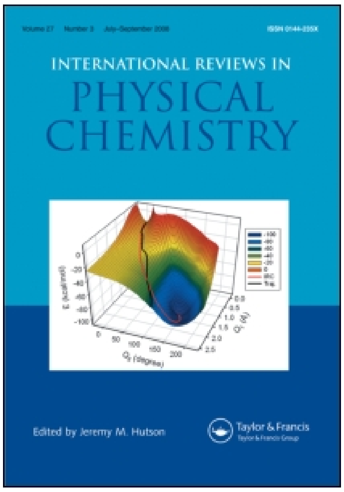

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Bretislav Friedrich[a]
[a] Department of Chemistry, Harvard University, Cambridge, MA, USA

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Electric dipole moments of pendular molecules

by BRETISLAV FRIEDRICH

Department of Chemistry, Harvard University, 12 Oxford Street,
Cambridge, MA 02138, USA

External electric fields can halt the rotation of polar molecules and produce pendular states in which the molecular dipole μ is confined to librate over a limited angular range about the space-fixed direction of the external field. The pendular eigenfunctions are hybrids of field-free rotor states, $|J, K, M\rangle$ with indefinite (for $K \neq 0$) or alternating (for $K = 0$) parities; this renders the parity of the hybrid wavefunctions indefinite for any values of the good quantum numbers K or M. As a result, the parity selection rule for the matrix elements of tensor operators in the pendular basis, notably the electric dipole moment, is lifted. We give the expectation values of the space-fixed dipole moment operator and of the orientation cosine of the figure axis and illustrate the lifting with field strength of the parity selection rule for prototype hybrid states of polar molecules. The symmetry properties of the pendular Hamiltonian are used to sort the eigenstates according to the sign of the product of K, M, and μ.

1. Introduction

Current work with spatially oriented molecular beams has prompted a new wave of studies of polar or paramagnetic molecules in strong external electric and magnetic fields. Despite previous analysis (Schlier 1955, von Meyenn 1970), it has been recognized (Loesch and Remscheid 1990, Friedrich and Herschbach 1991a) and demonstrated (Loesch and Remscheid 1990, Friedrich and Herschbach 1991b, Block *et al.* 1992, Rost *et al.* 1992) only recently that strong uniform electric fields can be used to hybridize *low* rotational states of polar molecules. The hybridization results in *pendular states* in which the molecular axis is confined to librate over a limited angular range about the field direction. The directional pendular states comprise coherent superpositions of rotational states $|J, K, M\rangle$ with a range of J values but fixed values of the good quantum numbers K and M. The directionality of the hybrids has enabled collision experiments probing steric effects (Loesch and Remscheid 1990, Friedrich *et al.* 1992, Loesch and Möller 1992, 1993). It has also found uses in spectroscopy to determine molecular parameters (Block *et al.* 1992, Friedrich *et al.* 1994, Slenczka *et al.* 1994), to provide intermediate states with widely tunable energies (Block *et al.* 1992, Slenczka *et al.* 1994). and to make accessible transitions that otherwise would be forbidden by the field-free selection rules (Block *et al.* 1992, Friedrich *et al.* 1994, Slenczka *et al.* 1994).

When $K = 0$, the molecule tumbles end-over-end (unless $J = 0$); states with the same value of $|M|$ remain degenerate and the energy shifts depend quadratically on the field strength at low fields (second-order Stark effect (Kronig 1926)). The tumbling tends to make the *space-fixed dipole moment* small. This led to a long-held but mistaken notion that for $K = 0$ it was not feasible to orient polar molecules (Ramsey 1956, Brooks 1976, Bernstein *et al.* 1987). When $K \neq 0$, the molecule *precesses* rather than tumbles. The energy shifts depend on the sign of M and are linear in both M and the field strength at low-fields (first-order Stark effect, e.g. Townes and Schawlow (1975)). For

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precessing molecules the dipole moment does not average out, so the molecular axis is intrinsically oriented. Thus for the lowest few rotational states with $K \neq 0$, molecular beams containing essentially a single oriented precessing state $|J, K, M\rangle$ can be obtained by use of inhomogeneous focusing fields (Kramer and Bernstein 1964, Stolte 1991).

For sufficiently high-fields, however, *both* $K = 0$ and $K \neq 0$ states become hybridized and descend to energies below their field-free levels, thus becoming pendular with angular amplitudes smaller than ± 180°. The existence of pendular states is made possible by non-zero space-fixed electric dipole moments and vice versa. However, the expectation values of tensor operators, such as the electric dipole moment, are subject to restrictions imposed by the *parity selection rule* (e.g., Bunker (1973), Landau and Lifshitz (1977)) summarized in Appendix A. Since the electric dipole moment operator is a true tensor of rank $k = 1$, equation (A 5 *b*) applies which means that there can be no space-fixed electric dipole moment in states of *definite* parity (e.g. Davydov (1965)). Does this mean that a molecule in a pure $|J, K, M\rangle$ state cannot have a static dipole moment? And are there any *other states* in which the expectation value of the space-fixed dipole moment is non-zero? In order to answer these questions (and save the phenomenon) we examine the inversion properties of polar linear as well as symmetric top molecules in *external electric fields*: We find that the parity of the hybrid eigenfunctions is indefinite so that the parity selection rule no longer applies. In such a case $\langle\mu_Q\rangle$ *can* be non-zero and the molecular axis oriented. We discuss the properties of pendular states relevant to their parity and illustrate, using exact calculations, the lifting with field strength of the parity selection rule for prototype hybrid states.

In this article, we first define electric dipole moments of pure $|J, K, M\rangle$ states and give a brief introduction to pendular states and to the problem of parity. Then we examine the inversion properties of pendular states and give their space-fixed dipole moments. Detailed exact calculations illustrate the mechanism of the relaxation of the parity selection rule with field strength. These calculations may also serve as a prototype for other situations governed by coherent superpositions of J-states in which similar calculations are not feasible. The paper also introduces a sorting scheme of pendular states relevant to both their focusing and spectroscopic properties. It identifies an octuplet of states arising for given non-zero $|K|$, $|M|$, and $|\mu|$ and gives a survey of their interrelations.

2. Electric dipole moments of pure states $|J,K,M\rangle$

The notion of a space-fixed electric dipole moment of a molecule is usually associated with the expectation value $\langle\mu_Q\rangle$ of the space-fixed component μ_Q of the dipole moment operator in the symmetric top basis, $|J, K, M\rangle$ (Klemperer *et al.* 1992, Kroto 1992)

$$\begin{aligned}\langle\mu_Q\rangle &= \langle J, K, M|\mu_Q|J, K, M\rangle \\ &= (2J+1)\sum_q \langle\mu_q\rangle\begin{pmatrix} J & 1 & J \\ -M & Q & M\end{pmatrix}\begin{pmatrix} J & 1 & J \\ -K & q & K\end{pmatrix} \\ &= \sum_q \langle\mu_q\rangle\frac{KM}{J(J+1)}.\end{aligned} \tag{1}$$

The $|J, K, M\rangle$ eigenstates correspond to motions in which the total angular momentum **J** has projection K on the figure axis, z, of the molecule and projection M on the space-fixed Z-axis; μ_q, $q = 0$, ± 1 are the spherical components of the dipole moment operator in the body-fixed frame *xyz* with expectation values $\langle \mu_q \rangle$, as endowed by the asymmetric charge distribution in a polar molecule (e.g., Zare (1988)). The body-fixed components μ_q are related to the spherical components μ_Q, $Q = 0, \pm 1$, in the space-fixed frame *XYZ* by the rotation

$$\mu_Q = \sum_{q=-1}^{+1} \mathbf{D}^{1*}_{Q,q}(\varphi, \theta, \chi)\mu_q, \tag{2}$$

where the Wigner matrices, $\mathbf{D}^1_{Q,q}$, are parametrized by the Euler angles φ, θ, χ (e.g., Zare (1988)). From the properties of the 3-*J* symbols we see that $\langle \mu_Q \rangle$ is non-zero only if $J > 0$ and $Q = q = 0$. The latter condition implies that the non-zero body-fixed component of the dipole moment operator is along the *z*-axis (figure axis) of the molecule and the non-zero space-fixed component of the dipole moment is along the quantization axis, *Z*; hence

$$\langle \mu_{Q=0} \rangle = \langle \mu_{q=0} \rangle \frac{KM}{J(J+1)}. \tag{3}$$

In the case when $K = 0$ (pertaining also to a $^1\Sigma$ linear molecule), or $M = 0$, the 3-*J* symbols of (1) vanish and, as a result, there is no static (i.e. space-fixed) permanent dipole moment.

A non-zero static dipole moment implies that the body-fixed dipole moment (and thus the figure axis of the molecule) is oriented. This is a corollary of (2) and (3): for $Q = q = 0$, we have $\mu_Q = \mu_q \cos\theta$ so that the expectation value of the orientation cosine, $\langle \cos\theta \rangle$, becomes

$$\langle \cos\theta \rangle = \frac{KM}{J(J+1)}. \tag{4}$$

Accordingly, a polar ($\langle \mu_q \rangle \neq 0$ for $q = 0$) symmetric top molecule in a pure state $|J, K, M\rangle$ can have a non-zero expectation value of the static dipole moment (or the orientation cosine) only if $J > 0$ and both M and $K \neq 0$.

3. Pendular Hamiltonian and its eigenproperties

The Hamiltonian of the polar symmetric top molecule in a homogeneous electric field ε_Q directed along the space-fixed *Z*-axis ($Q = 0$) can be written as

$$H = [\mathbf{J}^2 + (A/B - 1)J_z^2] - \omega\cos\theta, \tag{5}$$

with B the rotational constant about either the *x*- or *y*-axis and A the rotational constant about the figure axis *z* (we chose the case of a prolate top, $A > B = C$, without limiting the generality of the argument); the parameter $\omega \equiv \mu\varepsilon/B$ with $\mu \equiv \langle \mu_{q=0} \rangle$ and $\varepsilon \equiv \varepsilon_{Q=0}$ measures energies in units of the rotational constant B.

For given non-zero M, K, and ω, the Hamiltonian of (5) is determined by the 2^3 combinations of the signs of M, K, and ω, see Appendix B. Figure 1 illustrates the sign combinations for a symmetric top molecule with distinguishable orientation of the figure axis, *z*, and of the electric dipole moment, designated here by ω. The positive direction of *z* is defined as the one from the black end to the white end, the positive direction of ω as the one from the negative to the positive pole. The space-fixed axis *Z* (as defined by the direction of the electric field ε) is kept constant for all combinations. For given non-zero values of $|M|$, $|K|$, and $|\omega|$, there are two different symmetries, each specified by the sign of the product ωMK. These comprise two quadruplets with equal energies; for one quadruplet the product ωMK is positive, for the other negative.

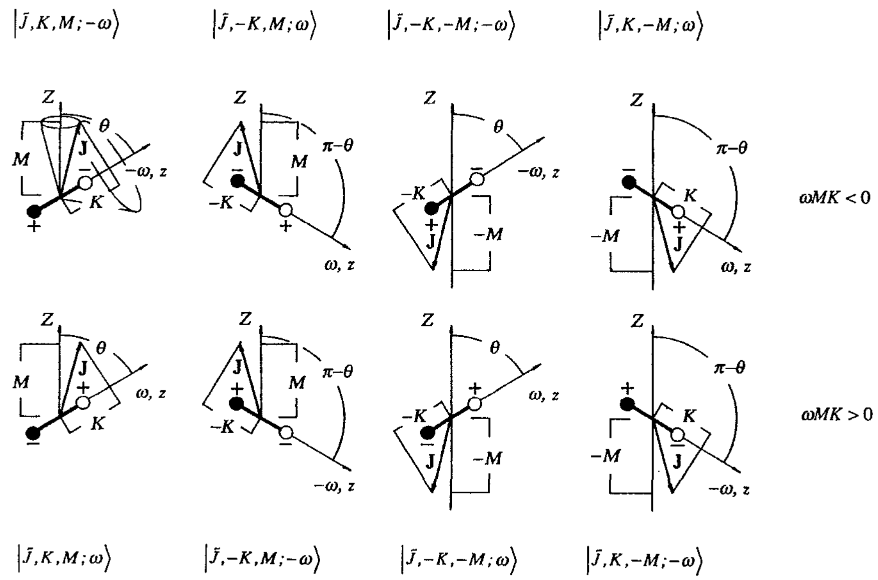

Figure 1. Vector model of angular momentum eigenstates due to the pendular Hamiltonian at fixed values of $\tilde{J}$, $|M|$, $|K|$, and $|\omega|$. There are 2^3 sign combinations of M, K, and ω for a symmetric top molecule with distinguishable orientation of the figure axis, z, and of the electric dipole moment, designated here by ω. The positive direction of z is defined as the one from the black end to the white end, the positive direction of ω as the one from the negative to the positive pole. The space-fixed axis Z (as defined by the direction of the electric field ε) is kept constant for all combinations. The inversion operation is effected by replacing θ by $\pi - \theta$, and K by $-K$. There are two different symmetries, each specified by the sign of the product ωMK. These comprise two quadruplets with equal energies; for one quadruplet the product ωMK is positive, for the other negative. The eigenenergies for $\omega MK > 0$ are lower than those for $\omega MK < 0$ at all field strengths. Within each isoenergetic quadruplet there are two pairs of states that differ in the sign of ω and hence the sense of figure axis orientation. See also text and Appendix B.

According to (3) applicable at low $|\omega|$ in the realm of the first-order Stark effect, we see that $\langle\mu_Q\rangle > 0$ for $\omega > 0$ and $MK > 0$ (i.e. for $\omega MK > 0$ the Stark energy is negative) whereas $\langle\mu_Q\rangle < 0$ for $\omega > 0$ and $MK < 0$ (i.e. for $\omega MK < 0$ the Stark energy is positive). Since the sign of ωMK remains the same at all field strengths, we conclude that the quadruplet with $\omega MK < 0$ has always higher eigenenergies than the $\omega MK > 0$ quadruplet:

$$E(\omega MK > 0) \leqslant E(\omega MK < 0). \tag{6}$$

Within each isoenergetic quadruplet there are two pairs of states that differ in the sign of ω and hence the sense of figure axis orientation. If either M or K is zero there is just one isoenergetic quadruplet of states consisting of two pairs of states differing on the sign of ω; for $M = K = 0$ there are just two states differing in the signs of ω. This scheme is referred to as the 'ωMK rule' (Friedrich *et al.* 1993). In a given electronic state the sign of the body-fixed electric dipole moment is fixed, i.e. either $\omega > 0$ or $\omega < 0$. This reduces the number of states within a given multiplet by half. The inversion of spatial coordinates is effected by replacing θ by $\pi - \theta$, K by $-K$; hence the multiplets are converted to one another by the inversion operation, see Appendix B.

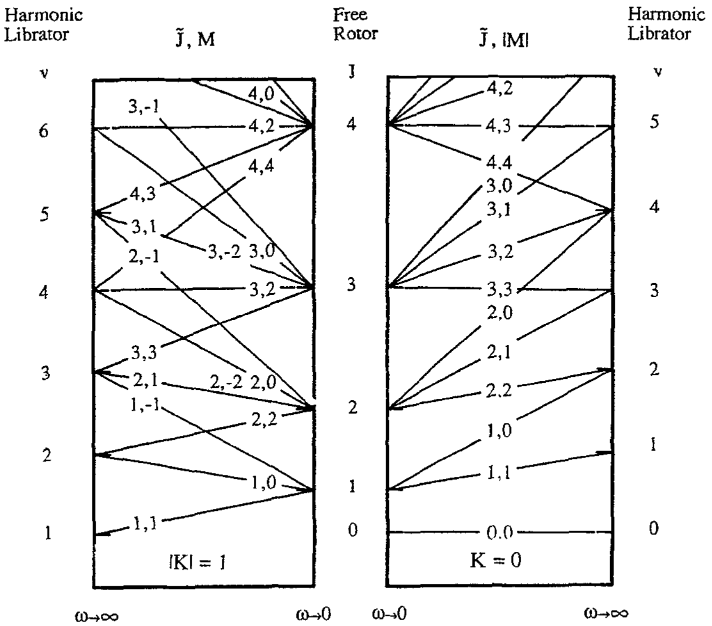

Figure 2. Correlation diagram between field-free rotor states, $\omega \rightarrow 0$, and harmonic librator states, $\omega \rightarrow \infty$, for $K = 0$ (right panel) and $|K| = 1$ (left panel).

The field free states, $|J, K, M\rangle$, provide a basis for the series expansion of the eigenfunctions of Hamiltonian (5)

$$|\tilde{J}, K, M; \omega\rangle = \sum_{J=\max(|K|,|M|)}^{\infty} a^{J}_{K,M}(\omega)|J, K, M\rangle \tag{7}$$

with coefficients a^{J}_{MK} (depending solely on the interaction parameter ω) that can be determined by standard methods with arbitrary accuracy (Schlier 1955, von Meyenn 1970, Rost *et al.* 1992). For any fixed values of the good quantum numbers K and M, the range of J involved in the coherent superposition or hybrid wavefunction, (7), increases with the $|\omega|$-parameter.

The eigenstates are labelled by K and M and the nominal value of $\tilde{J}$ of the angular momentum for the field-free rotor state that adiabatically correlates with the high-field hybrid function. In the field-free limit the (prolate) eigenenergies are $E_{JK}/B = J(J+1) + (A/B - 1)K^2$. In the high-field limit, pendular states become harmonic, corresponding to an angular oscillator with eigenenergies $E_\nu/B = -\omega + \nu(2\omega)^{1/2} + (A/B - 1)K^2$, where $\nu \equiv 2\tilde{J} - |M + K|$. Figure 2 summarizes these features in terms of correlation diagrams between the field-free rotor states ($\omega \rightarrow 0$) and the harmonic angular oscillator (librator) states ($\omega \rightarrow \infty$) for $|K| = 0$ and 1. Note that the correlation diagrams for different $|K| > 0$ have a similar structure except that levels with $J \leqslant |K|$ are missing.

4. Parity of pendular eigenstates

At vanishing interaction of the molecular dipole with the external field, $\omega \rightarrow 0$, the wavefunctions become those of a symmetric top:

$$|\tilde{J}, M, K; \omega \rightarrow 0\rangle \rightarrow |J, M, K\rangle \tag{8}$$

The parity operation applied to $|J, K, M\rangle$ leads to

$$P|J,K,M\rangle = (-1)^{J-K}|J,-K,M\rangle \neq p|J,K,M\rangle, \tag{9}$$

indicating that the state $|J,K,M\rangle$ is of *indefinite parity* if $J > 0$ and $K \neq 0$. Consequently, the static dipole moment is not necessarily zero (see similar argument based on the notion of double parity of Oka (1973), and an alternative argument based on the notion of degeneracy in, e.g., Mandl (1975)):

$$\begin{aligned}\langle J,K,M|\mu_Q|J,K,M\rangle &= \langle\mu_q\rangle\frac{KM}{J(J+1)}\\ &= (-1)^k\langle J,K,M|P^{\dagger}\mu_Q P|J,K,M\rangle\\ &= -(-1)^{2J-2K}\langle J,-K,M|\mu_Q|J,-K,M\rangle\\ &= \langle\mu_q\rangle\frac{KM}{J(J+1)}.\end{aligned} \tag{10}$$

However, field-free states with $J = 0$ or $J > 0$ and $K = 0$ do have definite parity, e.g.

$$P|J,0,M\rangle = (-1)^J|J,0,M\rangle = p|J,0,M\rangle, \tag{11}$$

and therefore in these states the polar molecules cannot have non-zero static electric dipole moments or exhibit figure axis orientation.

In the presence of an electric field the potential, $-\omega\cos\theta$, hybridizes the field-free rotor states (for any value of $\tilde{J}$, K or M), giving rise to *pendular states* with wavefunctions given by (7). The pendular Hamiltonian (5) is *not* invariant under inversion of spatial coordinates (for a fixed direction of the external field), and its wavefunctions are of *indefinite parity*, being comprised either of states with indefinite parity (for $K \neq 0$) or with alternating parities (for $K = 0$),

$$\begin{aligned}P|\tilde{J},K,M;\omega\rangle &= P\sum_J a^J_{MK}(\omega)|J,K,M\rangle = \sum_J a^J_{MK}(\omega)P|J,K,M\rangle\\ &= \sum_J a^J_{MK}(\omega)(-1)^{J-K}|J,-K,M\rangle\\ &= \sum_J a^J_{M,-K}(\omega)|J,-K,M\rangle \equiv |\tilde{J},-K,M;\omega\rangle\\ &\neq p|\tilde{J},K,M;\omega\rangle.\end{aligned} \tag{12}$$

5. Electric dipole moments of pendular states $|\tilde{J},K,M;\omega\rangle$

In consequence of (12), polar molecules in pendular states can have non-zero static dipole moments, without restrictions imposed by the parity selection rule. Moreover, the expectation value $\langle\mu_Q\rangle$ of the space-fixed component μ_Q of the dipole moment operator in a pendular state, $|\tilde{J},K,M;\omega\rangle$, is given by

$$\begin{aligned}\langle\mu_Q\rangle &= \langle\tilde{J},K,M;\omega|\mu_Q|\tilde{J},K,M;\omega\rangle\\ &= \sum_{J,J'=0}^{\infty}\sum_{q=-1}^{+1} a^J_{M,K}a^{J'}_{M,K}(2J+1)^{1/2}(2J'+1)^{1/2}\langle\mu_q\rangle\\ &\quad\times\begin{pmatrix} J & 1 & J'\\ -M & Q & M\end{pmatrix}\begin{pmatrix} J & 1 & J'\\ -K & q & K\end{pmatrix}\end{aligned} \tag{13}$$

indicating that this can be non-zero even if $\tilde{J}, M, K$ are *all* zero. For $Q = q = 0$, $\mu_Q = \mu_q \cos\theta$ we have

$$\langle \cos\theta \rangle = \sum_{J,J'=0}^{\infty} a^J_{M,K} a^{J'}_{M,K} (2J+1)^{1/2} (2J'+1)^{1/2} \begin{pmatrix} J & 1 & J' \\ -M & 0 & M \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -K & 0 & K \end{pmatrix} \tag{14}$$

which means that the figure axis of molecules in pendular states is *always oriented.*

Lifting of the restriction of type (A 5 *b*) on the matrix elements of the dipole moment, (12), can be demonstrated by evaluating explicitly the matrix element of the inverted dipole moment; this yields

$$\begin{aligned} &\langle \tilde{J}, K, M; \omega | P^{\dagger} \mu_Q P | \tilde{J}, K, M; \omega \rangle \\ &\quad = \sum_{J,J'=0}^{\infty} \sum_{q=-1}^{+1} (-1)^{J-J'-2K} a^J_{M,-K}(\omega) a^{J'}_{M,-K}(\omega) \\ &\qquad \times (2J+1)^{1/2} (2J'+1)^{1/2} \langle \mu_q \rangle \begin{pmatrix} J & 1 & J' \\ -M & Q & M \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ K & q & -K \end{pmatrix} \\ &\quad = -\sum_{J,J'=0}^{\infty} \sum_{q=-1}^{+1} a^J_{M,K}(\omega) a^{J'}_{M,K}(\omega) \\ &\qquad \times (2J+1)^{1/2} (2J'+1)^{1/2} \langle \mu_q \rangle \begin{pmatrix} J & 1 & J' \\ -M & Q & M \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ -K & q & K \end{pmatrix} \end{aligned} \tag{15}$$

in agreement with

$$\langle \tilde{J}, K, M; \omega | \mu_Q | \tilde{J}, K, M; \omega \rangle = (-1)^k \langle \tilde{J}, K, M; \omega | P^{\dagger} \mu_Q P | \tilde{J}, K, M; \omega \rangle, \tag{16}$$

for $k = 1$.

6. Discussion

Figure 3 illustrates the dependence on $|\omega|$ of energy levels, for all states with the nominal $\tilde{J} = 1$. These involve $(2\tilde{J}+1)^2 = 9$ states, only $3\tilde{J} + 2 = 5$ of which are non-degenerate. For the $K = 0$ case, states with the same value of $|M|$ are degenerate and the Stark shifts are quadratic in $|\omega|$ at low-field. For the $|K| = 1$ case, the shifts depend on the sign of M and are linear in both M and $|M|$ at low-field. For sufficiently high-fields *all* states descend to energies far below their field-free levels, thus becoming pendular. The angular amplitudes become smaller than $\pm 180°$ when $E_{\tilde{J}KM}(|\omega|)/B < |\omega|$ and decrease to less than $\pm 90°$ when $E_{\tilde{J}KM}/B < 0$. The eigenenergies of pendular states vary linearly with $|\omega|$ but the expectation values of their static dipole moments (and orientation cosines) are *positive* for $\omega > 0$ and *negative* for $\omega < 0$. This is illustrated in figure 4 that shows the dependence of $|\omega|$ of the expectation values of the orientation cosine for same states as in figure 3. These are conveniently evaluated from field-dependence of the energy levels by (e.g., Friedrich and Herschbach (1991a))

$$\langle \cos\theta \rangle = -\frac{\partial (E_{\tilde{J}KM}/B)}{\partial \omega}, \tag{17}$$

according to Hellmann–Feynman theorem. This relation also facilitates identifying the permutations of signs among M, K, and ω that pertain to equivalent or distinct orientations, see figure 1. For any given non-zero values of $|M|$, $|K|$ and $|\omega|$, reversing the sign of the dipole ($\omega \longrightarrow -\omega$) switches the system to a different level and always reverses the sign of $\langle \cos\theta \rangle$, see also Appendix B.

The hybridization of rotor states represents the quantum mechanism of creating the

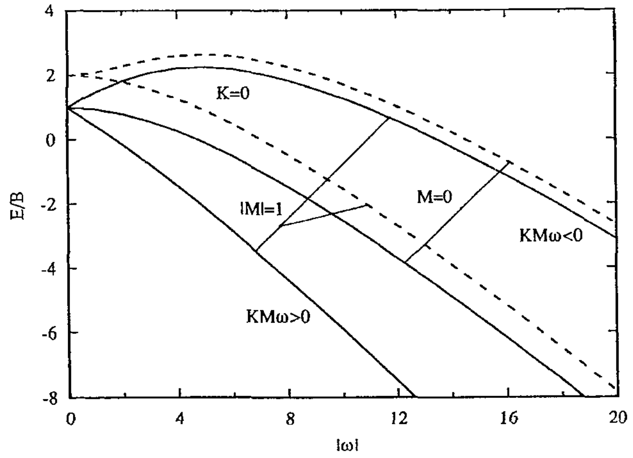

Figure 3. Energy levels of a rigid polar symmetic top in a uniform electric field, as functions of the Stark interaction parameter, $|\omega|$. Levels shown pertain to nominal $\tilde{J} = 1$ and to either $K = 0$ (dashed curves) or $K = \pm 1$ (full curves). States designated with M and K; the two states with $\tilde{J}$, M, K all non-zero are designated in accord with the ωMK rule, see text.

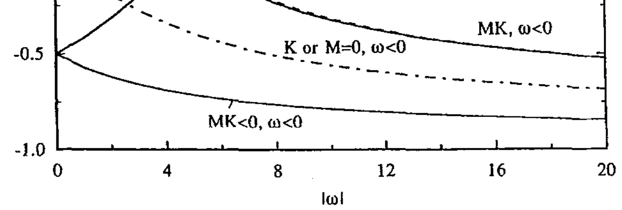

Figure 4. Expectation values of the orientation cosine as functions of the interaction parameter $|\omega|$, corresponding to states of figure 3. States designated with M, K, and ω. Dashed lines show the case when $K = 0$ and the solid lines when $K = \pm 1$; each of the dashed–dotted lines corresponds to two coincident values due to states with either M or $K = 0$; see also previous figure.

pendular states. Figure 5 illustrates for the case of the $\tilde{J} = 1$, $M = 0$, $K = 0$ state how the composition of the hybrid eigenfunction changes with the interaction parameter ω. The expansion coefficients $a^J_{MK}(\omega)$ of (7) are normalized such that the square of each gives the fractional contribution of the corresponding field-free wavefunction to the pendular hybrid. At $\omega = 0$, there is just one contributing free-rotor state, the parent state with $J = 1, M = 0, K = 0$. As the field strength increases, the parent component declines, reaches zero and then rises again, as $a^J_{00}(\omega)$ changes sign. However, the contributions from other components increase steadily with ω: first the isotropic one with $J = 0$, followed by the four-lobed $J = 2$ and by wavefunctions with higher J. At about $\omega = 5$ the contributions from $J = 0$, 1, and 2 become comparable, giving rise to a directional wavefunction with positive expectation value of the orientation cosine. This feature remains unaltered up to the harmonic librator limit at $\omega \rightarrow \infty$.

In order to show the 'devaluation' of the nominal inversion factor, $(-1)^{\tilde{J}-K}$, as a function of ω, we define a quantity

$$\Pi^{\tilde{J}}_{KM}(\omega) = \sum_{J=0}^{\infty} (-1)^{J-K} |a^J_{MK}(\omega)|^2, \tag{18}$$

which weighs the inversion factors, $(-1)^{J-K}$, of the $|J, K, M\rangle$ wave functions in a given pendular hybrid by their fractional contributions, $|a^J_{MK}(\omega)|^2$; note that $\Pi^{\tilde{J}}_{KM}(\omega \rightarrow 0) \rightarrow (-1)^{\tilde{J}-K}$. Hence $\Pi^{\tilde{J}}_{KM}(\omega)$ can be used to characterize the deviations from the nominal inversion factors at arbitrary ω and K. Figure 6 shows the dependence of $\Pi^{\tilde{J}}_{KM}(\omega)$ on ω for the $\tilde{J} = 1, M = 0, K = 0$ and $\tilde{J} = 1, M = 1, K = 1$ states: $\Pi^1_{1,1}$ deviates only slowly from the $\Pi^1_{1,1}(\omega = 0) = +1$ value; this is largely because the 1, 1, 1 hybrid is dominated, at low ω, by the parent wavefunction. The behaviour of the 1, 0, 0 hybrid is quite different: the wavefunction loses its parity eigenvalue of -1 very quickly as ω increases and, at higher ω, $\Pi^1_{0,0}$ even changes sign; this is due to the contributions from states with even J that dominate the hybrid there. In the high-field limit, however, both types of the pendular wavefunctions become strongly hybridized so that the positive and negative contributions to $\Pi^{\tilde{J}}_{KM}$ balance out, resulting in $\Pi^{\tilde{J}}_{KM}(\omega \rightarrow \infty) \rightarrow 0$ at the harmonic librator limit.

Although the second (and higher)-order Stark effect can create a linear superposition of the zero-order (rotational) wavefunctions (Hughes 1947), the resulting space-fixed dipole moments for $J > 0$ were considered to be impractically small. This led to a long-held belief that polar molecules with $K = 0$ cannot be oriented (e.g., Ramsey (1956), Brooks (1976), Levine and Bernstein (1987)).

Within the hybridizing field, the hybrid nature of the pendular states would not be altered by coupling of **J**, the angular momentum of the pendulum, with other angular momentum vectors. The pendular states comprise coherent superpositions of basis states with indefinite or with alternating parities, thus rendering the parity of the pendular wavefunctions indefinite. This puts the parity selection rule out of order. However, a coupling of the field-free $|J, K, M\rangle$ states to other states can result in a definite parity of the ensuing total wavefunctions, such as in the case of the Wang functions; then the parity selection rule would come into effect and the field-free symmetric top states coupled to other modes of motion would lose their static dipole moments (Klemperer *et al.* 1992).

Although field-free states $|J, K, M\rangle$ of molecules may exhibit orientation of the figure axis, (4), equilibrium ensembles of such molecules are isotropic. A perturbation of the equilibrium population can lead to a preference of some of the pure $|J, K, M\rangle$ states and thereby give rise to a net anisotropy of the ensemble, as shown by the work of Toennies

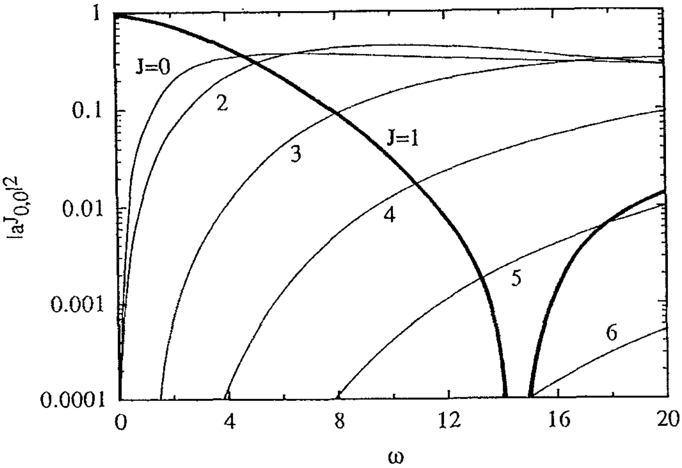

Figure 5. Change of the composition of the hybrid eigenfunction, $|\tilde{J}, K, M; \omega\rangle = \Sigma_J a^J_{K,M}(\omega)|J, K, M\rangle$, for $\tilde{J} = 1$, $M = 0$, $K = 0$ as a function of the interaction parameter ω. The expansion coefficients, $a^J_{K,M}$, are normalized such that the square of each gives the fractional contribution of the field-free wavefunction to the pendular hybrid. The thick line shows the parent state contribution ($J = 1$), the thin lines show contributions from other J-states.

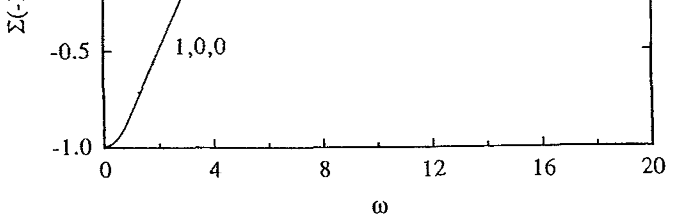

Figure 6. Deviation from the nominal inversion factors, $(-1)^{\tilde{J}-K}$, for the $\tilde{J} = 1$, $M = 1$, $K = 1$ and $\tilde{J} = 1$, $M = 0$, $K = 0$ states as a function of ω; this is expressed in terms of the quantity $\Pi^{\tilde{J}}_{KM}(\omega) = \Sigma_J(-1)^{J-K}|a^J_{MK}(\omega)|^2$ which weighs the inversion factor of each free-rotor state in a given hybrid by its fractional contribution.

(1962), Beuhler *et al.* (1966), Brooks (1966), Estler and Zare (1978), Treffers and Korving (1978), Stolte (1982), Mattheus *et al.* (1986), de Vries *et al.* (1987), McCaffery *et al.* (1988). However, since any field-free state can become a parent state of a pendular state, pendular orientation is not limited to systems out of equilibrium. Consequently, the pendular mode of motion can be described by the apparatus of equilibrium quantum statistical mechanics. Moreover, the partition function can be approximated analytically with high accuracy (Friedrich and Herschbach 1993); this enables calculating thermodynamic functions and ensemble averages in closed form at almost arbitrary field strengths and temperature. In particular, the treatment yields an expression for the polarization, $\langle\langle\cos\theta\rangle\rangle$, of an ensemble of weakly-interacting $^1\Sigma$ dipole molecules,

$$\langle\langle\cos\theta\rangle\rangle = \left(\coth\alpha - \frac{1}{\alpha}\right)\left(\frac{\alpha - (u/2)\coth(u/2)}{\alpha - 1}\right), \tag{19}$$

with $\alpha \equiv \omega/\Upsilon$ and $u \equiv (2\omega)^{1/2}/\Upsilon$; $\Upsilon \equiv kT/B$ is the reduced temperature. The Langevin–Debye formula (Langevin 1905, Debye 1929, Van Vleck 1932), represented by the first term of (19), fails at high field strengths and low temperatures, i.e. in the pendular orientation domain. In the classic treatment based on the second-order Stark effect, all contributions except those from the $J = 0$, $M = 0$ states cancel out (Van Vleck 1932). In contrast, formula (19) comprises non-zero contributions from all states in the ensemble.

7. Conclusions

The pendular potential, proportional to the cosine of the angle between the body-fixed dipole moment and the direction of an external electric field, hybridizes free rotor states of polar symmetric top molecules. The hybrid nature of the ensuing pendular states allows these molecules to possess non-zero space-fixed dipole moments. The underlying indefinite parity of pendular eigenfunctions is the key to figure-axis orientation of individual dipole molecules as well as to polarization of equilibrium ensembles. The non-diagonal elements of the space-fixed dipole moment matrix in the pendular basis are also generally non-zero, thus making possible dipole transitions otherwise forbidden by the parity selection rule. For a given value of body-fixed dipole moment and given non-zero values of the good quantum number $|K|$ and $|M|$, pendular states occur in pairs of isoenergetic doublets related to one another by spatial inversion

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Appendix A. Summary of the parity selection rule

The parity operator, P, reverses (inverts) the sign of the coordinates:

$$Pf(X, Y, Z) = f(-X, -Y, -Z); \tag{A 1}$$

(which is equivalent to transforming a left-handed coordinate system into a right-handed one or vice versa). It is a unitary operator, $P^\dagger = P^{-1}$, with the characteristic equation

$$Pf(X, Y, Z) = pf(X, Y, Z) \tag{A 2}$$

and eigenvalues $p = \pm 1$. Parity is said to be *positive* for $p = +1$ (and designated $+$) and *negative* for $p = -1$ (and designated $-$).

Parity is expressive of the left–right symmetry of space and is to be distinguished from inversion in the body-fixed frame, an operation that only exists for systems with a centre of symmetry such as homonuclear diatomics.

An operator A that transforms under rotation like a spherical tensor operator of rank k and under inversion according to

$$PAP^{\dagger} = (-1)^k A \tag{A 3}$$

is referred to as a *true* (*polar*) *tensor operator*; the operator has *positive* or *negative* parity for k even or odd. A spherical tensor operator A that transforms under inversion as

$$PAP^{\dagger} = -(-1)^k A \tag{A 4}$$

is referred to as a pseudo-tensor (*axial tensor*); it has *positive* or *negative* parity for k odd or even. For $k = 0$ the operator can be either a *true scalar* (with positive parity) or a *pseudoscalar* (with negative parity).

For the matrix elements of a *true tensor* operator, A, of rank k connecting states $|\psi_+\rangle$ or $|\psi_-\rangle$ of *definite parity* we have

$$\langle \psi_{-,+}|A|\psi_{+,-}\rangle = 0, \quad \text{for } k \text{ even}, \tag{A 5a}$$

$$\langle \psi_{-,+}|A|\psi_{-,+}\rangle = 0, \quad \text{for } k \text{ odd}. \tag{A 5b}$$

For the matrix elements of a *pseudo-tensor* operator, A, of rank k connecting states $|\psi_+\rangle$ or $|\psi_-\rangle$ of *definite parity* we have

$$\langle \psi_{-,+}|A|\psi_{-,+}\rangle = 0, \quad \text{for } k \text{ even}, \tag{A 6a}$$

$$\langle \psi_{-,+}|A|\psi_{+,-}\rangle = 0, \quad \text{for } k \text{ odd}. \tag{A 6b}$$

This can be proved from the definitions (A 3) and (A 4) and the unitarity property of P. For instance $\langle \psi_-|A|\psi_+\rangle = 0$ in (A 5a) obtains as follows: $\langle \psi_-|A|\psi_+\rangle = (-1)^k \langle \psi_-|P^{\dagger}AP|\psi_+\rangle = (-1)^k \langle \psi_- P^{\dagger}|A|P\psi_+\rangle = (-1)^k p_- p_+ \langle \psi_-|A|\psi_+\rangle = -\langle \psi_-|A|\psi_+\rangle$ for k even, which can only be fulfilled if $\langle \psi_-|A|\psi_+\rangle = 0$ (QED).

Appendix B. Properties of the pendular Hamiltonian

For given values of K, M, and ω the Hamiltonian, (5), can be recast into a form that depends solely on the polar angle θ (e.g., Friedrich *et al.* (1993))

$$H = H_{MK;\omega}(\theta) = H_{MK}(\theta) - \omega\cos\theta, \tag{B 1}$$

where

$$H_{MK}(\theta) = -\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\right)\frac{\partial}{\partial\theta} + \frac{(M - K\cos\theta)^2}{\sin^2\theta} - \left(\frac{A}{B} - 1\right)K^2 \tag{B 2}$$

is the field-free Hamiltonian for a symmetric top at fixed values of M, K. It is easily seen that

$$H_{M,K}(\theta) = H_{-M,-K}(\theta) = H_{M,-K}(\pi - \theta) = H_{-M,K}(\pi - \theta), \tag{B 3}$$

and

$$-\omega\cos\theta = -(-\omega)\cos(\pi - \theta), \tag{B 4}$$

so that the Hamiltonians with $\omega MK > 0$,

$$H_{H,K;\omega}(\theta) = H_{-M,-K;\omega}(\theta) = H_{M,-K;-\omega}(\pi-\theta) = H_{-M,K;-\omega}(\pi-\theta), \tag{B 5}$$

and their eigenvalues form an isoenergetic quadruplet:

$$E_{>} \equiv E_{\omega MK} = E_{\omega-M-K} = E_{-\omega-MK} = E_{-\omega M-K}. \tag{B 6}$$

By applying the inversion operation to the Hamiltonian (B 1), i.e. by replacing K by $-K$ and θ by $\pi-\theta$, we obtain

$$PH_{M,K;\omega}(\theta) = H_{M,K}(\theta) + \omega\cos\theta \equiv H_{M,K;-\omega}(\theta) \tag{B 7}$$

a new Hamiltonian. Using (B 3) and (B 4) we see that

$$H_{M,K;-\omega}(\theta) = H_{-M,-K;-\omega}(\theta) = H_{M,-K;\omega}(\pi-\theta) = H_{-M,K;\omega}(\pi-\theta), \tag{B 8}$$

whose eigenvalues form an isoenergetic quadruplet,

$$E_{<} \equiv E_{-\omega MK} = E_{-\omega-M-K} = E_{\omega-MK} = E_{\omega M-K}, \tag{B 9}$$

with $\omega MK < 0$.

The eigenfunctions with negative and positive ω within each quadruplet are oriented in the opposite sense to one another. Note that for $K=0$, the parity operation can be alternatively accomplished by replacing ω by $-\omega$. The general effect of the latter operation, $\omega \rightarrow -\omega$, can be summarized in term of the Fourier coefficients, $a_{JKM}(\omega)$, for either of the quadruplets,

$$\begin{aligned} a_{JKM}(\omega) &= a_{J-K-M}(\omega) \\ &= (-1)^{\tilde{J}-J} a_{J-KM}(-\omega) = (-1)^{\tilde{J}-J} a_{JK-M}(-\omega), \end{aligned} \tag{B 10}$$

for $\omega MK > 0$, and

$$\begin{aligned} a_{J-KM}(\omega) &= a_{JK-M}(\omega) \\ &= (-1)^{\tilde{J}-J} a_{JKM}(-\omega) = (-1)^{\tilde{J}-J} a_{J-K-M}(-\omega), \end{aligned} \tag{B 11}$$

for $\omega MK < 0$. For $K=0$ we see that indeed the reversal of sign of ω amounts to a transition between states given by the Fourier coefficients of (B 10) and (B 11)

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