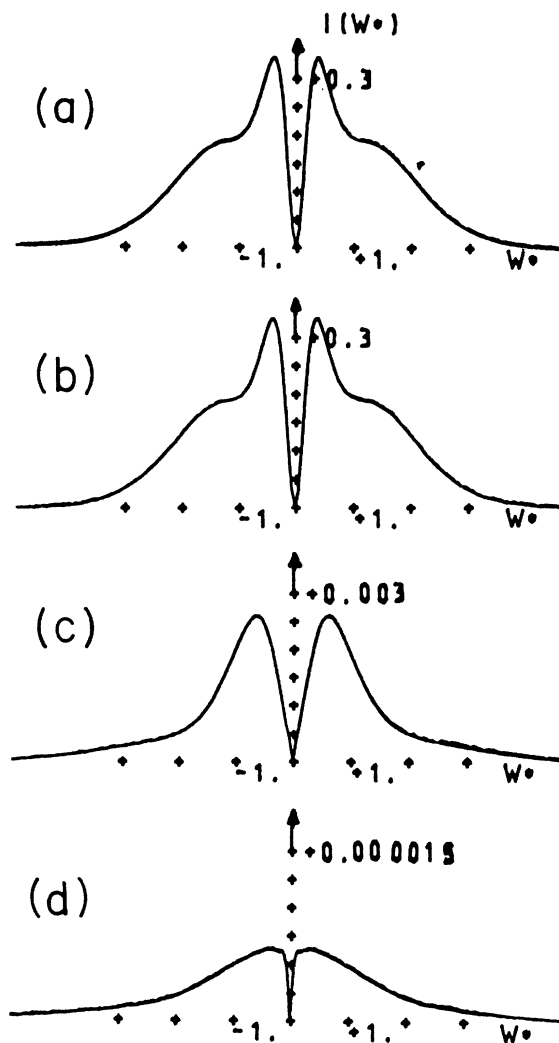

FIG. 3. Spectral density for a system of free asymmetric-top molecules with $I_x/I_y = 0.66$ and $I_z/I_y = 1.33$, corresponding to the median point, P_0, of the precedent figure. The unitary vector u is directed along with the y axis of intermediate moment of inertia. The frequency is in reduced units, $\omega^* = (I_y/k_B T)^{1/2}\omega$. The curve a corresponds to the exact profile. The curves (b), (c), and (d) give the contributions of the first ($s = 1$), second ($s = 3$), and third ($s = 5$) terms of the series. Note that the curves (c) and (d) have different scales.

small values of the nome q in all circumstances, except when θ is very near θ_m (Fig. 1).

C. Symmetric-top limit

When a molecule is a nearly symmetric top, its profiles are generally considered to be similar to the profiles of a symmetric top. To study the accuracy of this approximation, we compare a nearly planar asymmetric top (point P_2 of Fig. 2) with the corresponding symmetric top (point P_1 of Fig. 2). The resulting profiles for a dipolar transition parallel to the y axis, are reported in the Figs. 4(a)

and 4(b). One can observe that the two profiles present considerable analogies although not in all respects. As a consequence, the present theory justifies partially the symmetric-top approximation. In fact, at least ninety-nine percent of the spectral density comes from factors with $s = 1$ which can be associated term by term with the symmetric-top factors (see Sec. III C). In the asymmetric as in the symmetric case, the frequency dependence is contained in integrals over functions of the type $\alpha\omega^2\exp(-\beta\omega^2)$. However, there is a difference in the θ-dependent coefficients α and β.

D. Nearly linear-tops

One has to be much more cautious for nearly linear molecules. A certain similarity at large ω's certainly exists between the profile [Fig 4(d)] of an asymmetric top corresponding to the point P_4 of the Fig. 2 and the profile [Fig. 4(e)] of a symmetric top associated with the point P_5. But a large difference appears at the band centers. As the representative point of the top under consideration approaches that corresponding to the linear top (point L), central maximums on either side of the origin are increasing. This is the consequence of the fact that the probability density, $W(J,\theta)$, in Eq. (33), tends to a delta function, $\delta(\theta)$, when the smallest moment of inertia tends to zero. Particular care is required in this case when numerical calculations are executed. The analytical method presented in this paper appears much more convenient than pure numerical approaches.

E. Extended diffusion

The extended diffusion models have often been used to describe rotational molecular motions in liquids.[14] In these models, molecules are assumed to rotate like free rotors between collisions. These instantaneous collisions either randomize the orientation of the angular momentum (M model) or they randomize both its orientation and its modulus (J model). The calculations can then be developed by employing Laplace transformations. As the Laplace transform of spherical-top correlation function is expressible in terms of elementary functions, the series developed in this paper are well suited for practical computation. The technical procedure is similar to that given in Sec. III of Ref. 2. Generally speaking the present method will be useful for all models of molecular liquids in which torques act impulsively and the liquids exhibit gaslike properties.

F. Rotation-vibration coupling

A last comment concerns the rotation-vibration coupling. As the molecule vibrates, its inertia tensor varies. The effect of this coupling has been determined for zero-rank tensor correlation functions,[16] which are related to isotropic Raman spectra, by using an infinite q series. In a similar way, the present form of the theory for first-rank correlation function of asymmetric tops appears particularly well adapted to incorporate the rotation-
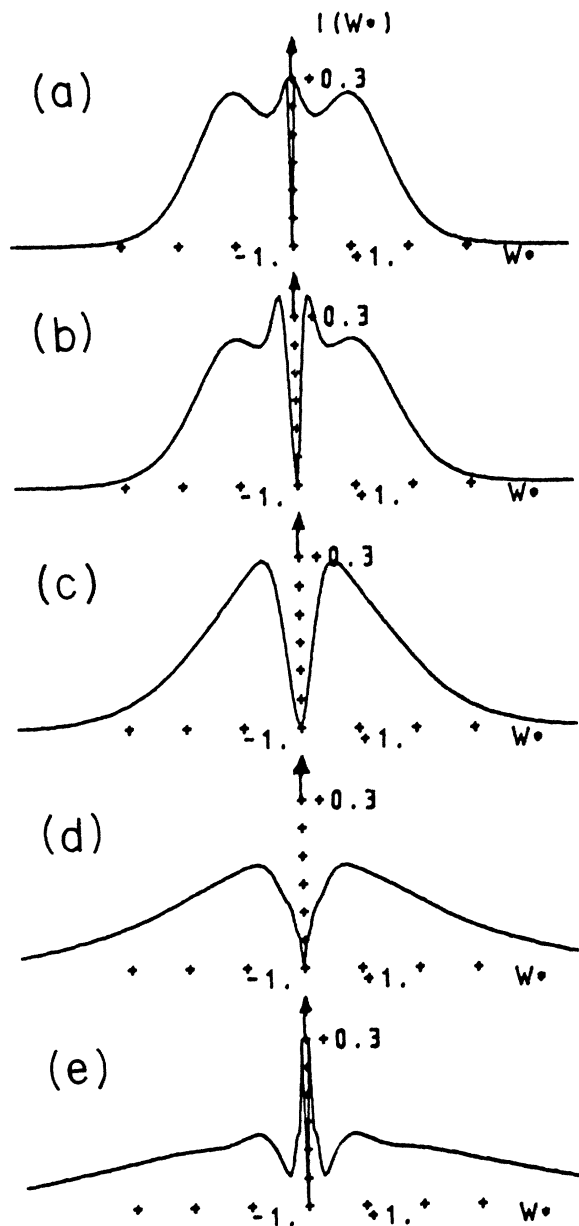

FIG. 4. Spectral density for systems of free asymmetric-top molecules. The unitary vector u is directed along with the y axis of intermediate moment of inertia. The curves (a)—(e) correspond to the points P_1 to P_5 of Fig. 2, respectively. The of I_x/I_y and I_z/I_y are the following: (a) 1 and 1.9, (b) 0.9 and 1.8, (c) 0.55 and 1.45, (d) 0.2 and 1.1, (e) 0.1 and 1.

vibration coupling effects. This last point will be developed in a future paper.

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APPENDIX

Explicit expressions for the time-independent coefficients Q_x, Q_y, and Q_z that appear in Eqs. (36)—(38) are as follows:

$$Q_x = 4\sin^2\theta k^{-2}A \; ,$$

$$Q_y = 4\sin^2\theta k^{-2}\mathrm{dn}^2(ia)A \; ,$$

$$Q_z = 4\cos^2\theta A \; ,$$

$$A = \frac{\pi}{2K}\mathrm{dn}(ia)(I_xI_yI_z)^{-1/2}\left[\frac{\cos^2\theta}{I_z}+\frac{\sin^2\theta}{I_x}\right]^{-3/2} \; .$$

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