

This article was downloaded by:

On: 21 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713724383>

### Statistical mechanics of pendular molecules

Bretislav Friedrich<sup>a</sup>; Dudley Herschbach<sup>a</sup>

<sup>a</sup> Department of Chemistry, Harvard University, Cambridge, MA, USA

**To cite this Article** Friedrich, Bretislav and Herschbach, Dudley(1996) 'Statistical mechanics of pendular molecules', *International Reviews in Physical Chemistry*, 15: 1, 325 – 344

**To link to this Article:** DOI: 10.1080/01442359609353187

**URL:** <http://dx.doi.org/10.1080/01442359609353187>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Statistical mechanics of pendular molecules

by BRETISLAV FRIEDRICH and DUDLEY HERSCHBACH

Department of Chemistry, Harvard University, Cambridge, MA 02138, USA

When molecules are subjected to an external electric field, static or radiative, the interaction with either permanent or induced dipole moments creates pendular eigenstates, directional superpositions or hybrids of the field-free rotational states. These hybrids reflect the anisotropy of the interaction; for a linear molecule this is proportional to  $\cos \theta$  for a permanent dipole and to  $\cos^2 \theta$  for an induced dipole, with  $\theta$  the angle between the molecular axis and the field direction. In the weak-field regime, the molecular axis tumbles through  $360^\circ$ , but in the strong-field limit it is confined to harmonic librations about the field direction. Here we treat the statistical mechanics of pendular states of linear molecules, either polar (with a permanent dipole moment  $\mu$ ) or nonpolar but polarizable (with a polarizability anisotropy  $\Delta\alpha$  contributing to an induced dipole moment). The partition function and the thermodynamic properties and other ensemble averages can be specified by two reduced variables involving  $\mu$  or  $\Delta\alpha$ , the field strength, rotational constant, and temperature. A simple approximation due to Pitzer enables the partition function to be cast in terms of the classical result with quantum corrections derived from the harmonic libration limit. This provides explicit analytic formulas which permit thermodynamic properties to be evaluated to good accuracy without computing energy levels and state sums. We also evaluate the average orientation or alignment of the molecular dipoles and examine field-induced shifts of chemical equilibria.

### 1. Introduction

The thermal properties of ensembles of molecules subject to electric or magnetic fields is a venerable subject (Langevin 1905, Debye 1929, Van Vleck 1932). However, although the major conceptual aspects are well-understood, virtually all simple working approximations, such as the Langevin–Debye function, pertain either to the classical limit or to the weak-field regime. This has been adequate for Kerr effect measurements and many other experiments dealing with weak field-induced orientation. Recent work focuses instead on the strong-field, low-temperature regime, where quantum effects become substantial. Since typically many eigenstates contribute, numerical calculations are tedious. Here we show that, for the prototype case of a linear molecule, remarkably simple and accurate approximations for the partition function and thermodynamic properties can be obtained by means of a scheme devised by Pitzer to treat hindered internal torsional vibrations (Pitzer 1937, Pitzer and Gwinn 1942). The results are applicable throughout the weak- to strong-field regime, for either static or radiative fields. We consider interactions with either permanent electric or magnetic dipole moments (see also Friedrich and Herschbach 1993) or with an induced dipole moment resulting from the molecular polarizability.

In §2, we outline pertinent aspects of the interaction potentials and eigenstates. The eigenproperties, which for fairly strong fields deviate markedly from second-order Stark or Zeeman effects, characterize pendular states intermediate between the free rotor and harmonic libration limits. The directional properties and field dependence of such states have been examined recently for molecules with permanent electric dipole moments (Friedrich and Herschbach 1991a, b, Block *et al.* 1992, Rost *et al.* 1992), magnetic dipole moments (Slenczka *et al.* 1994), both electric and magnetic dipoles

(Friedrich *et al.* 1994a, b), or only the polarizability interaction (Friedrich and Herschbach 1995, Kim and Felker 1996). Reactive and inelastic collisions of pendularly oriented polar molecules have also been studied (Loesch and Remscheid 1990, 1991, Friedrich *et al.* 1992, Loesch and Möller 1992, 1993, Van Leuken *et al.* 1995).

In §3 we obtain the partition function as a product of three factors, each dependent on a single dimensionless variable involving a reduced temperature and a reduced interaction parameter. The utility of the Pitzer scheme is demonstrated and limiting cases examined. In §4, corresponding approximations for the thermodynamic functions are obtained for the Gibbs free energy, enthalpy, entropy, and heat capacity functions, all given as explicit analytic formulas which permit the thermodynamic properties to be evaluated without computing energy levels.

In §5 we derive expressions for the average orientation of permanent and induced dipoles. These include explicit quantum corrections for the Langevin-Debye formula and its extension to the induced dipole case. In §6 we compute field-induced shifts of chemical equilibria for some simple exchange reactions of diatomic molecules.

## 2. Eigenproperties of pendular molecules

For simplicity we consider linear molecules without electronic angular momentum, but the chief results can be extended to other categories by standard means. The eigenenergies of the field-free rotor states  $|J, M\rangle$  are given by

$$E_J = BJ(J+1) \quad (1)$$

where  $B$  is the rotational constant,  $J$  is the total angular momentum quantum number, and  $M$  the projection on the space-fixed  $Z$ -axis. By virtue of the different orientations of the  $J$ -vector, these energy levels are  $(2J+1)$ -fold degenerate.

### 2.1. Permanent dipoles

For polar molecules, the interaction potential is given by

$$\frac{V_\mu(\theta)}{B} = -\omega \cos \theta \quad (2)$$

in units of the rotational constant  $B$ , where  $\theta$  is the angle between the molecular electric dipole moment  $\mu$  and the direction of the electric field  $\varepsilon$  and  $\omega \equiv \mu\varepsilon/B$  is a dimensionless interaction parameter. An analogous potential obtains for the case of a permanent magnetic dipole moment coupled to the internuclear axis, subject to a magnetic field (Friedrich and Herschbach 1992). The interaction (2) creates coherent superpositions or hybrids of the field-free rotor states in which the molecular axis librates about the direction of the field like a pendulum. These pendular states,  $|\tilde{J}, M; \omega\rangle$ , are labelled by the good quantum number  $M$  and the nominal value of  $\tilde{J}$ , the angular momentum of the field-free rotor state that adiabatically correlates with the high-field hybrid function,  $|\tilde{J}, M; \omega \rightarrow 0\rangle \rightarrow |J, M\rangle$ . For fixed values of  $\tilde{J}$  and  $M$  the pendular state depends solely on the interaction parameter  $\omega$  which determines the range of  $J$  involved in the hybrid wavefunction. For large  $\omega$ , the pendulum eigenstates become increasingly directional with energies that differ greatly from the rotor levels. In the harmonic limit ( $\omega \rightarrow \infty$ ) the levels become  $(N+1)$ -fold degenerate with eigenenergies

$$\frac{E_N}{B} = -\omega + (N+1)(2\omega)^{1/2} \quad (3)$$

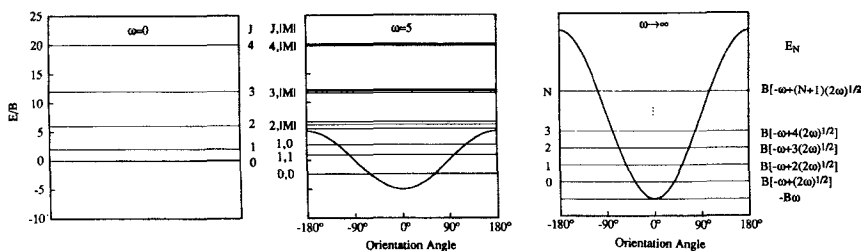


Figure 1. Eigenenergies for a rigid linear dipole in a static electric or magnetic field, in units of the rotational constant,  $B$ . On the left are the field-free rotor states  $|J, M\rangle$ ; these adiabatically correlate with the hybridized states  $|\tilde{J}, M; \omega\rangle$  created by the field. On the right are the equispaced harmonic librator states  $|N, M\rangle$  attained in the high-field limit. In the middle the energy levels for  $\omega = 5$  are shown together with the interaction potential,  $-\omega \cos \theta$ .

where  $N = 2\tilde{J} - |M|$  is the total number of the librator quanta;  $\tilde{J} - |M|$  is the number of  $\theta$ -nodes (in the range  $0^\circ - 180^\circ$ ) and  $|M|$  the number of  $\phi$ -nodes (in the range  $0^\circ - 360^\circ$ ). Figure 1 shows for  $\omega = 5$  the typical pattern of energy levels, in contrast to the free-rotor and harmonic librator limits. Qualitatively, the lowest states within the cosine potential well are librator-like whereas those appreciably above the barrier top ( $\theta \sim \pm 180^\circ$ ) become rotor-like.

## 2.2 Induced dipoles

For nonpolar but polarizable molecules the leading interaction with an electric field  $\varepsilon$  is with the polarizability tensor, which has components  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  parallel and perpendicular to the molecular axis. Even for polar molecules, the polarizability contributes the leading interaction with the electric field of nonresonant radiation, if the frequency is too high for the permanent dipole to follow. Then the interaction potential is

$$\frac{V_{\alpha}(\theta)}{B} = \omega_{\perp} - \Delta\omega \cos^2 \theta \quad (4)$$

again in units of the rotational constant, with  $\theta$  the angle between the molecular axis and the electric field direction. The coefficient

$$\Delta\omega \equiv \omega_{\parallel} - \omega_{\perp} \quad (5)$$

is a dimensionless anisotropy parameter, and

$$\omega_{\parallel, \perp} \equiv \left( \frac{\alpha_{\parallel, \perp} \varepsilon^2}{2B} \right). \quad (6)$$

For plane-wave radiation with electric field strength  $\varepsilon = \varepsilon_0 \cos(2\pi\nu t)$ , and nonresonant frequencies much greater than the reciprocal of the laser pulse duration,  $\nu \gg 1/\tau_p$ , averaging over the pulse period  $\tau_p$  converts  $\varepsilon^2$  in (6) to  $\frac{1}{2}\varepsilon_0^2$ . Since for linear molecules the polarizability component parallel to the axis always exceeds that perpendicular,  $\alpha_{\parallel} > \alpha_{\perp}$ , the anisotropy parameter  $\Delta\omega > 0$ ; hence  $V_{\alpha}$  is a double-well potential, with minima at  $\theta = 0^\circ$  and  $180^\circ$ . The eigenstates  $|\tilde{J}, M; \Delta\omega\rangle$  are labelled by  $|M|$  and the nominal value  $\tilde{J}$  designating the angular momentum for the field-free rotor state that adiabatically correlates with the high-field hybrid function.

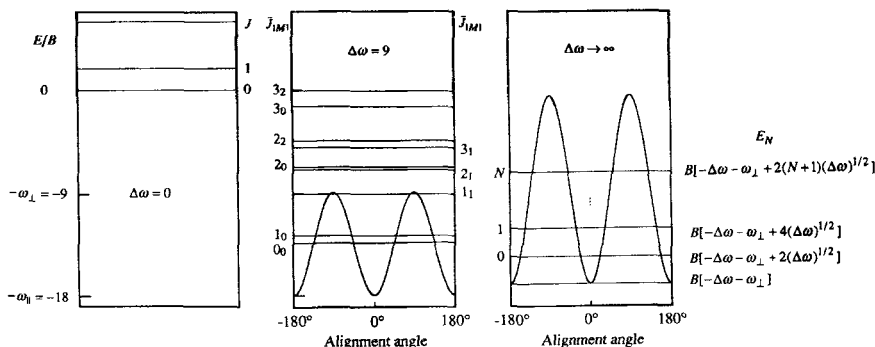


Figure 2. Eigenenergies for a linear induced dipole in an external electric field, in units of the rotational constant,  $B$ . On the left are the field-free rotor states  $|J, M\rangle$ ; these adiabatically correlate with the hybridized states  $|\tilde{J}, \tilde{M}; \Delta\omega\rangle$  created by the field. On the right are the equispaced harmonic librator states  $|N, M\rangle$  attained in the high-field limit. In the middle the energy levels for  $\Delta\omega = \omega_{\perp} = 9$  are shown together with the interaction potential,  $-\omega_{\perp} - \Delta\omega \cos^2 \theta$ .

In the high-field limit,  $\Delta\omega \rightarrow \infty$ , the range of  $\theta$  is confined near the potential minima and the eigenenergies become

$$\frac{E_{\tilde{J}, |\tilde{M}|}}{B} = -\Delta\omega - \omega_{\perp} + 2(\Delta\omega)^{1/2} + 2\tilde{J}(\Delta\omega)^{1/2} + \frac{|M|^2}{2} - \frac{\tilde{J}^2}{2} - \tilde{J} - 1 \quad (7a)$$

for  $(\tilde{J} - |M|)$  even, and

$$\frac{E_{\tilde{J}, |\tilde{M}|}}{B} = -\Delta\omega - \omega_{\perp} + 2\tilde{J}(\Delta\omega)^{1/2} + \frac{|M|^2}{2} - \frac{\tilde{J}^2}{2} - \frac{1}{2} \quad (7b)$$

for  $(\tilde{J} - |M|)$  odd. Hence states with  $\tilde{J} = N + 1$  for  $\tilde{J} - |M|$  odd and  $\tilde{J} = N$  for  $\tilde{J} - |M|$  even, with the same  $N = 2(k + |M|/2)$  and  $k = 0, 1, 2, \dots$  have equal energies,  $E_N/B$ :

$$\frac{E_N}{B} \cong -\Delta\omega - \omega_{\perp} + 2(N + 1)(\Delta\omega)^{1/2} \quad (8)$$

and each of the states is  $2(N + 1)$ -degenerate. Figure 2 shows the energy levels for a particular choice of the interaction parameter ( $\Delta\omega = 9 = \omega_{\perp}$ ), together with the levels in the field-free rotor and harmonic librator limits. Note that in the intermediate regime, tunnelling occurs between the two equidistant potential minima for the bound states (Friedrich and Herschbach 1996).

### 3. The pendular partition functions

We consider a canonical ensemble of molecules and as usual take the translational, electronic, vibrational, and rotational or pendular modes of motion as separable (although the Born–Oppenheimer approximation is somewhat less accurate in the presence of a strong field). For a given mode of molecular motion at temperature  $T$ , if Boltzmann statistics apply, the occupation number  $n_i$  of the  $i$ th energy level with energy  $E_i$  above the ground level  $E_0$  and degeneracy  $g_i$  is given by

$$\frac{n_i}{n} = g_i \frac{\exp[-(E_i - E_0)/kT]}{Q} \quad (9)$$

where

$$Q = \sum_{i=0}^{\infty} g_i \exp[-(E_i - E_0)/kT] \tag{10}$$

is the canonical molecular partition function pertaining to the given mode and  $n$  is the total number of molecules in the ensemble possessing that mode. In general, for the pendular mode the exact partition function (10) must be evaluated numerically, since as seen in figures 1 and 2 the spacing of the energy levels is not simple except in the free-rotor and harmonic librator limits. However, since the energy levels for any fixed field strength are proportional to the rotational constant  $B$ , the partition function and related quantities depend only on a reduced temperature,  $Y \equiv kT/B$ , in addition to the reduced interaction parameter. Accordingly, for permanent dipoles  $Q = Q(\omega, Y)$ ; for induced dipoles  $Q = Q(\Delta\omega, Y)$ . Note that, since in (4) the parameter  $\omega_{\perp}$  produces only a uniform shift of the energy levels, it does not contribute to the partition function (10); but  $\omega_{\perp}$  does enter  $E_0$  and thus affects the thermodynamic functions that involve  $E_0$ , the free energy and enthalpy.

We find that a simple procedure, utilizing the classical partition function  $Q_{cl}$  and subsequently applying quantum corrections, provides a remarkably accurate analytic approximation for the complete partition function  $Q$ . This procedure was introduced by Pitzer (Pitzer 1937, 1940, Pitzer and Gwinn 1942) in treating hindered internal rotation. The partition function  $Q_{cl}$  is given by the classical counterpart of (10), namely

$$Q_{cl} = \frac{2\pi I kT}{h^2} \int_0^{2\pi} d\phi \int_0^{\pi} \exp[-V(\theta)/kT] \sin \theta d\theta = \frac{1}{2} Y \int_0^{\pi} \exp[-V(\theta)/kT] \sin \theta d\theta \tag{11}$$

with  $h$  the Planck constant and  $I$  the moment of inertia, related to the rotational constant by  $B = \hbar^2/2I$ , with  $\hbar = h/2\pi$ ;  $V(\theta)$  is the potential energy of the permanent or induced dipole and  $Y \equiv kT/B$  the reduced rotational temperature.

The Pitzer–Gwinn *Ansatz* permits the partition function  $Q$  to be recast as product of three factors:

$$Q = Q_I Q_{II} Q_{III} \tag{12a}$$

given by

$$Q_I = Y \tag{12b}$$

$$Q_{II} = \frac{Q_{cl}}{Y} = \frac{1}{2} \int_0^{\pi} \exp[-V(\theta)/kT] \sin \theta d\theta \tag{12c}$$

$$Q_{III} = \left[ \frac{Q_q}{Q_{cl}} \right]_{lib} \tag{12d}$$

and enables a neat separation of variables: the first factor  $Q_I$  is independent of the field and depends only on  $Y$ ; the second factor,  $Q_{II}$ , depends only on the ratio of the interaction parameter ( $\omega$  or  $\Delta\omega$ ) to the reduced rotational temperature  $Y$ ; the third,  $Q_{III}$ , serves to correct the classical version of the partition function,  $Q_{cl} = Q_I Q_{II}$ , for the effects of quantization. For this we find it is a very good approximation to use the ratio  $[Q_q/Q_{cl}]_{lib}$  of the quantum partition function in the harmonic librator limit,  $[Q_q]_{lib}$ , to its classical limit,  $[Q_{cl}]_{lib}$ ; the correction  $[Q_q/Q_{cl}]_{lib}$  depends on the ratio of the level spacing in the harmonic librator limit to the reduced rotational temperature. The partition function  $Q$  of (12a) coincides with  $Q_{cl}$  at low fields and high temperatures

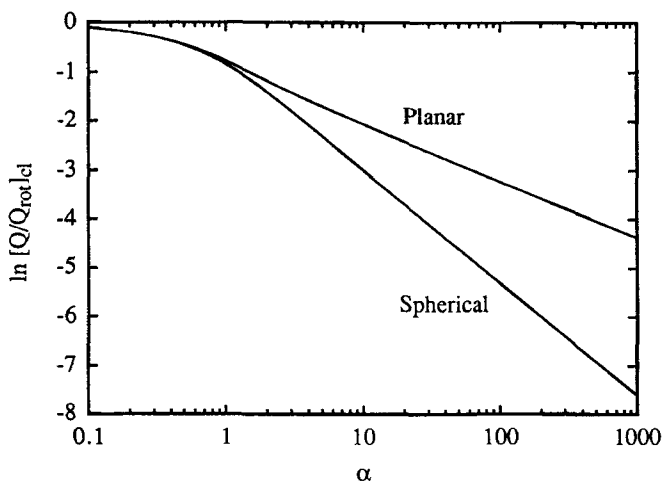


Figure 3. Field-dependent portion of classical partition function,  $Q_{cl} = Y Q_{II}(\alpha)$  of (12*b*, *c*) and (13), for permanent dipoles (spherical pendulum) as a function of the ratio  $\alpha \equiv \omega/Y = \mu F/kT$ . Also shown is the corresponding plot for a planar pendulum.

and with  $(Q_q)_{lib}$  at high fields and low temperatures. This limiting behaviour imposes restrictions on the choice of energy reference of the  $Q_{cl}$  and  $[Q_q/Q_{cl}]_{lib}$  terms and provides a consistency criterion for the definition of the respective independent variables.

Since the population of the ground state is related to the partition function by  $n_0 = n/Q$ ,  $n_0$  grows at a given temperature as the interaction parameter ( $\omega$  or  $\Delta\omega$ ) increases and the energy levels are drawn further apart. Because the lowest rotational states are hybridized most easily, such 'condensation' of molecules into the low-lying states occurs at field strengths substantially lower than those required to attain the harmonic libration limit.

Explicit analytic expressions are readily obtained for each factor of (12). Hence the partition function and thermodynamic properties can be evaluated to good accuracy without actually determining the field-dependent eigenenergies or computing the state sums called for in (10). We consider the two factors in turn for both polar (permanent dipole) and nonpolar (induced dipole moment) linear molecules.

### 3.1. Permanent dipoles

By referring the energy to the potential minimum, i.e. by taking  $V(\theta)/B = \omega + V_\mu(\theta) = \omega(1 - \cos \theta)$ , the integral (12*c*) yields

$$Q_{II}(\alpha) = \exp(-\alpha) \alpha^{-1} \sinh \alpha \quad (13)$$

where  $\alpha \equiv \omega/Y$ . Figure 3 plots the function  $Q_{II}(\alpha) = Q_{cl}/Y$  which approaches unity as  $\alpha \rightarrow 0$  and approaches  $1/(2\alpha)$  as  $\alpha \rightarrow \infty$ . Included for comparison is the corresponding result for the planar pendulum case,  $Q_{cl}/Q_t = \exp(-\alpha) I_0(\alpha)$ , for which the field-free rotor partition function is  $Q_t = (\pi Y)^{1/2}$ ;  $I_0$  is the modified Bessel function. The planar pendulum, solvable in terms of Mathieu functions, has long been employed in treating hindered internal rotation in molecules (Pitzer and Gwinn 1942, Li and Pitzer 1956) as well as an approximate model for the interaction of rotating molecules with an electric field (Friedrich and Herschbach 1991*a*, *b*, Friedrich *et al.* 1991).

In order to obtain the correction factor  $Q_{III}$  in (12*d*), we first consider the quantum

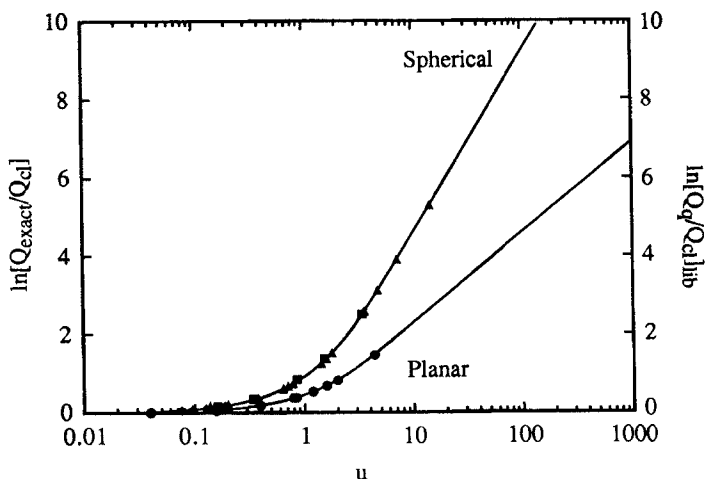


Figure 4. Points give ratio of exact partition function for permanent dipoles, as calculated from (10) for potential (2), to the classical partition function  $Q_{cl} = YQ_{II}(\alpha)$  of (12b, c) and (13), for  $\omega = 5$  (squares), 20 (triangles) and 100 (diamonds); full curve gives quantum correction factor  $\Gamma^2(u)$  computed for harmonic librator from (16). Corresponding points for a planar pendulum were obtained from tables of Pitzer and Gwinn (1942) and compared with correction factor  $\Gamma$  for a one-dimensional harmonic oscillator.

partition function in the limit  $\omega \rightarrow \infty$ , with energy levels given by (3): this is the partition function for an isotropic two-dimensional oscillator with frequency  $B(2\omega)^{1/2}$ . By referring the energy to the lowest librator level, i.e. by taking  $E_0/B = -\omega + (2\omega)^{1/2}$ , we obtain

$$[Q_q]_{lib} = \sum_{N=0}^{\infty} (N+1) \exp(-Nu) = [1 - \exp(-u)]^{-2} \equiv [Q_q(u)]_{lib} \quad (14)$$

where  $u \equiv (2\omega)^{1/2}/Y$ . The ratio of the partition function for the harmonic librator, as given in (14), to its classical limit ( $u \rightarrow 0$ ) is then

$$[Q_q/Q_{cl}]_{lib} = u^2 [1 - \exp(-u)]^{-2} \equiv \Gamma^2(u). \quad (15)$$

Combining (12), (13) and (15) yields the pendular partition function in the form

$$Q(\omega, Y) = Y [\exp(-\alpha)] \alpha^{-1} \sinh \alpha u^2 [1 - \exp(-u)]^{-2}. \quad (16)$$

The consistency of (13) and (15) is assured by the following limiting behaviour: at  $\alpha$  or  $u \rightarrow 0$ ,  $Q/Q_{cl} \rightarrow 1$  and simultaneously  $Q_{cl}/Y \rightarrow 1$  and  $\Gamma \rightarrow 1$  so that  $Q \rightarrow Y$  there. In the high-field limit, at  $\alpha, u \rightarrow \infty$ ,  $Q/(Q_q)_{lib} = u^2 Y Q_{II}(\alpha \rightarrow \infty) = 1$ .

Figure 4 displays a test of the approximation. The ratio of the exact quantum partition function from (10), for  $\omega = 5, 20, 100$ , to the classical version  $Q_{cl}$  is seen to depend essentially only on  $u$  and to agree closely with the librator ratio  $\Gamma^2(u)$ . Similar agreement obtains for the planar pendulum, in accord with the tests provided by Pitzer and Gwinn in terms of thermodynamic functions. Although  $Q_{lib}$  is not a good approximation to the partition function for either a spherical or a planar pendulum, except for large values of  $u$ , the quantum/classical ratio for the quadratic librator potential mimics very well that for the cosine potential almost over the full range. The exception occurs for very low values of the reduced temperature,  $Y < 1$ , when both  $\alpha \rightarrow \infty$  and  $u \rightarrow \infty$ ; then the librator ratio becomes much too large. In practice, this is not a significant limitation, since such low values of  $Y$  very seldom obtain.



Table 1. Values of the function  $A^{-1} \equiv \exp(-a)\pi^{1/2}(-a)^{-1/2}\text{erf}[(-a)^{1/2}]$ 

$a$	$A^{-1}$	$a$	$A^{-1}$	$a$	$A^{-1}$	$a$	$A^{-1}$
0.1	1.8719	1	1.0762	10	0.1061	100	0.0101
0.2	1.7535	2	0.6399	20	0.0514	200	0.0050
0.3	1.6442	3	0.4204	30	0.0339	300	0.0033
0.4	1.5431	4	0.3013	40	0.0253	400	0.0025
0.5	1.4496	5	0.2314	50	0.0202	500	0.0020
0.6	1.3630	6	0.1870	60	0.0168	600	0.0017
0.7	1.2829	7	0.1569	70	0.0144	700	0.0014
0.8	1.2087	8	0.1352	80	0.0126	800	0.0013
0.9	1.1399	9	0.1188	90	0.0111	900	0.0011

### 3.2. Induced dipoles

For the induced dipole moment interaction the integral (12c) is again analytic. By referring the energy zero to the potential minimum, i.e. by taking  $V(\theta)/B = \Delta\omega(1 - \cos^2\theta)$ , we have (Gautschi 1964)

$$Q_{\text{II}}(a) = \frac{1}{2A} \quad (17)$$

where  $A^{-1} \equiv [\exp(-a)]\pi^{1/2}(-a)^{-1/2}\text{erf}[(-a)^{1/2}]$  and  $a \equiv \Delta\omega/Y$ . The function  $A$  is tabulated for a range of the parameter  $a$  in table 1.

The quantum partition function in the harmonic librator limit, for  $E_0/B = -\Delta\omega - \omega_{\perp} + 2(\Delta\omega)^{1/2}$ , becomes

$$Q_{\text{lib}} = 2 \sum_{N=0}^{\infty} (N+1) [\exp(-Nv)] = 2[1 - \exp(-v)]^{-2} \equiv Q_{\text{lib}}(v) \quad (18)$$

where  $v \equiv 2(\Delta\omega)^{1/2}/Y$ . Consequently, the correction factor in (12d) becomes

$$Q_{\text{III}}(v) = [Q_q/Q_{\text{cl}}]_{\text{lib}} = v^2[1 - \exp(-v)]^{-2} \equiv \Gamma^2(v). \quad (19)$$

Combining (12), (17) and (19) yields the approximate partition function

$$Q(\Delta\omega, Y) = Y \frac{1}{2A} v^2 [1 - \exp(-v)]^{-2}. \quad (20)$$

Figure 5 displays a test of the approximation. The ratio of the exact quantum partition function from (10) evaluated for tabulated eigenenergies (Stratton *et al.* 1956), for  $\Delta\omega = 9, 25, 100$ , to the classical version  $Q_{\text{cl}}$  is again seen to depend essentially only on  $v$  and to agree closely with the librator ratio  $\Gamma^2(v)$ .

The partition function (20) is well-behaved in the low-field limit: for  $a, v \rightarrow 0$ ,  $Q/Q_{\text{cl}} \rightarrow 1$  and simultaneously  $Q_{\text{cl}}/Y \rightarrow 1$  and  $\Gamma \rightarrow 1$  so that  $Q \rightarrow Y$ ; in the high-field limit, at  $a, v \rightarrow \infty$ ,  $Q/(Q_q)_{\text{lib}} = v^2 Y Q_{\text{II}}(a \rightarrow \infty) = 1$  for  $v = (2\Delta\omega)^{1/2}/Y$ , a spacing that differs by a factor of  $2^{1/2}$  from that of (8). This follows from the asymptotic expansion  $\text{erf}[(-a)^{1/2}] \sim i[\exp(a)](\pi a)^{-1/2}$  at  $a \rightarrow \infty$ , yielding  $Q_{\text{II}}(a \rightarrow \infty) = (2a)^{-1}$ .

The reduced rotational temperature  $Y$  represents the classical limit of the rotational partition function

$$Q_{\text{rot}}(Y) = \sum_{J=0}^{\infty} (2J+1) \exp[-J(J+1)/Y]. \quad (21)$$

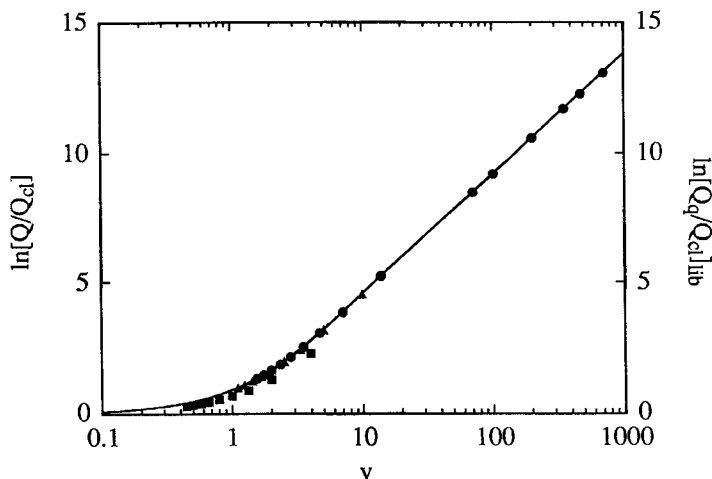


Figure 5. Points give ratio of exact partition function for induced dipoles, as calculated from (10) for potential (4), to the classical partition function  $Q_{cl} = YQ_{II}(a)$  of (12*b*, *c*) and (17), for  $\Delta\omega = 9$  (squares), 25 (triangles) and 100 (circles); full curve gives quantum correction factor  $\Gamma^2(v)$  computed for harmonic oscillator from (19).

At low temperatures  $Y$  and (21) differ appreciably. A correction for this can be made by inserting into (12*a*) another factor, the ratio of the quantum  $Q_{rot}$  to its classical limit. Unless the interaction ( $\omega$  or  $\Delta\omega$ ) is zero or much smaller than  $Y$ , however, such a correction is not warranted.

#### 4. The thermodynamic functions

Since the Helmholtz free energy  $F$ , integral energy  $U$ , entropy  $S$ , and heat capacity  $C$  are derived from the logarithm of the partition function (see e.g. Atkins 1990) the factorization provided by equations (16) and (20) gives the contribution of the pendular mode to all such functions  $\Phi$  as a sum of three terms, each dependent on a single dimensionless reduced variable:

$$\Phi(\omega, Y) = \Phi_I(Y) + \Phi_{II}(\alpha) + \Phi_{III}(u) \tag{22}$$

$$\Phi(\Delta\omega, Y) = \Phi_I(Y) + \Phi_{II}(a) + \Phi_{III}(v) \tag{23}$$

Tables 2 and 3 list these terms for the permanent and induced dipole moment interactions. The thermodynamic functions are as usual per mole rather than per molecule, so the gas constant  $R$  appears (rather than Boltzmann's constant  $k$ ). As the functions pertain to a nominal ideal gas, the Gibbs free energy is given by  $G = F + RT$ , the enthalpy by  $H = U + RT$ , and the heat capacities at constant pressure and volume are related by  $C_p = C_v + R$ . The contribution from the pendular mode thus is the same for  $G$  and  $F$ , for  $H$  and  $U$ , and for either heat capacity.

For convenience, we list the conversion factors relating the physical parameters in customary units to our dimensionless variables. With temperature in K and rotational constant  $B$  in  $\text{cm}^{-1}$ , for the permanent electric dipole moment  $\mu_{el}$  in Debye units and electric field strength  $\epsilon$  in  $\text{kV cm}^{-1}$ , or magnetic dipole moment  $\mu_m$  in Bohr magnetons and magnetic field strength  $H$  in Tesla units ( $= 10 \text{ kGauss}$ ), we have:

$$Y = 0.6961 T/B \tag{24a}$$

$$\omega_{el} = 0.0168 \mu_{el} \epsilon / B \tag{24b}$$

$$\omega_m = 0.4668 \mu_m H / B. \tag{24c}$$

Table 2. Thermodynamic functions,  $\Phi(\omega, Y) = \Phi_1(Y) + \Phi_{11}(\alpha) + \Phi_{111}(u)$ , for permanent dipoles.

$\Phi(\omega, Y)$	$\Phi_1(Y)$	$\Phi_{11}(\alpha)$	$\Phi_{111}(u)$
$\frac{F}{RT} = -\ln Q$	$-\ln Y$	$-\ln \left[ \frac{\sinh \alpha}{\alpha} \right] + \alpha$	$-2 \ln \left[ \frac{u}{1 - \exp(-u)} \right]$
$\frac{U}{RT} = T \frac{\partial \ln Q}{\partial T}$	1	$1 - \alpha \coth \alpha + \alpha$	$2 \left( \frac{u}{\exp(-u) - 1} \right)$
$\frac{S}{R} = \frac{U-F}{RT}$	$1 + \ln Y$	$\ln \left[ \frac{\sinh \alpha}{\alpha} \right] + 1 - \alpha \coth \alpha$	$2 \ln \left[ \frac{u}{1 - \exp(-u)} \right] + 2 \left( \frac{u}{\exp(-u) - 1} \right)$
$\frac{C}{R} = \frac{\partial}{\partial T} \left( T^2 \frac{\partial \ln Q}{\partial T} \right)$	1	$1 - \alpha^2 (\coth^2 \alpha - 1)$	$2 \left[ \frac{u^2 \exp(u)}{(\exp(u) - 1)^2 - 1} \right]$
$\omega \equiv \frac{\mu \varepsilon}{B}$	$Y \equiv \frac{kT}{B}$	$\alpha \equiv \frac{\omega}{Y}$	$u \equiv \frac{(2\omega)^{1/2}}{Y}$

Table 3. Thermodynamic functions,  $\Phi(\Delta\omega, Y) = \Phi_1(Y) + \Phi_{11}(a) + \Phi_{111}(v)$ , for induced dipoles.

$\Phi(\Delta\omega, Y)$	$\Phi_1(Y)$	$\Phi_{11}(a)$	$\Phi_{111}(v)$
$\frac{F}{RT} = -\ln Q$	$-\ln Y$	$\ln(2A)$	$-2 \ln \left[ \frac{v}{1 - \exp(-v)} \right]$
$\frac{U}{RT} = T \frac{\partial \ln Q}{\partial T}$	1	$\frac{1}{2} + a - A$	$2 \left( \frac{v}{\exp(-v) - 1} \right)$
$\frac{S}{R} = \frac{U-F}{RT}$	$1 + \ln Y$	$\frac{1}{2} - A + a - \ln(2A)$	$2 \ln \left[ \frac{v}{1 - \exp(-v)} \right] + 2 \left( \frac{v}{\exp(-v) - 1} \right)$
$\frac{C}{R} = \frac{\partial}{\partial T} \left( T^2 \frac{\partial \ln Q}{\partial T} \right)$	1	$\frac{1}{2} - A^2 - \frac{1}{2}A + aA$	$2 \left[ \frac{v^2 \exp(v)}{(\exp(v) - 1)^2 - 1} \right]$
$\Delta\omega \equiv \frac{1}{2} \Delta\alpha \frac{e^2}{B}$	$Y \equiv kT/B$	$a \equiv \Delta\omega/Y; A^{-1} \equiv \exp(-a) \pi^{1/2} (-a)^{-1/2} \operatorname{erf}[(-a)^{1/2}]$	$v \equiv \frac{2(\Delta\omega)^{1/2}}{Y}$

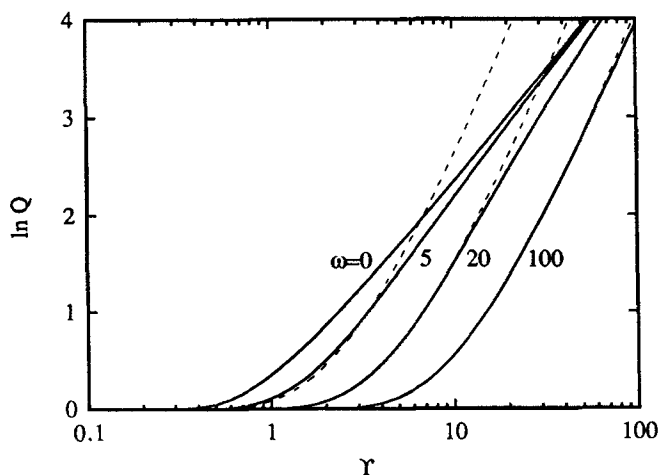


Figure 6. Total partition functions  $Q(\omega, Y)$  for permanent dipoles determined from (16) for pendular mode (full curves), as functions of reduced temperature  $Y$  for four values of reduced interaction strength  $\omega$ . The field-free limit ( $\omega = 0$ ) pertains to the rotational partition function  $Q_{\text{rot}}$  of (21); the high-field limit (dashed curves) to the harmonic librator function  $Q_{\text{lib}}(u)$  of (14). By virtue of the logarithmic ordinate scale, these plots also show the negative of the Helmholtz free energy function,  $-F/RT$ ; see table 2.

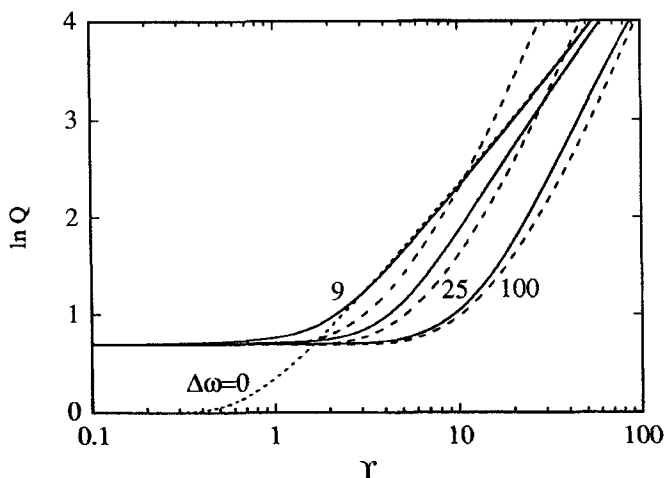


Figure 7. Total partition functions  $Q(\Delta\omega, Y)$  for induced dipoles determined from (20) for pendular mode (full curves), as functions of reduced temperature  $Y$  for four values of reduced interaction strength  $\Delta\omega$ . The field-free limit ( $\Delta\omega = 0$ ) pertains to the rotational partition function  $Q_{\text{rot}}$  of (21); the high-field limit (dashed curves) to the harmonic librator function  $Q_{\text{lib}}(v)$  of (18). By virtue of the logarithmic ordinate scale, these plots also show the negative of the Helmholtz free energy function,  $-F/RT$ ; see table 3.

For an induced dipole moment due to a polarizability anisotropy  $\Delta\alpha$  in  $\text{\AA}^3$  in an electric field  $\varepsilon$  in  $\text{kV cm}^{-1}$  the conversion is given by

$$\Delta\omega = 3 \times 10^{-8} \Delta\alpha \varepsilon^2 / B; \quad (25a)$$

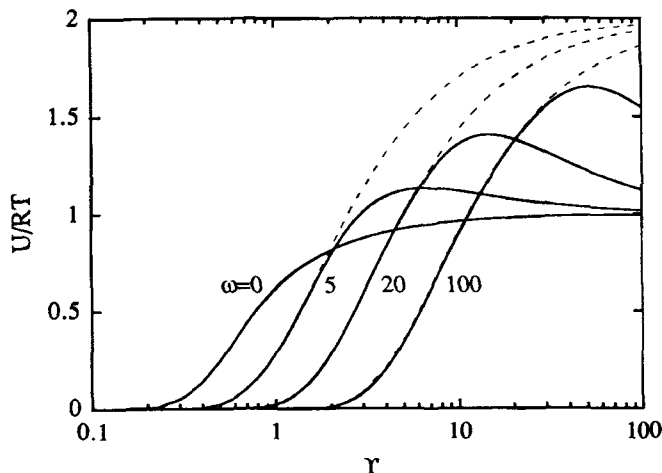


Figure 8. Internal energy,  $U/RT$ , for permanent dipoles as a function of reduced temperature, computed from (16) with factors listed in table 2, for  $\omega = 0, 5, 20$  and  $100$ . Dashed curves show the harmonic librator limit. Curve for  $\omega = 0$  calculated with  $Q_{rot}$  of (21).

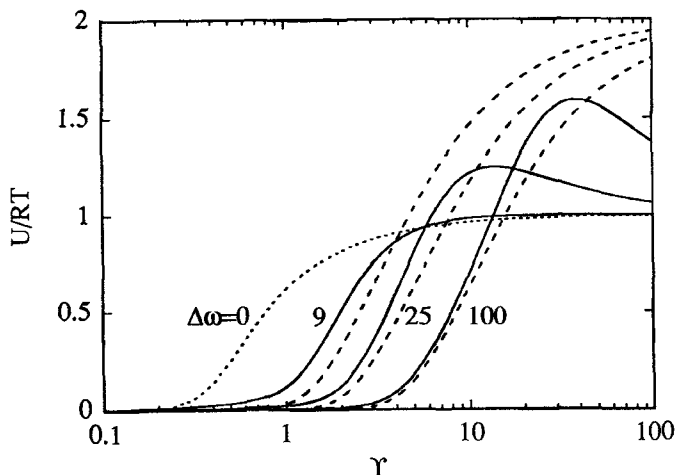


Figure 9. Internal energy,  $U/RT$ , for induced dipoles as a function of reduced temperature, computed from (20) with factors listed in table 3, for  $\Delta\omega = 0, 9, 25$  and  $100$ . Dashed curves show the harmonic librator limit. Curve for  $\Delta\omega = 0$  calculated with  $Q_{rot}$  of (21).

when the electric field is provided by a (nonresonant) electromagnetic wave with intensity  $I$  in  $\text{W cm}^{-2}$ ,

$$\Delta\omega = 5 \times 10^{12} \Delta\alpha I/B. \quad (25b)$$

Figures 6 and 7 illustrate the field dependence of the Helmholtz free energy, as  $-F/RT = \ln Q$  for ensembles of permanent and induced dipoles. At a given temperature, the presence of field reduces the partition function markedly below that for a free rotor, but, except in certain regions, it differs substantially from that for a harmonic librator. The results obtained from the Pitzer *Ansatz* of (16) and (20) coincide with our numerical calculations employing (10) within 5% and often fall within the width of the plotted curves. Figures 8–13 show corresponding results for the internal energy, entropy and heat capacity for the permanent and induced dipoles. In the presence of the field, the free energy and heat capacity increase, the internal energy and entropy decrease. Tables 4 and 5 give the leading terms for expansions that describe

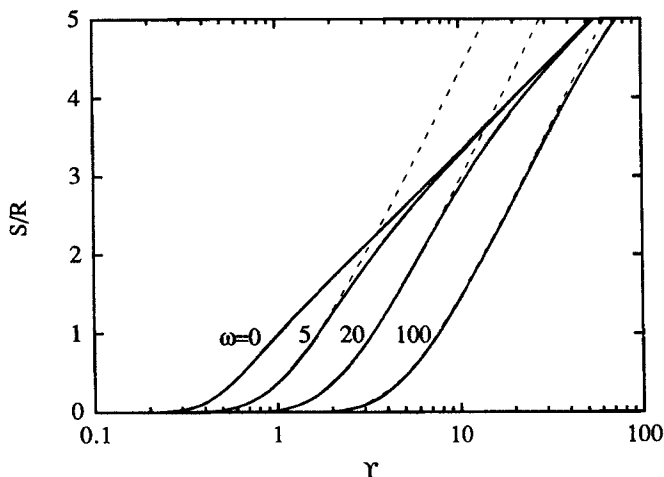


Figure 10. Entropy,  $S/R$ , for permanent dipoles as a function of reduced temperature, computed from (16) with factors listed in table 2, for  $\omega = 0, 5, 20$  and 100. Dashed curves show the harmonic librator limit. Curve for  $\omega = 0$  calculated with  $Q_{\text{rot}}$  of (21).

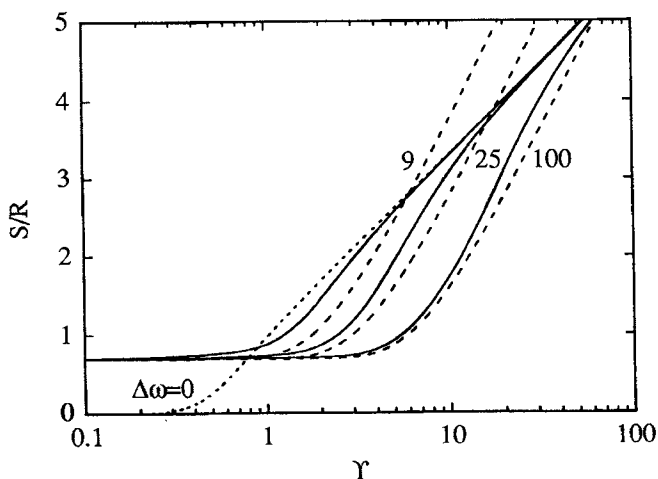


Figure 11. Entropy,  $S/R$ , for induced dipoles as a function of reduced temperature, computed from (20) with factors listed in table 3, for  $\Delta\omega = 0, 9, 25$  and 100. Dashed curves show the harmonic librator limit. Curve for  $\Delta\omega = 0$  calculated with  $Q_{\text{rot}}$  of (21).

the field-induced changes for small  $\omega$  and  $\Delta\omega$  or large  $Y$ . For sizeable values of the interaction parameter, the transition from dominantly librational motion at low temperatures to largely rotational motion at higher temperatures is evident in all the thermodynamic functions, but becomes most striking in the prominent bumps that appear in the temperature dependence of the internal energy and heat capacity.

Previous discussions of quantum statistical mechanics for molecules subject to electric or magnetic fields go back to Debye (1929) and Van Vleck (1932) but have been limited to the weak-field case, corresponding to a quadratic Stark or Zeeman effect. The partition function is then near the classical limit, and the results are essentially equivalent to including just the terms up through order  $\alpha^2$  in our table 4 or  $a^2$  in table 5. By means of the Pitzer procedure, however, it proves easy to attain good accuracy for the full range of interaction strengths.

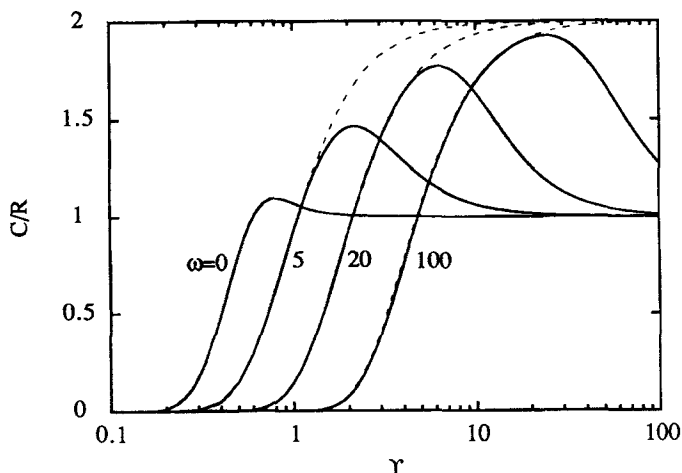


Figure 12. Heat capacity,  $C/R$ , for permanent dipoles as a function of reduced temperature, computed from (16) with factors listed in table 2, for  $\omega = 0, 5, 20$  and  $100$ . Dashed curves show the harmonic librator limit. Curve for  $\omega = 0$  calculated with  $Q_{\text{rot}}$  of (21).

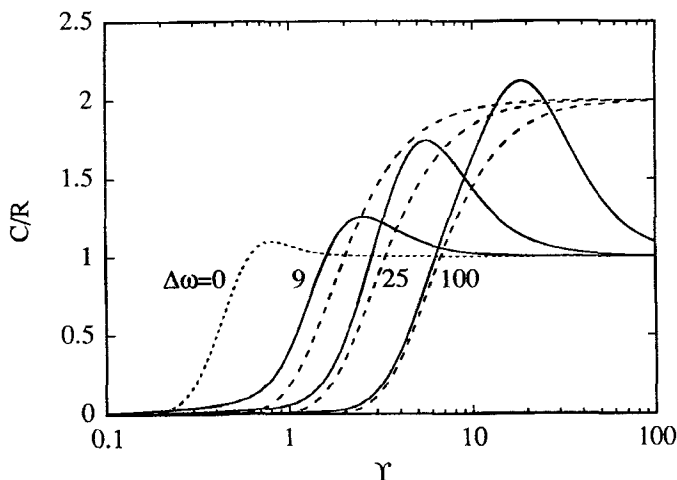


Figure 13. Heat capacity,  $C/R$ , for induced dipoles as a function of reduced temperature, computed from (20) with factors listed in table 3, for  $\Delta\omega = 0, 9, 25$  and  $100$ . Dashed curves show the harmonic librator limit. Curve for  $\Delta\omega = 0$  calculated with  $Q_{\text{rot}}$  of (21).

Although our treatment here is restricted to linear molecules without electronic angular momentum, we expect that more general cases can also be handled by augmenting standard methods with the Pitzer procedure. Often the classical partition function can be readily evaluated and separated into convenient factors (Herschbach *et al.* 1959) and the simple harmonic oscillator form for the quantum correction seems likely to be serviceable whenever the potential becomes quadratic in a suitable limit (Pitzer and Gwinn 1942, Li and Pitzer 1956).

### 5. Average molecular orientation and alignment

The Langevin–Debye function (Langevin 1905, Debye 1929) describes the average orientation of a Boltzmann distribution of rotating rigid permanent dipoles not

Table 4. Weak-field expansions of thermodynamic functions for permanent dipoles.

$\frac{\Delta F}{RT}$	$\alpha - \frac{\alpha^2}{6} \left( 1 - \frac{\alpha^2}{30} + \dots \right)$	$-2 \left( \frac{u}{2} - \frac{u^2}{24} + \dots \right)$
$\frac{\Delta U}{RT}$	$1 - \frac{\alpha^2}{3} \left( 1 - \frac{\alpha^2}{15} + \dots \right)$	$-2 \left( \frac{u}{2} - \frac{u^2}{12} + \dots \right)$
$\frac{\Delta S}{R}$	$1 - \alpha - \frac{\alpha^2}{6} \left( 1 - \frac{\alpha^2}{10} + \dots \right)$	$+2 \left( \frac{u^2}{12} - \dots \right)$
$\frac{\Delta C}{R}$	$\frac{\alpha^2}{3} \left( 1 - \frac{\alpha^2}{5} + \dots \right)$	$-2 \left( \frac{u^2}{12} - \dots \right)$

Table 5. Weak-field expansions of thermodynamic functions for induced dipoles.

$\frac{\Delta F}{RT}$	$\frac{2a}{3} - \frac{2a^2}{45} \left( 1 + \frac{4a}{63} + \dots \right)$	$-2 \left( \frac{v}{2} - \frac{v^2}{24} + \dots \right)$
$\frac{\Delta U}{RT}$	$\frac{2a}{3} - \frac{4a^2}{45} \left( 1 + \frac{2a}{21} + \dots \right)$	$-2 \left( \frac{v}{2} - \frac{v^2}{12} + \dots \right)$
$\frac{\Delta S}{R}$	$-\frac{2a^2}{45} \left( 1 + \frac{8a}{63} + \dots \right)$	$+2 \left( \frac{v^2}{12} - \dots \right)$
$\frac{\Delta C}{R}$	$\frac{4a^2}{45} \left( 1 + \frac{4a}{21} - \frac{4a^2}{105} + \dots \right)$	$-2 \left( \frac{v^2}{12} - \dots \right)$

interacting with each other but subject to an external field uniform in magnitude and direction. It corresponds to the classical limit of the partition function, which has been adequate for a host of experiments dealing with weak field-induced orientation, such as Kerr effect measurements. Quantum effects become substantial, however, in the strong-field, low-temperature regime explored in recent experiments (see e.g. Friedrich and Herschbach 1991 b). Numerical calculations are straightforward but tedious since for large  $\omega$  or  $\Delta\omega$  and small  $\alpha$  or  $a$  many pendular eigenstates typically contribute. We find that the Pitzer *Ansatz* again proves useful—for both the permanent and the induced dipole moment case; it provides an analytic approximation that supplants numerical computations for much of the range exhibiting marked quantum effects.

### 5.1 Permanent dipoles

The orientation of the molecular dipole in a given state  $i$  is specified by the expectation value of the cosine of the angle between the dipole axis and the field direction,  $\langle \cos \theta \rangle_i$ . The average orientation is then obtained from the ensemble average

$$\langle \langle \cos \theta \rangle \rangle = \sum_{i=0}^{\infty} \langle \cos \theta \rangle_i \frac{n_i}{n}. \tag{26}$$

According to the Hellmann–Feynman theorem,  $\langle \cos \theta \rangle_i$  can be evaluated for a given state from the  $\omega$ -dependence of the corresponding eigenenergy:

$$\langle \cos \theta \rangle_i = -\frac{\partial(E_i/B)}{\partial\omega}. \tag{27}$$



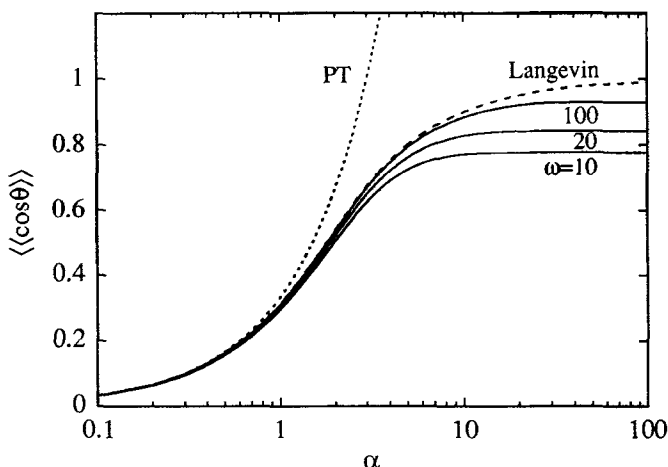


Figure 14. Average orientation cosine,  $\langle\langle \cos \theta \rangle\rangle$ , calculated from (31) for an ensemble of permanent dipoles as a function of  $\alpha = \omega/Y$ , at  $\omega = 10, 20$  and  $100$ . A numerical calculation for  $\omega = 20$  coincides with approximation (31) within the thickness of the plotted curve. Also shown (dashed) is the classical Langevin–Debye dependence (32) and its low-field limit (PT, dotted).

By combining (9), (10), (26) and (27) we obtain:

$$\langle\langle \cos \theta \rangle\rangle = \langle \cos \theta \rangle_0 + Y \frac{\partial \ln Q(\omega, Y)}{\partial \omega}. \quad (28)$$

The choice of  $E_0/B$  made in deriving  $Q(\omega, Y)$ , see (13) and (15), ensures the correct limiting properties of the thermodynamic potentials but, as seen from (28), this choice singles out the orientation cosine of the ground energy level in the average orientation. Consequently,  $\langle \cos \theta \rangle_0$  cannot be evaluated from  $Q(\omega, Y)$ . However, by shifting the energy zero to the minimum of the potential, see the appendix, we obtain a renormalized partition function

$$Q^0(\omega, Y) = \exp(-E_0/kT) Q(\omega, Y). \quad (29)$$

This yields the complete ensemble average:

$$\langle\langle \cos \theta \rangle\rangle = Y \frac{\partial \ln Q^0(\omega, Y)}{\partial \omega}. \quad (30)$$

As in the case of the entropy or heat capacity, the average orientation is independent of the choice of zero energy for the partition function; this makes (28) and (30) equivalent.

By substituting for  $Q^0(\omega, Y)$  into (30) from (A4) we obtain the result

$$\langle\langle \cos \theta \rangle\rangle = \coth \alpha + (2/\omega)^{1/2} [1 - \exp(u)]^{-1} - (2\omega)^{-1/2}. \quad (31)$$

We note that for  $u \rightarrow 0$  equation (30) yields the classical Langevin–Debye formula

$$\langle\langle \cos \theta \rangle\rangle_{cl} = \coth \alpha - \frac{1}{\alpha} = Y \partial \ln Q_{cl}^0(\omega, Y) / \partial \omega. \quad (32)$$

Figure 14 displays this approximation for  $\omega = 10, 20, 100$ . The chief effect is simply a ‘rounding-off’ of the Langevin–Debye result at large  $\alpha$ . This rounding becomes less

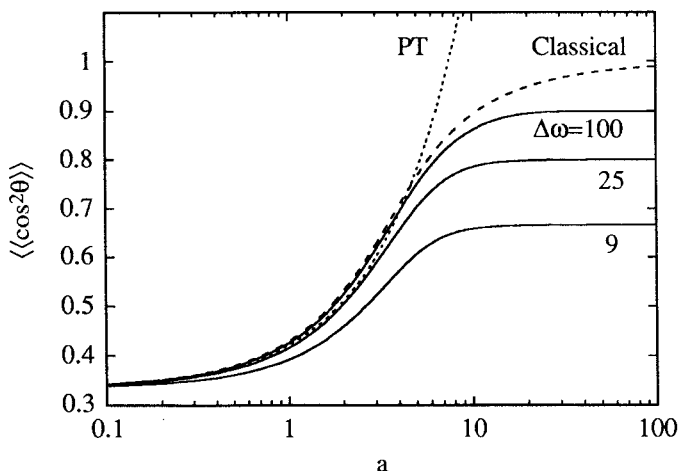


Figure 15. Average alignment cosine,  $\langle\langle \cos^2 \theta \rangle\rangle$ , calculated from (34) for an ensemble of induced dipoles as a function of  $a = \Delta\omega/Y$ , at  $\Delta\omega = 9, 25$  and  $100$ . A numerical calculation for  $\omega = 25$  coincides with approximation (34) within 5%. Also shown (dashed) is the classical dependence (35) and its low-field limit (PT, dotted).

pronounced as  $\omega$  increases. We find agreement with numerical calculations is good for  $\omega = 20$ . Also shown is the second-order expansion of (32) for  $\alpha \rightarrow 0$ ,  $\alpha/3$ , which coincides with average orientation obtained by second-order perturbation theory (PT).

### 5.2. Induced dipoles

The alignment of a nonpolar molecule in a given state  $i$  is specified by the expectation value of the squared cosine of the angle between the dipole axis and the field direction,  $\langle \cos^2 \theta \rangle_i$ , which, in turn, can be obtained from the field dependence of the eigenenergy via the Hellmann–Feynman theorem. Consequently, the ensemble polarization is given by

$$\begin{aligned} \langle\langle \cos^2 \theta \rangle\rangle &= \langle \cos^2 \theta \rangle_0 + Y \frac{\partial \ln Q(\Delta\omega, Y)}{\partial \Delta\omega} \\ &= Y \frac{\partial \ln Q^0(\Delta\omega, Y)}{\partial \Delta\omega} \end{aligned} \quad (33)$$

in analogy with the permanent dipole case described in the previous paragraph. Substitution from (A8) leads to the result

$$\langle\langle \cos^2 \theta \rangle\rangle = \frac{A}{a} - \frac{1}{2a} + \frac{1}{(\Delta\omega)^{1/2}} \left( \frac{2}{1 - \exp(v)} + \frac{2}{v} - 1 \right). \quad (34)$$

Again, for  $v \rightarrow 0$  we obtain the classical result

$$\langle\langle \cos^2 \theta \rangle\rangle_{\text{cl}} = \frac{A}{a} - \frac{1}{2a} = Y \frac{\partial \ln Q_{\text{cl}}^0(\Delta\omega, Y)}{\partial \Delta\omega}. \quad (35)$$

Figure 15 displays this approximation for  $\Delta\omega = 9, 25, 100$ . The chief effect is again a ‘rounding-off’ of the classical result at large  $a$ . This rounding becomes less pronounced as  $\Delta\omega$  increases. Also shown is the second-order expansion of (35) for  $a \rightarrow 0$ , which gives  $\frac{1}{3} + \frac{4}{45}a$ ; this coincides with the result of the second-order perturbation theory (PT).

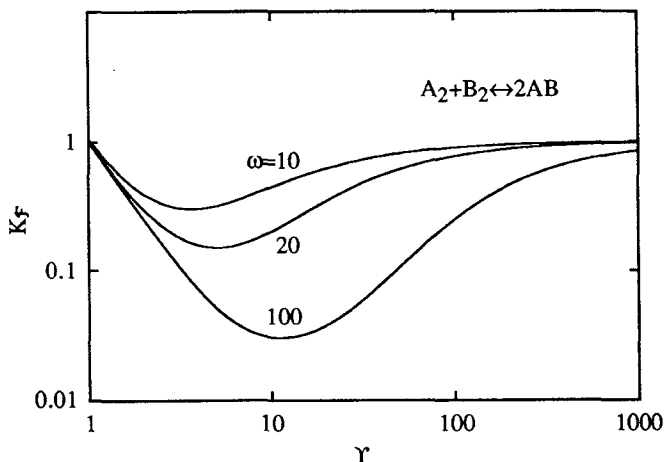
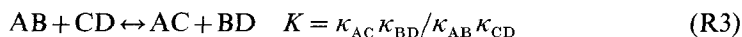
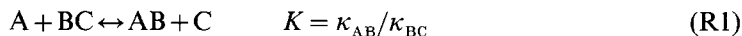


Figure 16. Field-dependent portion of equilibrium constant  $K_{\mathcal{F}}$  for permanent dipole reactions of type (R2) as a function of reduced temperature  $Y$  and reduced field strength  $\omega = 10, 20$  and  $100$ .

### 6. Field-induced shifts of chemical equilibria

The factorization provided in (12) by the Pitzer–Gwinn *Ansatz* facilitates evaluating equilibrium constants for reactions of molecules with permanent or induced dipole moments in the presence of strong external fields. The equilibrium constant for a chemical reaction thus takes the form  $K_0 K_{\mathcal{F}}$ , where  $K_0$  denotes the constant that pertains in the absence of the field. The factor  $K_{\mathcal{F}}$  for either the permanent or the induced dipole molecules has the same form as the usual equilibrium products but with the partial pressure or concentration  $[j]$  of each dipolar species replaced by  $\kappa_j(\omega, Y) = Q_j(\omega, Y)$  from (16), or  $\kappa_j(\omega_{\perp}, \Delta\omega, Y) = Q_j(\omega_{\perp}, \Delta\omega, Y)$ , from (21). Note that the effect of the  $\omega_{\perp}$  term, which shifts uniformly the energy levels of a given species, does not necessarily cancel out in the equilibrium product. Thus species with larger  $\omega_{\perp}$  have smaller  $\kappa_j(\omega_{\perp}, \Delta\omega, Y)$ . For each species that does not interact with the field (such as for atoms or spherical molecules), the  $[j]$ -factor is replaced by unity. Examples include three types of exchange reactions of diatomic molecules:



Type (R2) is typically expected to exhibit the strongest field dependence, since in (R1) and (R3) the factors tend to balance out. In (R2), since at a given temperature the free energy of the dipolar product  $AB$  increases, the reaction will be inhibited as  $\omega$  increases. Figure 16 displays the functional dependence of the  $K_{\mathcal{F}}(\omega, Y)$  factor. For instance, the curve for  $\omega = 10$  pertains to  $I_2 + Cl_2 \leftrightarrow 2ICl$  at a field strength of about  $50 \text{ kV cm}^{-1}$ ; the reduced temperature scale for  $ICl$  is such that the minimum of the curve (at  $Y \sim 5$ ) comes at about  $1 \text{ K}$ . Thus, field-induced shifts of such equilibria are typically quite small. Such shifts can become significant if exceptionally low temperatures can be attained (perhaps for reactions occurring in a supersonic expansion) or exceptionally large ratios of  $\mu/B$  (as for large, very polar molecules). Note that at very low temperatures,  $Y \rightarrow 0$ , the equilibrium constant is not affected by

the presence of the field; under such conditions only the ground state is populated and so the altered spacing between levels no longer matters.

## 7. Discussion

Our chief motivation has been to provide means to readily estimate thermodynamic properties for gas-phase molecules subject to strong external fields at relatively low temperatures. Both the method and results seem likely to find wider application. The simplicity and accuracy afforded by Pitzer's procedure, correcting the classical partition function by the harmonic oscillator ratio, recommend it for many problems involving strong perturbations. The results obtained here for pendular molecules are also applicable to condensed phase systems if interactions among the molecules are much less significant than with the external field.

The pendular functions may indeed even prove useful in modelling the effect of internal fields exerted by neighbours in a liquid or solid. The tumbling of a linear molecule in a condensed phase is more aptly represented by a spherical rather than a planar pendulum. At low temperatures or high density, the molecules in condensed phases are chiefly confined to librational or jostling motions, with occasional excursions to adjacent potential minima. This is much like hindered internal torsion within molecules such as ethane. The hindering potential barrier is not a constant, however, but depends on the orientation and density of packing of neighbouring molecules. As the temperature is increased or density lowered, the jostling increasingly turns into tumbling. Heat capacity curves of molecular solids often show anomalies resembling the bumps seen in figures 12 and 13, although sometimes much sharper. These are usually attributed to a rather sudden transition from librational to rotational motion. The sharpening stems from the cooperative effect of the mutual rotation of neighbouring molecules, which weakens the hindering potential and so makes the transition occur more abruptly. The cooperative behaviour thus might be simulated by averaging over a range of the interaction parameter. In such ways, the easily evaluated pendular properties may serve to induce useful hybridization among treatments of many dynamical phenomena involving inhibiting but pliable barriers.

## Acknowledgments

We dedicate this paper to Michael Henschman, in admiration of his masterful applications of thermodynamics to chemical processes. We are grateful for support of this work by the National Science Foundation.

## Appendix: Partition functions with shifted reference energy

### A.1. Permanent dipoles

An alternative choice refers the energy zero to the ground field-free state; then  $V(\theta) = V_\mu(\theta)$ , and integral (12c) yields

$$Q_{\text{II}}^0(\alpha) = \alpha^{-1} \sinh \alpha \quad (\text{A1})$$

A consistent expression for the  $Q_{\text{III}}(u)$  term is obtained by referring the libration energy limit to the potential minimum, i.e. by taking  $E_0/B = -\omega$ :

$$[Q_{\text{q}}^0(u)]_{\text{lib}} \equiv \sum_{N=0}^{\infty} (N+1) \exp[-(N+1)u] = \exp(-u) [1 - \exp(u)]^{-2} \quad (\text{A2})$$

and thus

$$Q_{\text{III}}^0(u) = u^2 \exp(-u) [1 - \exp(-u)]^{-2} = [Q_{\text{q}}^0/Q_{\text{cl}}^0]_{\text{lib}}. \quad (\text{A3})$$

The resulting approximation to the partition function then becomes

$$Q^0(\omega, Y) = Y \alpha^{-1} \sinh \alpha u^2 \exp(-u) [1 - \exp(-u)]^{-2}. \quad (\text{A4})$$

#### A.2. Induced dipoles

Alternatively, by taking  $V(\theta) = V_a(\theta)$ , integral (12c) yields

$$Q_{\text{II}}^0(a) = \frac{\exp(a)}{2A} \quad (\text{A5})$$

The corresponding librator partition function is obtained with  $E_0/B = -\Delta\omega - \omega_{\perp}$ :

$$Q_{\text{lib}}^0(v) = 2 \sum_{N=0}^{\infty} (N+1) \exp[-(N+1)v] = 2 \exp(-v) [1 - \exp(-v)]^{-2}. \quad (\text{A6})$$

Thus

$$Q_{\text{III}}^0(v) = v^2 \exp(-v) [1 - \exp(-v)]^{-2} = [Q_a^0 / Q_{\text{cl,lib}}^0] \quad (\text{A7})$$

and the alternative approximate partition function is

$$Q^0(\Delta\omega, Y) = Y \frac{\exp(a)}{2A} v^2 \exp(-v) [1 - \exp(-v)]^{-2}. \quad (\text{A8})$$

### References

- ATKINS, P. W., 1990, *Physical Chemistry*, 4th Edn (New York: W. H. Freeman), pp. 566–615.
- BLOCK, P. A., BOHAC, E. J., and MILLER, R. E., 1992, *Phys. Rev. Lett.*, **68**, 1303.
- DEBYE, P., 1929, *Polar Molecules* (New York: Chemical Catalogue, reprinted by Dover).
- FRIEDRICH, B., and HERSCHBACH, D., 1991a, *Z. Phys. D*, **18**, 153.
- FRIEDRICH, B., and HERSCHBACH, D., 1991b, *Nature (London)*, **353**, 412.
- FRIEDRICH, B., and HERSCHBACH, D., 1992, *Z. Phys. D*, **24**, 25.
- FRIEDRICH, B., and HERSCHBACH, D., 1993, *Collect. Czech. Chem. Commun.*, **58**, 2458.
- FRIEDRICH, B., and HERSCHBACH, D., 1995, *J. Phys. Chem.*, **99**, 15686.
- FRIEDRICH, B., and HERSCHBACH, D., 1996, *Z. Phys. D* (in press).
- FRIEDRICH, B., PULLMAN, D., and HERSCHBACH, D., 1991, *J. phys. Chem.*, **95**, 8118.
- FRIEDRICH, B., RUBAHN, H.-G., SATHYAMURTHY, N., 1992, *Phys. Rev. Lett.*, **69**, 2487.
- FRIEDRICH, B., SLENCZKA, A., and HERSCHBACH, D., 1994a, *Chem. Phys. Lett.*, **221**, 333.
- FRIEDRICH, B., SLENCZKA, A., and HERSCHBACH, D., 1994b, *Can. J. Phys.*, **72**, 897.
- GAUTSCHI, W., 1964, *Handbook of Mathematical Functions*, edited by M. Abramowitz, and I. Stegun (New York: Dover), p. 303.
- HERSCHBACH, D. R., JOHNSTON, H. S., and D. RAPP, 1959, *J. chem. Phys.*, **31**, 1652.
- KIM, W., and FELKER, P. M., 1996, *J. chem. Phys.*, **104**, 1147.
- LANGEVIN, P., 1905, *J. de phys.*, **4**, 678.
- LI, J. C. M., and PITZER, K. S., 1956, *J. phys. Chem.*, **60**, 466.
- LOESCH, H. J., and MÖLLER, J., 1992, *J. chem. Phys.*, **97**, 9016; 1993, *J. phys. Chem.*, **97**, 2158.
- LOESCH, H. J., and REMSCHEID, A., 1990, *J. chem. Phys.*, **94**, 4479; 1991, *J. phys. Chem.*, **95**, 8194.
- PITZER, K. S., 1937, *J. chem. Phys.*, **5**, 469; 1940, *ibid.*, **8**, 711.
- PITZER, K. S., 1953, *Quantum Chemistry* (New York: Prentice-Hall), pp. 227; 325–9.
- PITZER, K. S., and GWINN, W. D., 1942, *J. chem. Phys.*, **10**, 428.
- ROST, J.-M., GRIFFIN, J. C., FRIEDRICH, B., and HERSCHBACH, D. R., 1992, *Phys. Rev. Lett.*, **68**, 1299.
- SLENCZKA, A., FRIEDRICH, B., and HERSCHBACH, D. R., 1994, *Phys. Rev. Lett.*, **72**, 1806.
- STRATTON, J. A., MORSE, P. M., CHU, L. J., LITTLE, J. D. C., and CORBATÓ, F. J., 1956, *Spheroidal Wavefunctions* (New York: Wiley).
- VAN LEUKEN, J. J., BULTHUIS, J., STOLTE, S., and LOESCH, H. J., 1995, *J. phys. Chem.*, **99**, 13582.
- VAN VLECK, J. H., 1932, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press).