Dynamics of dipole molecules in strong inhomogeneous fields

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We consider the classical dynamics of the one-dimensional motion of a dipole molecule (a rotator or a symmetric top) along the vector of an inhomogeneous electric (or magnetic) field. Assuming that the changes in the magnitude of the field are small during the periods of the rotational or orientational oscillations of the dipole moment vector relative to the field vector we construct an adiabatic theory which describes the dependence of the average translational kinetic energy of the molecule on the magnitude of a field of arbitrary shape. We determine the regions for the values of the initial parameters of the motion (in the absence of a field) corresponding to a molecule being ejected from the active zone of the field or to falling into a force center. We evaluate the fraction of molecules from a Maxwellian beam ejected by a strong field.

1. INTRODUCTION

The interest in the study of beams of polar molecules in electric fields is connected with the dependence of the sign of the polarizability of a molecule on the rotational quantum numbers. For instance, the polarizability of a dipole rotator with the dipole moment p and moment of inertia I in a state with orbital quantum number j and magnetic quantum number m is given by the relation:[1]

$$\varkappa_{jm} = \begin{cases} \dfrac{2Ip^2}{3\hbar^2}, & j = m = 0 \\[2ex] -\dfrac{2Ip^2}{\hbar^2 j(j+1)} \dfrac{j(j+1) - 3m^2}{(2j-1)(2j+3)}, & |m| \le j \ne 0 \end{cases} \quad (1)$$

from which one can see that the action of an inhomogeneous field on a molecule can be different in its ground state and in its excited states. This is, in particular, used in lasers for selecting excited molecules by means of electric fields transverse to the axis of a beam[2] and for the electrostatic confinement of polar molecules in Penning traps.[3]

In the present paper we consider the dynamic action of a strong inhomogeneous field on the translational motion of a polar molecule along the field vector. Since the temperature T (in energy units) satisfies the inequality $T \gg \hbar^2/2I$ over a broad range it is possible to restrict our considerations to the framework of classical mechanics. An important simplifying assumption which enables us to construct an analytic theory valid for fields of arbitrary shape is the adiabatic approximation, which assumes that the magnitude of the field changes little over the periods of the rotational and orientational oscillations of the dipole moment vector of the molecule. The interaction of a molecule with the field is then satisfactorily described by the dipole approximation $-\mathbf{pE}$ and the results of the theory are invariant under a change of the electric dipole moments $\mathbf{p}$ and fields $\mathbf{E}$ by their magnetic counterparts. One further simplification consists in considering an inhomogeneous field directed only along the velocity vector of the translational motion of the molecule; this is, for instance, realized when a molecule falls centrally toward a point field source.

From the point of view of existing theories of the interaction of gases with surfaces[4] the problem discussed here, on the one hand, strongly restricts the possible types of surface electric fields and the range of explainable effects but, on the other hand, contains all the advantages of an analytical approach which completely traces the effect of perturbations of the intramolecular degrees of freedom on the dynamics of the center of inertia of the molecule.

Indeed, the electric fields at the surfaces of crystals are inhomogeneous both in magnitude and in direction and decrease rapidly, exponentially with distance from the surface, so that the adiabatic approximation is hardly applicable to them. It is true that the surfaces of ferroelectrics[5] or of oxides with orientationally ordered dipole radicals[6,7] and also charged adsorption centers may be sources for rather strong and slowly decreasing electric fields, but the problem of in how far they can be comparable with the quantity T/p can significantly change the nature of the translational motion remains open to discussion.

Moreover, in almost all theories of scattering of a gas by a surface the gas consists of structureless point particles without internal degrees of freedom.[4] The quasiclassical scattering theory developed by Bogdanov (see the Appendix to Ref. 4) using action-angle variables for intramolecular motions contained an assumption that the dynamic picture of scattering is independent of perturbations of the intramolecular motions.[8] The same limitation is also characteristic for nonstationary theories[9], although attempts were made in Ref. 10 to introduce in such models the action of intramolecular motions on the scattering dynamics.

In contrast to the earlier approaches mentioned here[4,8–10] the possibility of the expulsion by a strong surface electric field of dipole molecules of the gas phase due to the perturbation of the rotational motion was discussed in Refs. 11 and 12. An analytical expression was obtained in Ref. 13 for the adiabatic invariant of the motion of a dipole rotator, which was generalized in Ref. 14 to the case of a symmetric top.

A rather complete analysis of the dynamics of a dipole rotator with an estimate of the fraction of such molecules in a Maxwellian beam which are expelled from the region where a strong field acts was given in Refs. 13 and 15. Since these results are necessary for solving the more general problem, in the present paper we shall give a detailed summary of them. In Sec. 2 we shall pay special attention to the case of plane rotation; it is particularly illuminating, since it provides a good illustration of the physical mechanism of the appearance of repulsive force, and it is the limiting case of the asymptotic solution obtained in Sec. 3 for symmetric

tops with any ratio of their principal moments of inertia (and, in particular, for rotators). Unfortunately, this asymptotic expression contained an error in Ref. 14 which made it impossible to explain the other limiting case of the strong ejection of a dipole top oriented antiparallel to the field vector. This important special case, which allows a simple and exact solution, is also considered in Sec. 3. Finally, we find in Sec. 4 the fraction of dipole symmetric tops forming a Maxwellian beam outside the active region of the field, which are expelled by the field as a function of the ratio of their principal moments of inertia. In Sec. 5 we discuss the results of the adiabatic theory and their application to systems studied experimentally.

2. PLANE ROTATION OF THE DIPOLE MOMENT VECTOR

The plane rotation of the dipole moment vector $\mathbf{p}$ of a polar molecule in an electric field is the simplest case illustrating both the appearance of a decelerating or accelerating effective force when the field gradient is nonvanishing and the classical nonlinear resonance in the field of circularly polarized radiation.[16] It is characteristic for rotators with an angular momentum oriented at right angles to the field vector E, and can be realized for symmetric tops in the absence of rotation around an axis of symmetry which is coincident with the direction of $\mathbf{p}$.

We write down the Hamiltonian of the translational motion (along the z-axis) and the plane rotational motion of a molecule in an inhomogeneous field $E(z)$:

$$H = \frac{P_z^2}{2m} + H_{rot}, \qquad H_{rot} = \frac{M_\theta^2}{2I} - pE(z)\cos\theta, \qquad (2)$$

where θ is the angle between the vectors $\mathbf{p}$ and $\mathbf{E}$ (Fig. 1). $P_z = m\dot{z}$ and $M_\theta = I\dot{\theta}$ are the total impulse. The force and the moment of the force are determined by the equations of motion:

$$\dot{P}_z = p\frac{dE(z)}{dz}\cos\theta, \qquad \dot{M}_\theta = -pE(z)\sin\theta. \qquad (3)$$

We shall assume that the function $E(z)$ decreases with increasing distance z from the source of the field, situated at the point $z = 0$. For sharp angles θ ($|\theta| < 90°$) the acting force will then be attractive and for obtuse angles it will be repulsive. At the same time for angles lying in the range $0 < \theta < 180°$ the torque will decelerate the rotation, while for $180° < \theta < 360°$ it will accelerate it. We show that the average force acting over a period τ of the rotation or of the orienta-

tional oscillation of the vector $\mathbf{p}$ will be repulsive for fields of moderate strength.

Using Eq. (2) to get an expression for $\dot{\theta}$ we can write down the average value of $\cos\theta$ over the period τ:

$$\langle\cos\theta\rangle_t = \frac{1}{\tau}\int_0^\tau \cos\theta \, dt,$$

$$dt = \left(\frac{2}{I}\right)^{1/2}\frac{d\theta}{[H - m\dot{z}^2/2 + pE(z)\cos\theta]^{1/2}}. \qquad (4)$$

If the kinetic energy $m\dot{z}^2/2$ changes little over a time τ we can replace it by its average value $\langle m\dot{z}^2/2\rangle_t$, and introducing the convenient dimensionless variables

$$y = \frac{\langle m\dot{z}^2/2\rangle_t}{H}, \qquad x = \frac{pE(z)}{H}, \qquad \varepsilon = \frac{x}{1-y}, \qquad (5)$$

we can easily get the integrals in (4):

$$f(x, y) \equiv \langle\cos\theta\rangle_t$$

$$= \int_{\theta_{min}}^{\theta_{max}}\frac{\cos\theta \, d\theta}{(1 - y + x\cos\theta)^{1/2}} \bigg/ \int_{\theta_{min}}^{\theta_{max}}\frac{d\theta}{(1 - y + x\cos\theta)^{1/2}}$$

$$= \begin{cases} \varepsilon^{-1}[(1 + \varepsilon)E(k^{-1})/K(k^{-1}) - 1], & \varepsilon \le 1 \\ 2E(k)/K(k) - 1, & \varepsilon \ge 1 \end{cases}, \qquad (6)$$

$$k = [(1 + \varepsilon)/2\varepsilon]^{1/2}.$$

Here $K(k)$ and $E(k)$ are complete elliptic integrals of the first and second kind. In Fig. 2 we show f as function of ε.

The vector $\mathbf{p}$ performs complete revolutions ($\theta_{min} = 0$, $\theta_{max} = 2\pi$) for $\varepsilon \le 1$ and the average force is repulsive. In sufficiently strong fields ($\varepsilon \ge 1$) the rotational regime changes to an oscillatory one and the average force, which is proportional to $\langle\cos\theta\rangle_t$, changes sign when the conditions

$$2E(k_c) = K(k_c) \approx 2,321, \qquad k_c \approx 0,9089, \qquad \varepsilon_c \approx 1,533 \qquad (7)$$

are satisfied.

The result obtained has a rather obvious physical meaning. A molecule which performs complete (or nearly complete) revolutions finds itself longer in states in which its dipole moment is oriented at obtuse angles with respect to the field vector and therefore is subject to the action of a repulsive force directed antiparallel to the field gradient. If
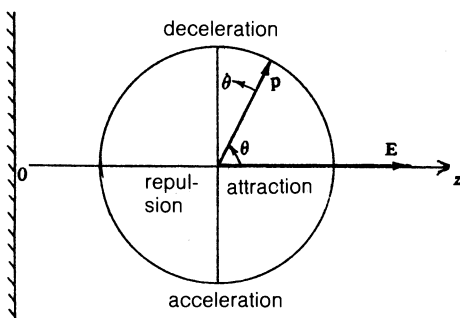

FIG. 1. Mechanism for the appearance of a repulsive force in the case of plane rotation of a dipole moment vector $\mathbf{p}$ in an inhomogeneous field $E(z)$.
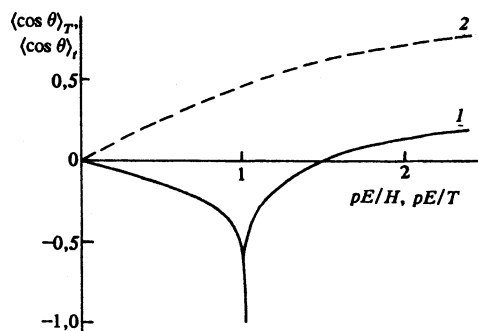

FIG. 2. The cosine of the angle of the orientation of the dipole moment with respect to the field, averaged over the period of the rotational or the oscillatory motion (curve 1) and averaged over a Gibbs ensemble (curve 2) as function of pE/H and pE/T, respectively.

the values of the field are so large ($\varepsilon > \varepsilon_c$) that the molecule can only perform small angular oscillations about the field vector the acting force becomes an accelerating one.

The dynamic mechanism considered is realized in low-density gases or in molecular beams of polar molecules for which the mean free path l exceeds the average action range R of the fields and the molecules do not exchange energy with one another in the field. In the opposite case $l \ll R$, the thermodynamic average orientations of the molecular dipole moments determined for the planar rotation considered here by Gibbs averaging,

$$\langle \cos \theta \rangle_T = I_1(pE/T)/I_0(pE/T) \tag{8}$$

[$I_n(z)$ is a Bessel function of imaginary argument of the first kind and of order n], always make a sharp angle with the field vector (Fig. 2) which guarantees the well known increase in the density of dipole particles in the active region of a field.

We turn to the consideration of the dynamics of the translational motion of a molecule. We shall be interested in the possibility of a regime of motion such that the acting force, before it changes its sign, manages to reverse the direction of the motion of the molecule and to eject it from the action zone of the field. In terms of the variables introduced in (5) we must find the function $y = y(x)$. The differential equation for this function follows directly from the first equation of motion in (3):

$$dy/dx = f(x, y). \tag{9}$$

The determination of the adiabatic invariant for an arbitrary mechanical system performing a one-dimensional finite motion and characterized by some parameter which changes slowly in time was carried out in Ref. 17. We show that the adiabatic invariant determined by the average value of the angular momentum $M_\theta = i\dot{\theta}$,

$$J(x, y) = \frac{1}{2\pi} \int_{\theta_{min}}^{\theta_{max}} M_\theta d\theta = \frac{(2IH)^{1/2}}{2\pi} \int_{\theta_{min}}^{\theta_{max}} (1 - y + x \cos \theta)^{1/2} d\theta$$

$$= \frac{4}{\pi}(IHx)^{1/2} \cdot \begin{cases} kE(k^{-1}), & \varepsilon \leq 1 \\ [E(k) - (1 - k^2)K(k)], & \varepsilon \geq 1 \end{cases} \tag{10}$$

[the parameter k was introduced in (6)] is a constant of the differential equation (9). To do this we use the following identity which follows from (6) and (10):

$$f(x, y) = -\frac{\partial J/\partial x}{\partial J/\partial y} \tag{11}$$

and we find the total derivative of $J(x,y)$ with respect to x:

$$\frac{d}{dx} J(x, y) = \frac{\partial J}{\partial x} + \frac{\partial J}{\partial y}\frac{dy}{dx} = \frac{\partial J}{\partial y}\left[\frac{dy}{dx} - f(x, y)\right] = 0. \tag{12}$$

The vanishing of (12) due to Eq. (9) means that the quantity $J(x,y)$ is conserved when the field parameter x changes. The required function $y(x)$ is thus implicitly determined by the following equation:

$$J(x, y) = J(0, y_0), \quad y_0 = y(0), \tag{13}$$

where

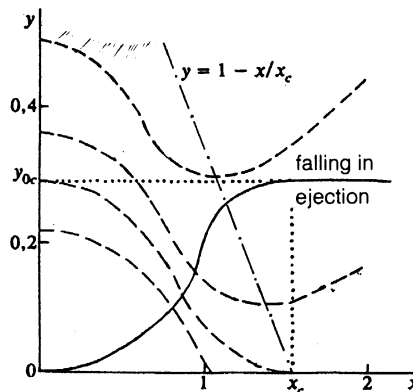$$J(0, y_0) = (2IH)^{1/2}(1 - y_0)^{1/2}. \tag{14}$$

FIG. 3. The relative translational kinetic energy y as function of the dimensionless field x acting on a molecule in the case of plane rotation (dashed lines). The continuous trace separates the xy diagram (x is the maximum value of the field) into regions where the molecule is "ejected" or where it "falls into" the force center.

We show in Fig. 3 the function $y = y(x)$ for various initial values of the parameter y_0 which gives the redistribution of the translational and rotational kinetic energies in zero field. In weak fields ($\varepsilon \ll 1$) we have

$$f(x, y) \approx -\frac{1}{4}\varepsilon, \quad y = y_0 - \frac{1}{8}\frac{x^2}{1 - y_0} \tag{15}$$

and the function $y(x)$ decreases to its minimum values determined by condition (7) which in the x,y coordinate plane are situated on the line $y = 1 - x/\varepsilon_c$. An especially critical regime corresponds to the conditions $dy/dx = 0$, $y = 0$ which are realized for

$$x_c = \varepsilon_c, \quad y_{0c} = 1 - \frac{2}{\pi^2 x_c} K^2(k_c) \approx 0,2879. \tag{16}$$

If the molecule is initially decelerated by the field for $y_0 > y_{0c}$ and later when well defined field values are reached it starts to be accelerated, for $y_0 = y_{0c}$ and $x = x_c$ the deceleration leads to the turning point ($y = 0$) and a subsequent reversed translational motion. For sufficiently strong fields ($x > x_c$) the electric field will thus eject plane-rotating dipole molecules with initial parameter values $y_0 \leqslant y_{0c}$.

The solid trace $y_0 = y_0(\tilde{x})$ in Fig. 3 separates the values of the initial relative translational kinetic energies y_0 and of the maximal fields x near the field source into two regions corresponding to the molecule falling into the force center or being expelled from the active region of the field. For $\tilde{x} < x_c$ the parameter $\tilde{x}$ corresponds to the turning points of the molecule ($y = 0$). In sufficiently strong fields $\tilde{x} > x_c$ the fraction of molecules ejected by the field, which is characterized by the quantity y_{0c}, is independent of the magnitude of the field.

3. DYNAMICS OF ROTATORS AND OF SYMMETRIC TOPS

We consider a symmetric top with principal moments of inertia $I_1 = I_2 = I$ and I_3 along the moving x_1, x_2, and x_3 axes, where we shall assume that the dipole moment vector $\mathbf{p}$ is oriented along the x_3 axis. The analysis of the dynamics of rotators will follow from the general relations for a top in the limit $I_3 \to 0$. It is convenient to express the rotational part H_{rot} of the Hamiltonian H of (2):
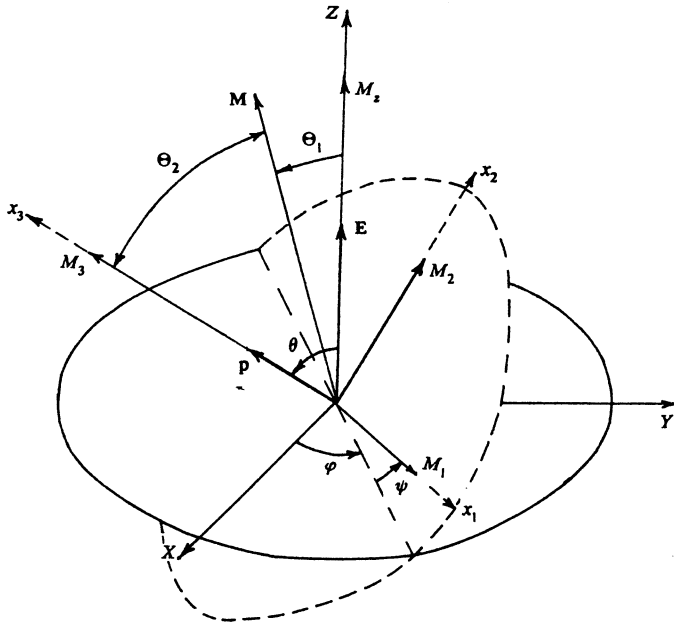
FIG. 4. Sketch of the orientations of the vectors and of the angular variables used to describe the dynamics of a dipole top in an external field.

$$H_{rot} = \frac{1}{2I}(M_1^2 + M_2^2) + \frac{1}{2I_3}M_3^2 - pE(z)\cos\theta \qquad (17)$$

(the M_i are the components of the angular momentum along the x_i axes) in terms of the Euler angle variables θ, ψ, and φ in a fixed X, Y, Z coordinate system with the Z axis oriented along the field vector E (see Fig. 4) and the generalized momenta $M_\theta = I\dot\theta$, $M_\psi = M_3$, $M_\varphi = M_z$:[17]

$$H_{rot} = \frac{M_\theta^2}{2I} + \frac{(M_z - M_3\cos\theta)^2}{2I\sin^2\theta} + \frac{M_3^2}{2I_3} - pE(z)\cos\theta. \qquad (18)$$

Note that the absolute magnitude of the total angular momentum vector is equal to

$$M = \left[M_\theta^2 + \frac{1}{\sin^2\theta}(M_z - M_3\cos\theta)^2 + M_3^2\right]^{1/2} = (2IH'_{rot})^{1/2}, \qquad (19)$$

where

$$H'_{rot} = H_{rot} - \frac{1}{2}\left(\frac{1}{I_3} - \frac{1}{I}\right)M_3^2, \qquad (20)$$

and its orientation in space can be given by the angles Θ_1 and Θ_2 with the Z and x_3 axes which are determined by the relation

$$\alpha_1 \equiv \cos\Theta_1 = \frac{M_z}{(2IH'_{rot})^{1/2}}, \qquad \alpha_2 \equiv \cos\Theta_2 = \frac{M_3}{(2IH'_{rot})^{1/2}}. \qquad (21)$$

The components M_z and M_3 are invariants of the motion in an external field, whereas the quantity H'_{rot}, determined in the adiabatic approximation by the equations

$$H'_{rot} = (1 - y)H', \qquad y \equiv \frac{\langle m\dot{z}^2/2\rangle_t}{H'},$$

$$H' = H - \frac{1}{2}\left(\frac{1}{I_3} - \frac{1}{I}\right)M_3^2 \qquad (22)$$

depends on the parameter y which changes with time. The parameters α_1 and α_2 are therefore not invariants, although they are convenient for giving the initial orientation (for $E = 0$) of the vector M. We shall use for the dimensionless invariants of the motion the parameters

$$\gamma_1 = \frac{M_z}{(2IH')^{1/2}} = (1 - y)^{1/2}\alpha_1,$$

$$\gamma_2 = \frac{M_3}{(2IH')^{1/2}} = (1 - y)^{1/2}\alpha_2, \qquad (23)$$

which are determined by the conserved part H' of the Hamiltonian H. The required adiabatic invariant then takes the form:

$$J(x, y) = \frac{1}{2\pi}\int_{\theta_{min}}^{\theta_{max}} M_\theta d\theta$$

$$= \frac{(2IH')^{1/2}}{\pi}$$

$$\times \int_{t_2}^{t_1} \frac{[(1 - y + xt)(1 - t^2) - (\gamma_1^2 + \gamma_2^2 - 2\gamma_1\gamma_2 t)]^{1/2}}{1 - t^2} dt$$

$$= \frac{(2IH')^{1/2}}{\pi}\left(\frac{x}{t_1 - t_3}\right)^{1/2}\Bigg[2(t_1 - t_3)E(k) - 2(t_1 + t_2)K(k)$$

$$+ \frac{1}{x}\left[\frac{(\gamma_1 - \gamma_2)^2}{t_1 - 1}\Pi\left(\frac{t_1 - t_2}{t_1 - 1}, k\right)\right]$$

$$- \frac{(\gamma_1 + \gamma_2)^2}{t_1 + 1}\Pi\left(\frac{t_1 - t_2}{t_1 + 1}, k\right)\Bigg]\Bigg\},$$

$$(24)$$

$$x = \frac{pE(z)}{H'}, \qquad k = \left(\frac{t_1 - t_2}{t_1 - t_3}\right)^{1/2}.$$

Here we have $t = \cos\theta$, $t_1 \geqslant t_2 \geqslant t_3$ are the roots of the cubic polynomial in the integrand, and $K(k)$, $E(k)$, and $\Pi(n,k)$

are complete elliptic integrals of, respectively, the first, second, and third kind. In the initial state $x = 0$, $y = y_0$, $\alpha_i = (1 - y_0)^{-1/2}\gamma_i$ we have

$$J(0, y_0) = [2IH'(1 - y_0)]^{1/2}$$

$$\times\left(1 - \frac{1}{2}|\alpha_1 - \alpha_2| - \frac{1}{2}|\alpha_1 + \alpha_2|\right). \quad (25)$$

Equating expressions (24) and (25) (as in (13)) we get the implicit function $y(x)$ for all initial values of y_0, α_1, and α_2. The average value of the force acting upon a molecule [see the first formula in (3)] is as before determined by the function $f(x,y) \equiv \langle\cos\theta\rangle_t$, which is now equal to:

$$f(x, y) = \frac{dy}{dx} = -\frac{\partial J/\partial x}{\partial J/\partial y} = (t_1 - t_3)\frac{E(k)}{K(k)} + t_3. \quad (26)$$

Equations (24) to (26), which determine the dynamics of a rotator for $\alpha_2 = 0$ were obtained in Ref. 13. Equations (24) and (26) for a symmetric top can be found in Ref. 14, but Eq. (25) in Ref. 14 contained an error which made correct analysis of the results impossible; we shall now turn to such an analysis.

In the case of weak fields $(x/(1 - y_0)\ll 1)$ we have

$$f(x, y) \approx \frac{1}{1 - y}\left\{\gamma_1\gamma_2\right.$$

$$\left. - \frac{1}{4}x\left[1 - \frac{3}{1 - y}\left(\gamma_1^2 + \gamma_2^2 - 3\frac{\gamma_1^2\gamma_2^2}{1 - y}\right)\right]\right\}, \quad (27)$$

$$y \approx y_0 + \alpha_1\alpha_2 x - \frac{1 - 3\alpha_1^2 - 3\alpha_2^2 + 5\alpha_1^2\alpha_2^2}{8(1 - y_0)}x^2. \quad (28)$$

We note that when we neglect the translational degrees of freedom $(y = y_0 = 0$, $\gamma_1 = \alpha_1)$, the asymptotic behavior (27) for a rotator $(\gamma_2 = 0)$ is the same as the classical limit of Eq. (1) (for $|m| \ll j \gg 1$ we have: $H_{\rm rot} = \hbar^2 j^2/2I$, $\alpha_1 = m/j$,

and $\varkappa_{jm} \approx -(p^2/4H_{\rm rot}(1 - 3\alpha_1^2))$ and for comparatively small inclinations of the initial plane of rotation to the field vector $(|\alpha_1| < 3^{-1/2})$ a repulsive force acts on the rotator which leads to a deceleration of the translational motion [decrease in the function $y(x)$]. In the case of a symmetric top deceleration occurs in the initial stage of the motion for $\alpha_1 < 0$ and afterwards for somewhat larger values of x for $\alpha_1 < [(1 - 3\alpha_2^2)/(3 - 5\alpha_2^2)]^{1/2}$, and also for $\alpha_1 = -\alpha_2 = -1$ (top oriented antiparallel to the field vector).

We obtain the asymptotic parameter y_{0c} of the critical regime of motion $y(x_c) = 0$, $f(x_c, 0) = 0$ for the case where the initial state differs little from that of a plane rotation of the dipole moment vector $(\alpha_1^2, \alpha_2^2 \ll 1)$ considered in Sec. 2. For $\alpha_1 = \alpha_2 = 0$ the roots of the cubic polynomial in the integrand in (24) are $t_1 = 1$, $t_2 = -\varepsilon_c^{-1}$ [see (7)], $t_3 = -1$, and the corrections to these roots will be quadratic in α_1 and α_2. The function $f(x_c, 0)$ of (26) in the linear approximation in α_1 and α_2 is therefore the same as (6) and we have $x_c \approx \varepsilon_c$. In the same approximation, by taking in (24) the contribution which is linear in $|\gamma_1 - \gamma_2|$ to the function

$$\frac{(\gamma_1 - \gamma_2)^2}{t_1 - 1}\Pi\left(\frac{t_1 - t_2}{t_1 - 1}, k\right)$$

$$\approx -\frac{\pi}{2}\frac{(\gamma_1 - \gamma_2)^2}{[(1 - t_1)(t_1 - t_2)]^{1/2}} \approx -\frac{\pi}{2}|\gamma_1 - \gamma_2|(2x)^{1/2},$$

we find

$$J(x_c, 0) \approx (2IH')^{1/2}\left[\left(\frac{2}{\pi^2 x_c}\right)^{1/2}K(k_c) - \frac{1}{2}|\gamma_1 - \gamma_2|\right]. \quad (29)$$

We denote the required linear asymptotic expression by $y_{0c}(\alpha_1, \alpha_2)$, where $y_{0c} = y_{0c}(0,0)$ refers to the value (16). Using (23) to equate (29) with $y = y_{0c}(\alpha_1, \alpha_2)$ to expression (25) for $J[0, y_{0c}(\alpha_1, \alpha_2)]$, we then get

$$y_{0c}(\alpha_1, \alpha_2) \approx y_{0c} - (1 - y_{0c})|\alpha_1 + \alpha_2|. \quad (30)$$

For the case of a rotator $(\alpha_2 = 0)$ the functions $y_{0c}(|\alpha_1|)$ and $x_c(|\alpha_1|)$ were tabulated in Ref. 13; they are shown in Fig. 5. Deviations of the exact function $y_{0c}(|\alpha_1|)$ from the asymptotic expression $y_{0c}(\alpha_1, 0)$ of (30) show up, starting with $|\alpha_1| \gtrsim 0.3$. By virtue of the invariance of Eqs. (24) to (30) under the substitution $\alpha_1 \leftrightarrow \alpha_2$ the functions $y_{0c}(\alpha_2)$ and $x_c(\alpha_2)$ will have exactly the same form for $\alpha_1 = 0$. It is interesting that for $\alpha_2 = -\alpha_1 \ll 1$, when the limiting position of the precessing top is strictly oriented antiparallel to the field vector $(\Theta_1 + \Theta_2 = 180°$, $\Theta_1 \sim \Theta_2 \sim 90°)$, a regime of maximum repulsion is reached, as in the case of plane rotation.

Expression (25) vanishes when $|\alpha_1|$ and (or) α_2 are equal to unity. The zero value of the adiabatic invariant distinguishes a special class of exact solutions corresponding to the absence of oscillations of the angular variable θ. The values of $\cos\theta$ are then equal to the two coincident roots $t_1 = t_2$ of the cubic polynomial of the integrand in (24) and can change when we change the parameters x and y.

Finding the conditions for which the equality $t_1 = t_2$ is realized is made easier because at that point the cubic polynomial has a local maximum and becomes equal to zero. In
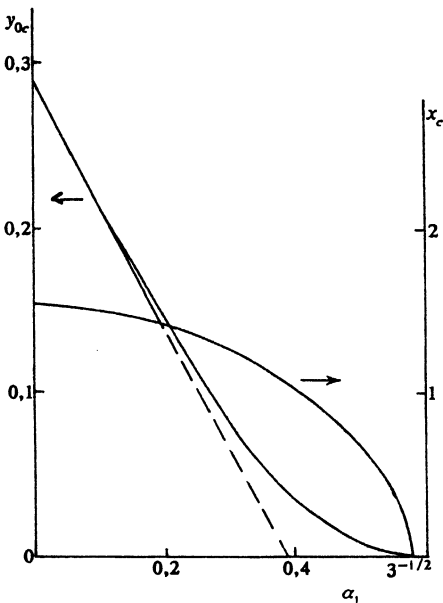
the case of most interest to us, that of a top with a dipole moment vector oriented antiparallel to the field vector, these conditions lead to simple functions $y(x)$ and $\theta(x)$:

$$y(x) = \begin{cases} y_0 - x, & x \le (1 - y_0)/2 \\ 1 + x - [8(1 - y_0)x]^{1/2}, & x \ge (1 - y_0)/2 \end{cases}, \quad (31)$$

$$\cos\theta = \begin{cases} -1, & x \le (1 - y_0)/2 \\ -[2(1 - y_0)/x]^{1/2} + 1, & x \ge (1 - y_0)/2 \end{cases}. \quad (32)$$

In Fig. 6 we show the functions $y(x)$ for different initial values y_0. The line $y = 1 - 3x$ splits the diagram into two regions in which there is no precession ($\theta = 180°$) and in which precession of the dipole moment about the field vector ($\theta < 180°$) occurs, and thus corresponds to points where the top loses its stability in an external field.

The critical trajectory $y(x)$ separating expulsive and attractive regimes of motion can be found from the conditions $y(x_c) = 0$, $y'(x_c) = 0$, and is characterized by the parameters:

$$x_c(-1, 1) = 1, \qquad y_{0c}(-1, 1) = 1/2. \quad (33)$$

The critical values of the field x_c and of the initial translational kinetic energy $y_{0c}(-1,1)$ found here turn out to be, respectively, less and larger than the analogous parameters (16) of the plane rotation case, so that the largest expulsive action is felt by a top oriented antiparallel to the field vector. The solid curve in Fig. 6, determined by the equations $y = x$ for $x < 1/3$ and $y = 1 - (1 + x)^2/(8x)$ for $1/3 < x < 1$, separates the xy diagram into two regions of parameter values (x is the maximum field value in the force center and y is the initial value outside the field) which correspond to the ejection of molecules from the action zone of the field and falling into the force center.

4. STATISTICS OF A MAXWELLIAN BEAM OF MOLECULES INCIDENT UPON THE ACTIVE ZONE OF A STRONG FIELD

We shall assume that outside the active zone of the field there is a gas of dipole molecules with number density n in thermodynamic equilibrium. The mean free path of the mol-
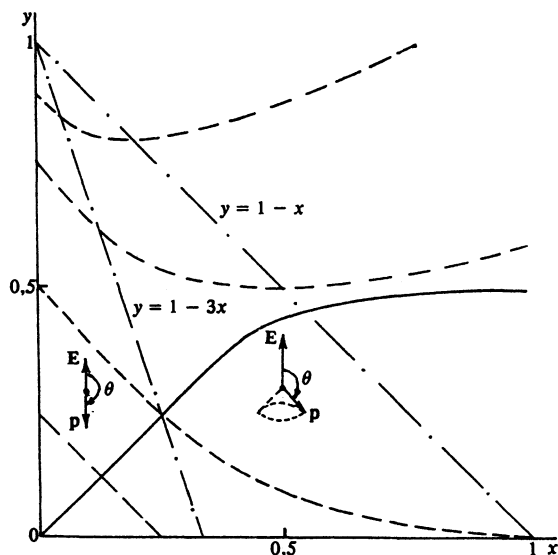

FIG. 6. Exact solutions of the problem of a symmetric top with a dipole moment oriented in its initial state antiparallel to the field vector.

ecules is assumed to be much longer than the linear dimensions of the active zone of the field, so that molecules in that zone do not suffer collisions and the action upon them by the field is purely dynamic. We calculate the fraction of molecules from a Maxwellian beam ejected by a strong field. To do this we need first of all obtain the equilibrium distribution function of the initial parameters H, y_0, α_1, and α_2 [see (21) and (22)] for the motion when there is no field.

The fraction of molecules which have values of the original initial parameters of the motion in the vicinity of $v_z = \dot{z}$, M_θ, M_ψ, M_φ, θ, ψ, and φ,

$$dW(v_z, M_\theta, M_\psi, M_\varphi, \theta, \psi, \varphi)$$

$$\propto \exp(-H/T) dv_z dM_\theta dM_\psi dM_\varphi d\theta d\psi d\varphi \quad (34)$$

is determined by the Hamiltonian (2) with H_{rot} from (18) for $E(z) = 0$. The original variables v_z, M_θ, M_ψ, and M_φ are connected with the new variables H, y_0, α_1, and α_2 through the relations

$$v_z = A(H, y_0, \alpha_2) B(y_0),$$

$$M_\theta = A(H, y_0, \alpha_2) C(\alpha_1, \alpha_2),$$

$$M_\psi = M_3 = A(H, y_0, \alpha_2)\alpha_2,$$

$$M_\varphi = M_z = A(H, y_0, \alpha_2)\alpha_1, \quad (35)$$

$$A = \left[\frac{2IH(1 - y_0)}{1 + (\lambda - 1)(1 - y_0)\alpha_2^2}\right]^{1/2},$$

$$B = \left[\frac{y_0}{mI(1 - y_0)}\right]^{1/2},$$

$$C = \left[1 - \frac{\alpha_1^2 + \alpha_2^2 - 2\alpha_1\alpha_2\cos\theta}{\sin^2\theta}\right]^{1/2},$$

where

$$\lambda \equiv I/I_3. \quad (36)$$

The corresponding Jacobian of the transformation has the form

$$|\partial(v_z, M_\theta, M_\psi, M_\varphi)/\partial(H, y_0, \alpha_1, \alpha_2)|$$

$$= \left[\frac{I^3(1 - y_0)}{my_0(1 - \alpha_1^2 - \alpha_2^2 + 2\alpha_1\alpha_2\cos\theta - \cos^2\theta)}\right]^{1/2}$$

$$\times \frac{H\sin\theta}{[1 + (\lambda - 1)(1 - y_0)\alpha_2^2]^2}. \quad (37)$$

Integrating over the angular variables θ, ψ, and φ we get the following expression for the fraction of molecules in the vicinity of the parameters H, y_0, α_1, and α_2, normalized to unity (for $0 \le H < \infty$, $0 \le y_0 \le 1$, $-1 \le \alpha_1 \le 1$, $0 \le \alpha_2 \le 1$):

$$dW(H, y_0, \alpha_1, \alpha_2) = f(H, y_0, \alpha_1, \alpha_2) dH dy_0 d\alpha_1 d\alpha_2, \quad (38)$$

$$f(H, y_0, \alpha_1, \alpha_2) = \frac{\lambda^{1/2}}{\pi T^2}\left(\frac{1 - y_0}{y_0}\right)^{1/2}$$

$$\times \frac{H\exp(-H/T)}{[1 + (\lambda - 1)(1 - y_0)\alpha_2^2]^2}. \quad (39)$$

We draw attention to the absence in the distribution function (39) of the symmetry between the variables α_1 and α_2 which occurred in Eqs. (24) to (30). This is connected with the fact that in the absence of an external field the total angular momentum vector can be oriented in any direction (the α_1 variable) whereas the precession angle (the α_2 variable) of the dipole moment vector relative to the total angular momentum vector is distributed according to the law

$$f(\alpha_2) = \int\limits_0^\infty dH \int\limits_0^1 dy_0 \int\limits_{-1}^1 d\alpha_1 f(H, y_0, \alpha_1, \alpha_2)$$

$$= \frac{\lambda^{1/2}}{[1 + (\lambda - 1)\alpha_2^2]^{3/2}} \tag{40}$$

and has the average value

$$\langle \cos \Theta_2 \rangle_T = \langle \alpha_2 \rangle_T = \frac{\lambda^{1/2} - 1}{\lambda - 1}, \tag{41}$$

which depends only on the ratio λ of the principal moments of inertia. We show in Figs. 7 and 8 the function $f(\alpha_2)$ for different $I_3/I = \lambda^{-1}$ and $\langle \cos \Theta_2 \rangle_T$ as function of λ^{-1}. The value $\lambda^{-1} = 0$ corresponds to a rotator ($\langle \alpha_2 \rangle_T = 0$), $\lambda = 1$ to a spherical top ($\langle \alpha_2 \rangle_T = 1/2$), and $\lambda^{-1} = 2$ to a plane molecule ($\langle \alpha_2 \rangle_T = 2 - \sqrt{2}$). The distribution function for a rotator, which has one rotational degree of freedom less, was obtained in Refs. 13 and 15 in the variables H, y_0, and α_1 and has the following form:

$$f(H, y_0, \alpha_1) = \frac{1}{2\pi^{1/2}T^{3/2}} \left(\frac{H}{y_0}\right)^{1/2} \exp\left(-\frac{H}{T}\right). \tag{42}$$

The analogous plane rotation distribution function for a model with one rotational degree of freedom ($\alpha_1 = \alpha_2 = 0$) is given by the expression

$$f(H, y_0) = \frac{1}{\pi T} \frac{\exp(-H/T)}{[y_0(1 - y_0)]^{1/2}}. \tag{43}$$

We now evaluate the average number of molecular collisions per unit time with a unit area positioned in the active zone of a strong field $\tilde{x} = p\tilde{E}/H$ and oriented at right angles to the field vector:
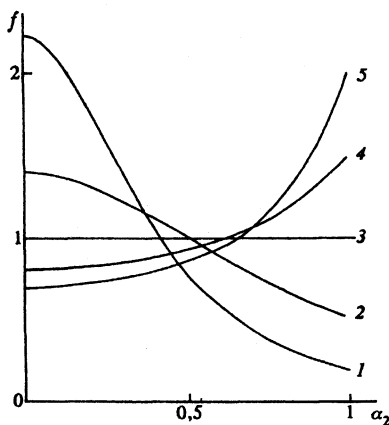
FIG. 7. Equilibrium distribution functions of the cosines of the precession angles of the dipole moment of a symmetric top for different ratios of the principal moments of inertia: $I_3/I = 0.2$ (1); 0.5 (2); 1.0 (3); 1.5 (4); 2.0 (5).
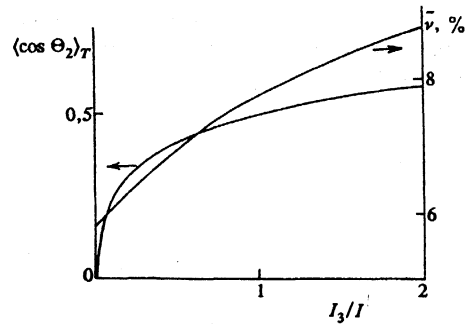
FIG. 8. The thermodynamic averages of the cosine of the precession angle and of the fraction $\tilde{v}$ of dipole molecules of a Maxwellian beam, ejected by the field, as functions of the ratio I_3/I of the principal moments of inertia.

$$v = \frac{1}{2} n \int\limits_0^\infty dH \int\limits_{-1}^1 d\alpha_1 \int\limits_0^1 d\alpha_2 \int\limits_{y_0(\tilde{x},\alpha_1,\alpha_2)}^1 dy_0 v_z f(H, y_0, \alpha_1, \alpha_2). \tag{44}$$

The factor 1/2 here takes into account the fact that only half of the molecules from the volume $nv_z dt\, dS$ can reach the area dS. The lower limit of the integration over y_0 follows from considering molecules which are ejected by the field. For instance, for the plane rotation case the function $y_0(\tilde{x})$ is represented by the solid curve in Fig. 3 and is the same as y_{0c} for $\tilde{x} > x_c = \varepsilon_c$. In the general case for $\tilde{x} > x_c(\alpha_1,\alpha_2)$ the function $y_0(\tilde{x},\alpha_1,\alpha_2)$ is the same as $y_{0c}(\alpha_1,\alpha_2)$, for which we found the asymptotic behavior (30) and the particular value (33). If the maximum values of the field $\tilde{E}$ are sufficiently large ($p\tilde{E} \gg T$) the function $y_0(\tilde{x},\alpha_1,\alpha_2)$ can be replaced by $y_{0c}(\alpha_1,\alpha_2)$ and we can integrate over H in (44) using the explicit expressions (39) for $f(H,y_0,\alpha_1,\alpha_2)$ and (35) for v_z:

$$v = v_0 \frac{\lambda^{1/2}}{2} \int\limits_{-1}^1 d\alpha_1 \int\limits_0^1 d\alpha_2 \left\{\frac{1 - y_{0c}(\alpha_1, \alpha_2)}{1 + (\lambda - 1)\alpha_2^2[1 - y_{0c}(\alpha_1, \alpha_2)]}\right\}^{3/2} \tag{45}$$

Here

$$v_0 = \frac{1}{2} n \left(\frac{2T}{\pi m}\right)^{1/2} \tag{46}$$

is the standard expression for the average number of collisions per unit time with unit area by gas molecules when there is no field (for $y_{0c}(\alpha_1,\alpha_2) = 0$ Eq. (45) gives $v = v_0$, as should be the case).

In the case of a rotator the function $y_{0c}(\alpha_1,0)$ is independent of α_2, one can easily integrate over α_2 in (45), and we find for the fraction of molecules which are ejected from the action zone of the field the result of Refs. 13 and 15:

$$\tilde{v} = 1 - \frac{v}{v_0} = \int\limits_0^1 d\alpha_1 y_{0c}(\alpha_1, 0). \tag{47}$$

The required fraction of dipole rotators from a Maxwellian beam is thus determined by the area under the graph of the function $y_{0c}(\alpha_1,0)$ in Fig. 5 and is approximately equal to 6.3%. Just as Eq. (47) can be obtained from the general expression (44) (without integration over the absent variable α_2) with a distribution function of the form (42), for the plane rotation case use of the corresponding distribution

function (43) gives

$$\tilde{v} = 1 - (1 - y_{0c})^{1/2} \approx 15{,}6\%. \tag{48}$$

Note that if we use for the rotator the linear approximation (30) (with $\alpha_2 = 0$) we have $\tilde{v} = \frac{1}{2} y_{0c}^2 / (1 - y_{0c}) \approx 5.8\%$, which is somewhat less than the exact value 6.3%. In the case of a symmetric top one can therefore also use the approximation (30) for a lower estimate of the integrals in (45) in the range of parameter values $|\alpha_1 + \alpha_2| < y_{0c} / (1 - y_{0c}) \approx 0.404$ and put $y_{0c} (\alpha_1, \alpha_2) = 0$ in the remaining region of α_1, α_2 values. The function $\tilde{v}$ of the ratio of the principal moments of inertia $I_3 / I = \lambda^{-1}$ obtained in this way is shown in Fig. 8. The values of $\tilde{v}$ change from 5.8% for rotators ($I_3 = 0$) to 8.8% for plane molecules ($I_3 = 2I$). Exact values of $\tilde{v}$ may be somewhat larger due to the nonvanishing values of $y_{0c} (\alpha_1, \alpha_2)$ extending to points α_1 or α_2 equal to $3^{-1/2} \approx 0.577$ (rather than 0.404, as in the linear approximation) and also because of the increase of the values of $y_{0c} (\alpha_1, \alpha_2)$ from $y_{0c} \approx 0.2879$ to 0.5 [see (33)] along the intersection $\alpha_1 = -\alpha_2$.

5. DISCUSSION

If the magnitude of an inhomogeneous electric field $E(z)$ changes little as the angle θ between the dipole moment and field vectors changes (adiabatic approximation), one can find a simple analytical description of the translational motion of a dipole molecule along the vector of this field in terms of the functional dependence of the translational kinetic energy, y, measured in units of the total energy of the molecule, on the magnitude of the field, x. The function $y(x)$ is characterized by two regions of monotonic behavior (see Figs. 3 and 6): the deceleration region in weak fields, $x < \varepsilon_c$, with large amplitudes of the change in the angle θ so that at the decisive times we have $\theta \sim 180°$, and an acceleration region in strong fields, $x > \varepsilon_c$, with small oscillations of the angle θ about the field vector. This last regime is realized only for sufficiently large initial values y_0 when the deceleration region does not reach the turning points $y = 0$, after which the direction of the motion is reversed and the molecule is ejected from the action zone of the strong field.

The diagram of initial translational kinetic energy y_0 vs maximum field value x therefore splits into two regions, characterized by falling into the force center and ejection from the active zone of the field. For a Maxwellian beam the fraction of ejected molecules is a quantity of the order of 10% and depends on the ratio of the principal moments of inertia. The strongest ejection is characteristic for the plane rotation of a rotator or for a symmetric top oriented with its dipole moment antiparallel to the field vector.

Specially prepared beams of fast rotating polar molecules are of interest from the point of view of applying the results obtained; by means of them one can study the scattering by regions with strong electric fields. Such regions are realized, e.g., near charged adsorption centers, or near the surfaces of ferroelectrics or oxides with orientationally ordered dipole radicals.[5-7]

It is well known that powders of $BaTiO_3$ (Ref. 18) and SiO_2 (Ref. 19) do not absorb gas molecules at temperatures corresponding to strong surface fields of $\sim 10^6 - 10^7$ V/cm ($T < T_c$, where T_c is the Curie temperature), whereas when there are no fields ($T > T_c$) the same molecules are adsorbed. A direct application of the results obtained in Sec. 4 to such systems cannot explain the complete absence of adsorption for $T < T_c$, since even in much stronger electric fields the fraction of ejected molecules from a Maxwellian beam is less than 10%. Nonetheless, one must take into account that a real molecular beam may differ from a Maxwellian one due to the multiple scattering by the grains of the powder with strong surface fields. Moreover, at distances from the field source (the surface) on the order of the molecular dimensions the adiabatic approximation used here must be replaced by the sudden perturbation approximation,[8,20] in which fast scattering or attraction occurs for a fixed orientation of the dipole moment. Since on the adiabatic portion of the motion with $x < x_c$ those average orientations of the dipole moments which correspond to a deceleration of the molecule in the field are depleted (see Figs. 2, 3, and 6), one must expect that when the molecule approaches the field source it undergoes fast scattering.

The considerations show that the results of the adiabatic approximation obtained in the present paper are useful also for interpreting actual experimental data.

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