Brute Force Orientation of Asymmetric Top Molecules

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The versatility of the brute force orientation of polar asymmetric top molecules in a molecular beam has been investigated. In symmetric top molecules the electric field only mixes free rotor basis functions with different *J* but equal *K* and *M* values, but in asymmetric top molecules the mixing includes *K*, because of the asymmetry, in addition to field-induced *J*-mixing. This distinction is important with respect to the orientation behavior. For asymmetric top molecules all Stark curves for different *J*-states and different *K*-values, but equal *M*, in the corresponding symmetric eigenbasis, feature avoided crossings. Dependent on the velocity with which the molecules pass through the orientation field, these avoided crossings will be traversed adiabatically or nonadiabatically. For near-symmetric top molecules, such as iodobenzene, the crossings will in general be nonadiabatic, and, as expected, the behavior is similar to that of the corresponding symmetric top. If the crossings are adiabatic, the orientation behavior can be drastically different from the behavior of the corresponding symmetric top molecule. A strong asymmetry need not always be prohibitive in attaining a perceptible degree of orientation, as is demonstrated by the case of water.

1. Introduction

The introduction of the brute force orientation technique in molecular beam experiments by Loesch and Remscheid[1] in 1990, and, independently, by Friedrich and Herschbach in 1991,[2] made it possible to carry out experiments on oriented molecules not being symmetric tops—or their equivalents—as was necessary for applying the hexapole state selection method.

The brute force method has proved its feasibility now in a large number of experiments on oriented symmetric top molecules.[3] Recently, reactive scattering experiments on a number of asymmetric top molecules have been carried out in Bielefeld.[4] The results show significant orientation effects, of the order of what could be expected for the symmetric top equivalents. For an appropriate analysis of the experimental results it is necessary to make an assessment of the differences that can be expected between symmetric and asymmetric top molecules, and this is the aim of this paper.

In section 2 some basic theory is summarized for the calculation of the Stark effect of asymmetric molecules.[6−9] The assumption that will be made throughout this paper is that the molecular dipole moment is along one of the principal axes of inertia. In bromoethene, one of the molecules for which also orientation dependent scattering results have been observed recently,[4] the dipole moment is not along one of the principal axes. Then the description is complicated by the mixing of all *K*-states, including those between even and odd *K*-states. Another, less serious, complication we will not deal with here, is formed by hyperfine couplings, including nuclear quadrupole interactions. These couplings, which *e.g.* for methyl iodide can have a substantial effect up to field strengths of about 1 kV/cm, are much weaker than the Stark interaction in field strengths that are normally used for brute force orientation.

Some computational considerations are given in section 3. One of the main problems one has to cope with in an exact calculation (*i.e.* leading to a converged result) is the many crossings that may occur between Stark curves, in particular if part of these crossings are nonadiabatic, which is likely to be the case if the asymmetry is weak and the rotational constants are small.

In section 4 we compare the orientation behavior of polar asymmetric and symmetric top molecules for some specific eigenstates in an electric field. In section 5 a thermal distribution over rotational eigenstates is considered. The results are illustrated by calculations on iodobenzene, which is a nearly symmetric top and is exemplary for many weakly asymmetric molecules, and on water, which, in contrast, is a strongly asymmetric molecule, with very large rotational constants.

2. Theory

For a dipolar, prolate symmetric top molecule the rotational Hamiltonian in the presence of an electric field E can be written as

$$H = C\{\mathbf{J}^2 + (A/C - 1)J_z^{\,2} - w\cos\vartheta)\} \qquad (1)$$

where the reduced field strength, $w = \mu E/C$, characterizes the interaction energy relative to the smallest rotational constant. Energies are expressed in frequency units.

The eigenfunctions of the Hamiltonian in eq 1 are to lowest order equal to the free rotor functions $|JKM\rangle$, which can be expressed in Wigner rotation matrices $D^J_{MK}(\phi,\vartheta,\chi)$, where ϕ, ϑ, and χ are the Euler angles for the transformation from laboratory to molecular axes. The Stark energy is to first order equal to $-wKM/(J(J+1))$, which is linear in the field strength. With increasing field strength, mixing between states with J differing by unity, but equal K and M, has to be taken into account, leading to a tridiagonal Hamiltonian matrix of infinite dimension.[1,8]

For an asymmetric top K is not a good quantum number anymore. If symmetric top functions are used as a basis for describing the asymmetric top eigenfunctions, functions with K differing by 2 are being mixed (for the corresponding matrix elements, see *e.g.* ref 8). It is common practice[6,8] to denote the asymmetric top functions by the J quantum number with

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two subscripts K_- and K_+. K_- denotes the value of $|K|$ in the prolate symmetric top limit ($B = C$) and K_+ the value of $|K|$ in the oblate top limit ($A = B$).

To make full use of the D_2-group to which also the asymmetric top functions still belong, the symmetrized, or Wang, functions are normally used as a basis[8]

$$|JKMs\rangle = \frac{1}{\sqrt{2}}[|JKM\rangle + (-1)^s|J{-KM}\rangle] \qquad (2)$$

where for $K = 0$, $|J0Ms\rangle = |J0M\rangle$, and $s = 0$ or 1 for $K \neq 0$.

In calculating the eigenfunctions and energies of a dipolar asymmetric top in an electric field, the Hamiltonian matrix is truncated to the appropriate size (see section 3), such that a converged result is obtained. The eigenfunctions corresponding to a given parent state, defined by $J^{\mathrm{p}}_{K_-K_+}$ and M_{p} can then be written as

$$|J^{\mathrm{p}}_{K_-K_+},M_{\mathrm{p}};w\rangle = \sum_{J'=J_{\min}}^{J_{\max}} \sum_{K'_-=K_-^{\min}}^{K_-^{\max}} \sum_{s=0}^{1} c_{J_{K_-K_+}}(J',K'_-,M,s;w)\cdot|J',K'_-,M,s\rangle \qquad (3)$$

Here, p denotes the parent state. Only M_{p} is a good quantum number; *i.e.* $M = M_{\mathrm{p}}$. $J_{\min}$ is determined by either $|K_-|$ or $|M|$, whichever is largest, or by the lower cut-off value; $J_{\max}$ is the upper cut-off value of J. Similarly, $K_-^{\min}$ and $K_-^{\max}$ are the lower and upper cut-off values of K'_-, where $K_-^{\max} \leq J_{\max}$ and $|K_-^{\min}| \leq J_{\max}$. The summation is taken to include all positive−negative K'_- pairs. The difference of the wavefunction with the parent state function at zero field is indicated by the parametric dependence on the reduced field strength. The expansion has been written in terms of prolate symmetric top functions, and therefore K_+ is only used as a formal parameter to refer to the parent state.

The orientation probability density function (opdf, which is the probability of finding an orientation of the molecular axis system, such that the Euler angles ϑ and χ are in intervals (ϑ, $\vartheta + d\vartheta$) and (χ, $\chi + d\chi$)) can be obtained as shown previously for the case of a symmetric top.[1,9] In contrast to the symmetric top case, the opdf not only depends on ϑ but also on χ since states with different *J and K* (where we will henceforth drop the subscript (−)) do mix. If the dipole moment is along a principal axis, as we have assumed here, states with either even or odd K values mix, so that only rotation matrix elements $D^n_{0k}(\vartheta,\chi)$ with k even occur in the opdf. Then the opdf can be written as

$$P(\cos\vartheta,\chi) = {}^1\!/_2\Big(1 + \sum_{n=1}^{\infty} a^0_n P_n(\cos\vartheta) + \sum_{n=2}^{\infty} a^2_n[D^n_{02}(\vartheta,\chi) + D^n_{0-2}(\vartheta,\chi)] + \sum_{n=4}^{\infty} a^4_n[D^n_{04}(\vartheta,\chi) + D^n_{0-4}(\vartheta,\chi)] + \ldots\Big) \qquad (4)$$

The rotation matrix elements $D^{\,j}_{0k}(\vartheta, \chi)$ are directly related to the spherical harmonics $Y_{j-k}(\vartheta,\chi)$.[8] For a symmetric top there is not only axial symmetry around the electric field axis, but also around the molecular dipole axis, so that the χ dependence vanishes. In the scattering experiments we are interested in,[4] only the spatial distribution of the dipole is relevant and thus only the Legendre expansion coefficients, or orientational constants, a^0_n need to be considered. These coefficients are related to the averages of the Legendre polynomials as

$$a^0_n = (2n + 1)\langle P_n(\cos\vartheta)\rangle \qquad (5)$$

The most important parameter for the present study is $\langle P_1(\cos\vartheta)\rangle = \langle\cos\vartheta\rangle = a^0_1/3$, the "orientation".

TABLE 1: Rotational Constants and Dipole Moments of Iodobenzene and Water[a]

	iodobenzene	water
A (cm^{-1})	0.18919[b]	27.33[c]
B	0.02503[b]	14.575[c]
C	0.02210[b]	9.499[c]
μ (D)	1.70	1.82[e]
w	32.3	0.08

aAlso given are the reduced field strengths w for a field of 25 kV/cm. [b] Reference 10. [c] Reference 11. [d] Reference 12. [e] Reference 13.

3. Computational Considerations

For the calculation of the Stark effect for a pure state, mixing with a limited number of other J states is sufficient to lead to a converged result. The minimum size of the matrix that leads to convergence is, of course, dependent on the value of w. This means that a larger matrix should be taken if the rotational constant C is small. If a thermal distribution of rotational states is to be calculated, then, if C is small, many states are involved and many large matrices have to be diagonalized, unless extremely low rotational temperatures can be attained. For iodobenzene, all rotational constants are small and so is the difference between B and C (see Table 1, where also the rotational constants of water are given).

In the specific case of iodobenzene for each parent state, which to first order is given by symmetric top quantum numbers J_{p}, K_{p}, and M_{p}, we built a Hamiltonian matrix including J-values in the range ($J_{\mathrm{p}} - \Delta J$, $J_{\mathrm{p}} + \Delta J$) and K-values in the range ($K_{\mathrm{p}} - \Delta K$, $K_{\mathrm{p}} + \Delta K$), with $\Delta J = 8$ and $\Delta K = 8$. Later calculations showed that $\Delta J = 6$ and $\Delta K = 6$ give approximately the same result, although for the lower J_{p} values $\Delta J = 6$ does not yet lead to complete convergence. Probably, the range of K-values can be reduced further. Actually, since we use Wang functions, the calculation is done simultaneously for positive and negative K-values, but the matrix contains either only even or only odd K's. By including both signs of K, the calculations may be restricted to positive values of M, since $|J{-KM}\rangle$ and $|JK{-M}\rangle$, as well as $|JKM\rangle$ and $|J{-K}{-M}\rangle$, are always degenerate.

A J range of $J_{\mathrm{p}} \pm 8$ leads to a converged result when the opdf was calculated for the symmetric top that iodobenzene nearly is (taking $B_{\mathrm{s}} = C_{\mathrm{s}} = (B_{\mathrm{as}} + C_{\mathrm{as}})/2$). If the calculation is done for the K_{p} and M_{p} substates of a single J_{p} state in the asymmetric top case, the results may appear surprisingly sensitive to the choice of the J-range and convergence seems to be difficult to achieve. Such behavior, however, turns out to be a consequence of the assumption of avoided crossings, rather than of lack of convergence. As long as the crossings are avoided, all energy levels keep the order they have at zero field. This is a favorable situation from a computational point of view, because the bookkeeping is simple. If, however, some crossings are nonadiabatic, then a calculation is not feasible if many crossings occur as is the case for iodobenzene. For the latter molecule most, if not all, crossings will be traversed nonadiabatically. Then a calculation assuming avoided crossings can be expected to lead to completely incorrect orientation distributions for the various parent states in a thermal distributions. Carrying more J-states in the matrix can make things even worse, if one or more of these states have energy levels higher than the parent state at zero field, but lower at the orientation field strength, or just the other way around, since the parent state is then identified with yet another state. This

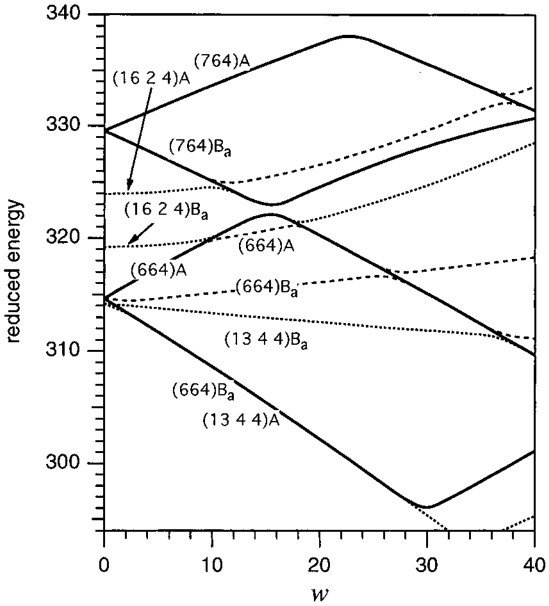

Figure 1. Effect of different degrees of mixing on the calculation of the orientation for parent states $|JKM\rangle = |6 \pm 6\ 4\rangle$ and $|JKM\rangle = |7 \pm 6\ 4\rangle$ (notation for the prolate top limit) of iodobenzene. The solid Stark curves are calculated allowing interactions with states up to $J = 12$. The dashed curves show the deviations from the the solid curves if, for the same (6 6 4) and (7 6 4) states, additional mixing with states up to $J = 16$ is allowed. The effect of this increased mixing is particularly large for the (6 6 4)B_a state, where the curve takes a completely different course as a result of an avoided crossing with the (13 4 4)B_a state near zero field. The change of the orientation on increased mixing can be appreciated by comparing the slopes of the dashed and solid curves, as far as they do not coincide, at the field strength of interest (here 25 kV/cm, corresponding with $w = 32.3$). The bends in the lowest and highest curves are due to avoided crossings with curves that are not shown. The gaps at the crossings appear greatly exaggerated as a result of the limiting number of calculated points (one per two w-units) and graphical smoothing of the curves.

point is illustrated in Figure 1 for two rather arbitrarily chosen states, $|JKM\rangle = |6 \pm 6\ 4\rangle$ and $|7 \pm 6\ 4\rangle$ (symmetric top limit) of iodobenzene. If many states are populated, one may expect that the incorrect identification of states, due to the inadvertent assumption of adiabatic crossings, averages out, and this appears to be the case indeed, as will be shown in the next sections. Then the number of J-states that is allowed to mix with a given parent state also does not seem to be critical.

The time determining step in the calculation is the diagonalization of the Hamiltonian matrices for all parent states that contribute to the distribution at a given (rotational) temperature. The diagonalization was carried out in two steps, by first bringing the matrix on tridiagonal form and then diagonalizing the resulting matrix.[16]

As stated before, the Hamiltonian matrix was built around the parent state diagonal matrix element(s) in a symmetric fashion. This is not at all the most efficient way for a computation. Since the distance between subsequent J-levels is $2J$, for given K and M values, whereas the off-diagonal matrix elements, $H_{J+1,J}$ and $H_{J-1,J}$, do not change much with J; if J is not too small, it would be obvious to take more lower-lying and less higher-lying J-levels. Due to the interfering level identification problems mentioned above, we have not attempted to optimize the computation by such an approach.

Another way to reduce the size of the matrix, which for iodobenzene with ΔJ, $\Delta K = 8$ can be up to 306 × 306, or with ΔJ, $\Delta K = 6$ up to 182 × 182, is to use nonsymmetrized symmetric top functions, rather than Wang functions. Using the latter means that the matrix always contains elements for states with positive as well as negative K. Using the unsymmetrized functions implies that the size of the matrix can be reduced by a factor of 2, giving a reduction in computational time by a factor of, roughly, 8.[16] Since the number of matrices to be diagonalized doubles, the net reduction in computation time will be about a factor of 4. An additional advantage is that the computer program can be simplified very much. We have pursued this idea, but for reasons explained below, it did not work out as anticipated.

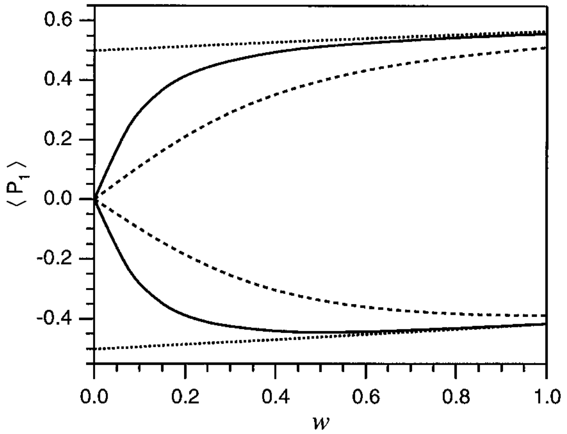

Figure 2. Average orientations as a function of reduced field strength w for the 1_{11} and 1_{10} states of iodobenzene (lower and upper solid curve, respectively), the corresponding symmetric top states $|1\ 1\ 1\rangle$ and $|1\ {-1}\ 1\rangle$ (dotted), and the 1_{11} and 1_{10} states of fluorobenzene (dashed). The latter has rotational constants $A = 0.1895$, $B = 0.0857$, and $C = 0.0589$ (see ref 6, p 633).

The above considerations are not important for the calculations on the water molecule. Here the number of parent states at a rotational temperature of 15 K is small (values up to $J_p = 3$ are sufficient for getting a converged result!), because of the large rotational constants. Moreover, because of the large asymmetry, the curve crossings are adiabatic.

Once the eigenfunction for the parent state has been calculated, the components of the opdf can be calculated very fast by using a recursive procedure for the computation of the three-j symbols in the Clebsch−Gordan series expansion of all products of rotation matrix elements that are contained in the square of the wavefunction.[9,14]

4. Selected *J*-States

Often the orientation distribution of the molecular z-axis, for iodobenzene coinciding with the dipole moment and the axis with largest rotational constant, is dominated by the orientation $\langle P_1(\cos\vartheta)\rangle = \langle\cos\vartheta\rangle$ and/or the alignment $\langle P_2(\cos\vartheta)\rangle = \langle(3\cos^2\vartheta - 1)/2\rangle$. In Figure 2 we have plotted the orientation as a function of the electric field to illustrate the principal distinction between asymmetric and symmetric top dipolar molecules. Plots are displayed for the 1_{11} and 1_{10} states for iodobenzene. The field dependence for the corresponding states $|1\ 1\ 1\rangle$ and $|1 - 1\ 1\rangle$ of a symmetric top with $C = (B_{as} + C_{as})/2$ are also shown. The molecular z-axis is chosen in the direction of the dipole moment so that the Stark effect is positive if K and M have equal signs and negative if the signs are opposite.

Clearly, because K is not a good quantum number, there is no first order linear Stark effect for the asymmetric top even if the asymmetry is very small. At $w \approx 0.6$, corresponding to a field strength of about 500 V/cm, the curve nearly coincides with that of the corresponding hypothetical symmetric top molecule. Because of the strong nuclear quadrupole coupling constant of iodine, even the symmetric top would actually not have a linear Stark effect up to about 1 kV/cm.[20] This does

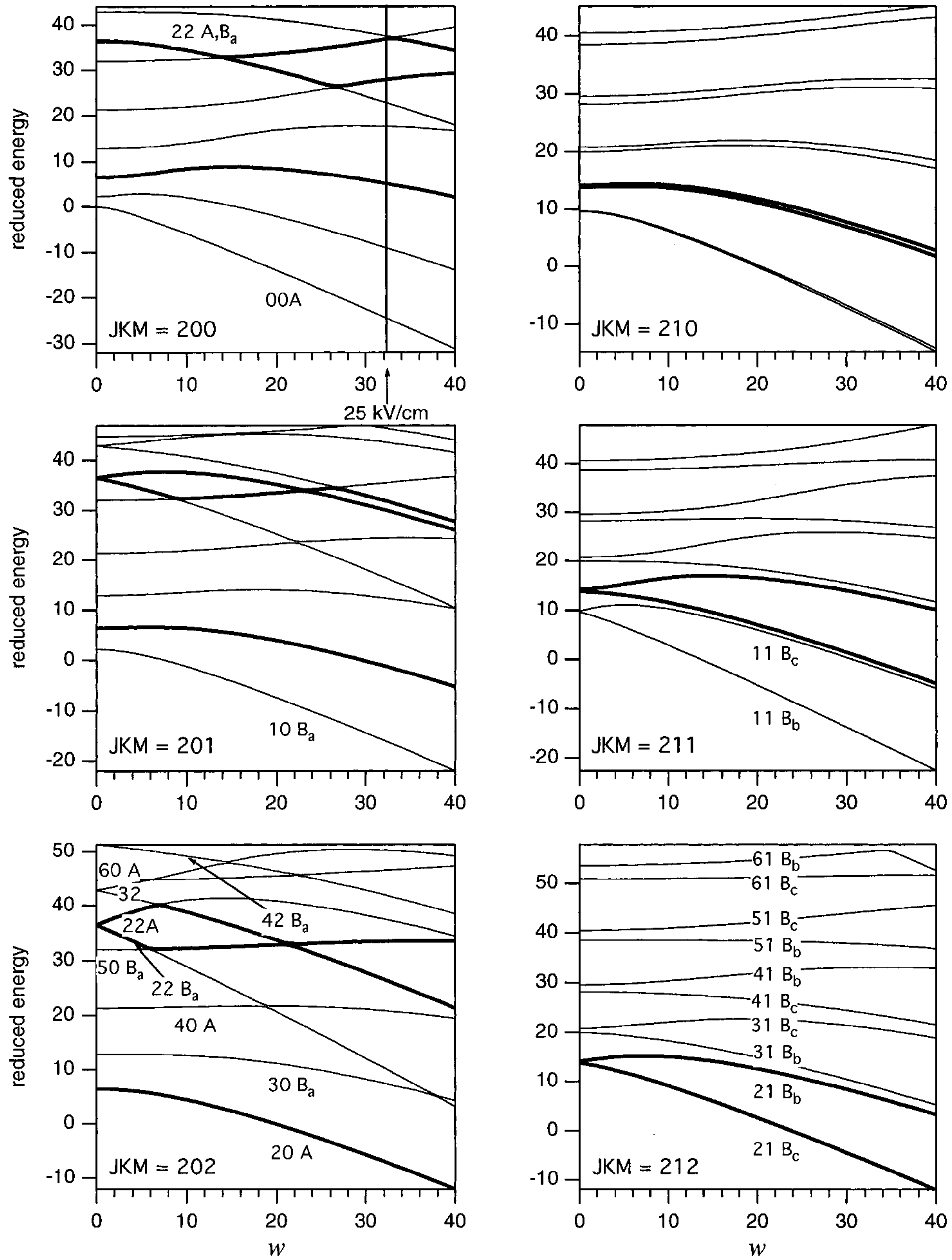

Figure 3. Stark curves for the $J = 2$ substates, and their closest neighbors with which they can interact, of iodobenzene. The parent state is indicated in the bottom left corner of each panel by the J, K_-, and M quantum numbers of the corresponding prolate symmetric top. Negative values of K_- are included by the use of Wang functions. Negative M values are not included; they lead to the same sets of curves. States are characterized by their J- and K_--values (M is always as in the parent state) and symmetry species given in the bottom panels; in the remaining panels the assignment is only given if new levels are involved, or for clarity, if curves coincide. All curves with $J = 2$ are drawn thick. The experimental field strength of 25 kV/cm,[4] corresponding with $w = 32.3$, has been indicated in the upper left panel.

not preclude molecules such as methyl iodide to be state-selected in an electrostatic hexapole field. The same will hold for iodobenzene, which only has some additional nonlinearity due to the asymmetry. So in practice the behavior of an asymmetric top could be much the same as that of its symmetric counterpart with only a small deterioration of the focusing due to the asymmetry. This is well-known, and it has been demonstrated a long time ago by Jones and Brooks.[15]

For the near-symmetric top molecule we consider here, the rotational constants are rather small, and in a thermal mixture molecules in many different rotational states are present, even at a low rotational temperature of 15 K. Then setting the hexapole field for selection of a specific $|JKM\rangle$ state (in the symmetric top limit) will also lead to focusing of molecules in a number of other states that have the same value of $KM/(J(J + 1))$. As a result, the virtue of the hexapole method, state selection, is largely lost.

The Stark interaction to first order only mixes A and B$_a$ symmetry species for K even and only B$_b$ and B$_c$ for K odd. In other words, the D_2 symmetry is broken by the electric field. Therefore, as suggested before in section 3 for computational reasons, one might as well choose to classify the asymmetric top functions to even and odd values of K of the symmetric top basis functions. Using the D_2 symmetry representations has, however, certain merits, as we will demonstrate below.

For the $J = 1$ states, the orientation of iodobenzene in a strong electric field is about the same as it would be in case of its symmetric equivalent. This seems, however, not to be the case for the $J = 2$ states. The reason is that here interactions with other states begin to interfere because of the presence of avoided

TABLE 2: Orientational Constants (See Equation 4) for the $J = 2$ Substates of Iodobenzene, Assuming Adiabatic and Diabatic Crossings and Using the Symmetric Top Approximation[a]

	asymmetric							
	adiabatic						diabatic	symmetric
	$w = 32.3$			$w = 33.6$			$w = 32.3$	$w = 30.6$
n	a_n^0	a_n^2	a_n^4	a_n^0	a_n^2	a_n^4	a_n^0	a_n^0
1	1.230			1.360			1.752	1.704
2	0.450	0.025		0.374	0.025		0.905	0.614
3	−0.374	0.005		−0.315	0.005		0.081	−0.344
4	−0.111	−0.022	0.000	−0.188	−0.024	−0.066	0.062	−0.246
5	0.494	−0.009	0.000	0.522	−0.015	−0.044	0.170	0.116
6	0.565	0.020	0.000	0.509	0.018	0.000	0.183	0.125
7	0.107	0.030	−0.000	0.007	0.031	−0.000	0.094	−0.029
8	−0.007	0.022	−0.000	−0.051	0.013	−0.035	0.088	−0.079

[a] For the adiabatic case results for two *w*-values (32.3 and 33.6) are given, corresponding to a dipole moment of 1.70 and 1.77 D, respectively. The other results are for a dipole moment of 1.70 D only. The field strength is 25 kV/cm. See text for further explanation.

TABLE 3: Orientational Constants of Iodobenzene, Calculated as Averages over a Thermal Rotational Distribution, with $T_{\text{rot.}} = 15$ K[a]

	I			II			III	D−L
n	a_n^0	a_n^2	a_n^4	a_n^0	a_n^2	a_n^4	a_n^0	a_n^0
1	0.064			0.060			0.060	0.071
2	0.002	−0.001		−0.001	0.000		0.001	
3	−0.003	0.000		0.016	−0.002		0.000	
4	0.004	0.002	0.000	0.001	0.011	0.005	0.000	
5	0.002	−0.000	0.000	0.010	−0.001	0.000	0.000	
6	0.011	0.002	−0.001	0.003	0.004	0.005	0.000	
7	−0.001	−0.001	−0.000	0.011	−0.001	0.000	0.000	
8	−0.002	0.001	−0.000	0.005	0.001	0.002	0.000	

[a] The field strength is 25 kV/cm. Results are given for three types of calculation: using a symmetrized symmetric top basis (I), using a nonsymmetrized basis (II), and assuming a symmetric top (III). The definition of the orientational constants is given in eq 4. Also given is the value of a_1^0 using the Debye−Langevin equation (D−L).

crossings of Stark curves. In Figure 3 the thick curves are the Stark curves for all different $J = 2$ parent states. Only for $K = 2$ are there avoided crossings with other states. If the crossings are traversed adiabatically, as is suggested by the thick curves, then one ends up with an orientation that is lower than is to be expected for the symmetric top case where the curves shown do cross. Indeed, if the calculation is repeated under the assumption of nonadiabatic crossings, the orientation (determined by the value of a_1^0) is comparable to that for the symmetric case. In Table 2 the first eight Legendre coefficients for the expansion of the orientation probability density in terms of Legendre polynomials are given for three calculations, with adiabatic—for two *w* values—and nonadiabatic crossings, and with the approximation of a symmetric top.

The rotational temperature was taken to be 15 K and the field strength 25 kV/cm. For iodobenzene this field strength corresponds with $w = 32.3$, indicated by the vertical line in the top left panel in Figure 3. If the dipole moment is assumed to be 5% higher, *i.e.* 1.77 D, then $w = 33.6$, which is just at the opposite side of the crossing of the upper $|2\ 2\ 0\rangle$ curve with the lower $|3\ 2\ 0\rangle$ curve (upper left panel). As a result, the orientation at this *w*-value is expected to be disproportionately higher than the one at $w = 32.3$, and this is indeed what is found (see Table 3).

The degree of orientation for nonadiabatic crossings is larger than for the symmetric top approximation. This can be attributed to the larger rotational constant $C' = (B + C)/2$ for the symmetric top and a correspondingly smaller value of *w*. The higher Legendre moments are apparently much more sensitive to a change of *w*, which concurs with previous results.[9] The orientation constants $c_n{}^2$ and $c_n{}^4$ are even more sensitive on the particular state and to changes in *w*, to such an extent that we consider their values dubious.

Though not so relevant for the present comparison, we have assumed that the distribution over the *K*-states is given by a Boltzmann distribution at zero field and that it can be characterized by a single rotational temperature. Furthermore, we have taken into account the spin statistics (*vide infra*).

The assumption of adiabatic crossings for a near-symmetric top, such as iodobenzene, is unlikely to be justified. The criterion for adiabatic passage is given by the inequality (ref 17)

$$\frac{(\partial H_{\text{Stark}}/\partial t)_{ij}}{\omega_{ij}(E_i - E_j)} \ll 1 \qquad (6)$$

where $(\partial H_{\text{Stark}}/\partial t)_{ij}$ is the time derivative of the matrix element of the Stark interaction that couples states *i* and *j*, and ω_{ij} is the frequency gap in the crossing point, corresponding to the energy difference $E_i - E_j$. The gaps at the curve crossings are very narrow, of the order of 100 kHz, and are therefore not perceptible in Figure 3. The region where the electric field is 25 kV/cm is roughly 1 cm and is passed by the molecules in about 5 μs. Assuming that the matrix element varies linearly with the field, the left hand term in eq 6 is about 250, so that the adiabatic condition is not fulfilled.

Admittedly, this estimation is crude, because the field gradient at the field strength where the crossing occurs is decisive for evaluating inequality 6, but it is still fair to say that most of the crossings, not only for $J = 2$, in iodobenzene will be nonadiabatic. A quantitative analysis of the crossings can, in principle, be done by a Landau−Zener type of approach.[18,19] But such an analysis is fully untractable for a thermal distribution of rotational states of iodobenzene or comparable, nearly symmetric top molecules for two reasons: first, because of the formidable computational capacity required and, second, because of the small gain in accuracy compared to a calculation based on the assumption of adiabatic crossings.

5. Thermal Distributions of Rotational States

For the lowest *J*-states it is a simple matter to analyze the results of the opdf calculation by studying the crossings of Stark curves, as we have just done for $J = 2$ (Figure 2) in the case of iodobenzene. This molecule has small rotational constants, and therefore the rotational temperature has to be made very low in order to get a reasonably narrow distribution of states. In Figure 4 the distribution over the *J* states is plotted, assuming a Boltzmann distribution with a rotational temperature of 15 K. The population of each *J*-state is summed over all *M*-states and all *K*-substates. The latter are also assumed to be populated

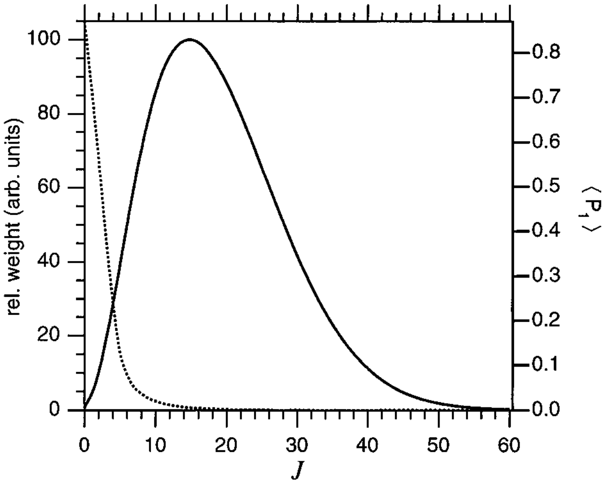

Figure 4. Boltzmann distribution of J-states of iodobenzene at zero field, for a rotational temperature of 15 K. J is taken to be a continuous variable. Also shown is the calculated orientation $\langle P_1 \rangle$ (right hand axis) as a function of J.

according to a Boltzmann distribution with a rotational temperature of 15 K. The population of states with $|K| > 16$ can be neglected. The curve in Figure 4 up to $J = 40$ has been calculated by considering iodobenzene as an asymmetric top. For $J > 40$ this curve has been extrapolated to smoothly follow the curve for the symmetric top case. The difference between the two curves for $J < 40$ is very small and not visible on the scale in Figure 4. Evidently, many J-states are populated, with a maximum at $J = 14$. To reduce the computation time calculations were done up to $J = 40$, whereas $|K|$-values up to 16 were included. Since only the tail of the distribution is left out, the error in extrapolating the results to $J = 60$ is small. Also shown in Figure 4 is $\langle P_1 \rangle$, also given as a continuous function of J. For each J the ensemble average over all K- and M-substates is taken. Clearly, $\langle P_1 \rangle$ decreases rapidly with J, but the weight function increases sharply, so that results around $J = 5$ will have a relatively large effect on the thermal average over all J-values.

The results of three types of calculation are shown in Table 3. The expansion coefficients of the opdf are the result of ensemble averaging and should be distinguished from those for molecules in a single state. Type I calculations make use of a symmetrized Wang basis, so each matrix diagonalization is done for positive and negative K-values simultaneously. In other words, nearly degenerate K-states with positive and negative Stark effects at weak field are included. For type II calculations the computer program was simplified by using the symmetric top eigenbasis. Then for each parent state a matrix has to be diagonalized that involves only K-substates within a certain range of only one component of a nearly degenerate K-substate (at zero field). Type III calculations are done by neglecting the asymmetry of iodobenzene. Here, for parent states with $J = 35$ and higher, numerical instabilities are observed, which manifest themselves by rather large discontinuities in the values of the Legendre moments c_2 and higher. These values are discarded in the extrapolation to $J = 60$.

In addition, the calculations should take care of the proper spin statistics. For iodobenzene the symmetric top basis functions are symmetric under rotation over π about the symmetry axis for K even and antisymmetric for K odd. Since by this rotation two pairs of spins $-\,{}^1/_2$ are interchanged, spin statistics gives weights 10 and 6 for K even and K odd states, respectively (see ref 6, p 104). Type II and III calculations have been carried out using an unsymmetrized basis, but this does not affect the statistical weights. Including the spin statistics only gives rise to small oscillations in the results for subsequent J values, but owing to the many J-states involved, the net effect on the thermally averaged results is negligible.

The results in Table 3 show that type I and III calculations give approximately the same value of a_1^0, the parameter that determines the average orientation of the dipole moment. The value for type I is slightly higher, which is in agreement with the difference in w, caused by the larger value for the rotational constant C for the symmetric top.

The value of a_1^0 found from type II is not equal to the value from type I, but slightly smaller. So it appears that the two types of calculation are not completely equivalent. This can be explained as follows. In type I calculations (nearly) degenerate K-states are treated on the same footing, so that Stark curves with positive and negative initial slopes are included. As a result, the incidence of curve crossing with a given parent state, which may correspond to a Stark curve with either a negative or positive slope, is enhanced. In type II calculations half of the curves are left out. This reduces the number of curve crossings, but curve crossings that do occur will in general correspond to zero-field states that are further apart than in type I calculations. As a consequence, since all crossings are treated as avoided crossings, states are interchanged that may have an appreciably different statistical weight. Then the effect of an exchange of states is self-compensating to a lesser extent.

A same reasoning may apply to the higher Legendre coefficients. These show much larger fluctuations between J-states than does a_1^0. As has been shown previously,[9] and as also can be seen in the calculation for the $J = 2$ states given above, the dependence of these coefficients on the particular state is much stronger than for a_1. Then an interchange of states may not be self-compensating anymore, even if the zero-field energies of these states do not differ very much. Therefore we do not regard these thermally averaged higher order coefficients as reliable. Accurate values can only be obtained by a careful analysis of all crossings, and even then accumulation of round-off errors may spoil the results. Since in the case of iodobenzene most crossings will be traversed nonadiabatically, the results for the symmetric top approximation can be expected to be more reliable. In the latter approximation the higher Legendre polynomials are very small compared to $\langle P(\cos \vartheta) \rangle$. This is in agreement with earlier results for methyl iodide.[1,21]

It is of interest to compare the values of a_1^0 with that obtained by the Debije−Langevin equation, which in the present case can be written as $a_1^0 \approx \mu E/(2kT)$. The value so obtained, $a_1^0 = 0.068$, is larger than the other a_1^0 values in Table 3, but in the Debije−Langevin approximation the dipoles are in thermal equilibrium in the presence of the field, whereas in the above calculation the distribution of states is for zero field.

The larger part of the above discussions was devoted to calculations on iodobenzene, because of the complications that arise from the abundancy of (weakly) interacting states. For the water molecule the calculations are simple by comparison.

The rotational constants of water are given in Table 1. Since the smallest rotational constant is still large, very strong fields are necessary in order to attain reasonable w-values. With a field strength of 25 kV/cm, w is only 0.08, in large contrast to iodobenzene where $w = 32.3$. The coupling to the electric field is therefore very weak, and by no means is a “brute force” exerted. The orientation that nonetheless can be obtained is mainly to be attributed to the rotational cooling. In Table 4 the calculated orientational constants are given for a field strength of 25 kV/cm and a rotational temperature of 15 K. At this rotational temperature the $J = 3$ population is negligible.

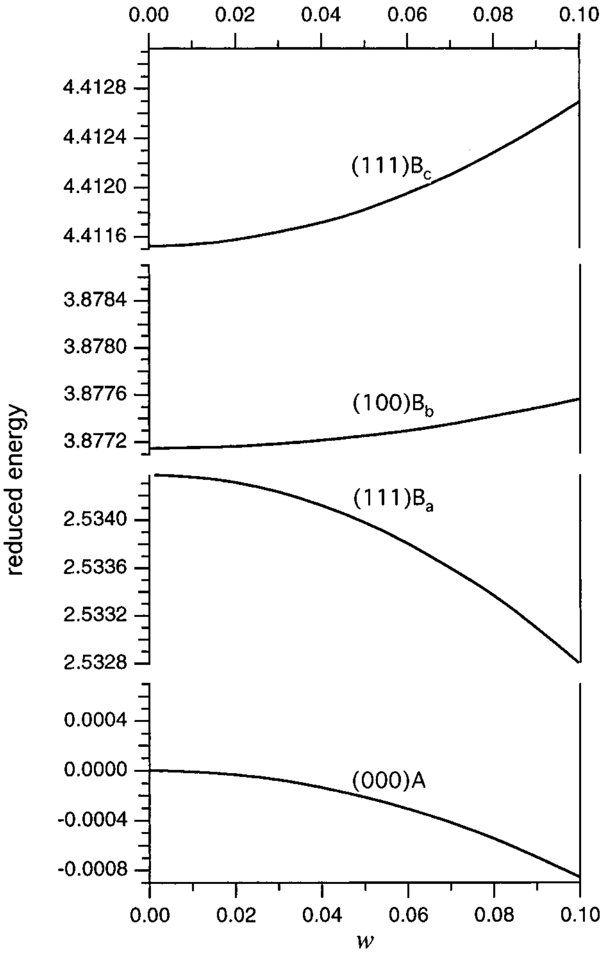

Figure 5. Stark curves for H_2O. Only those states are represented that give significant, if small, Stark effects. States are denoted by J, $|K|$, and $|M|$, and D_2 symmetry representation, defining the corresponding parent state Wang functions. K represents the projection of **J** on the molecular symmetry axis in the intermediate case symmetric top limit. All curves are on the same scale.

TABLE 4: Orientational Constants of Water, Calculated as Averages over a Thermal Rotational Distribution, with $T_{\mathrm{rot.}}$ = 15 K, for Two Field Strengths

	E = 50 kV/cm		E = 25 kV/cm	
n	a_n^0	a_n^2	a_n^0	a_n^2
0	1.0000		1.0000	
1	0.0826		0.0414	
2	0.0015	0.0013	0.0004	0.0003

The Stark curves for the four only relevant states are shown in Figure 5. The energies for higher J-states, which have no significant population anyway, are virtually field independent over the small w-range of Figure 5. Because of the dominance of the lowest states, it is not surprising that all Legendre moments, except $\langle P_1\rangle$ and $\langle P_2\rangle$, are found to be zero. Of the average spherical harmonics, only $\langle Y_{22}\rangle$ is nonzero. In the calculation, the molecular z-axis has been chosen as the b-axis, so K refers to this axis. States with even K have a spin-statistical weight of 1; states with odd K, a weight of 3 (see ref 6, p 104). The populations of even and odd K-states must be in the same proportion as in the initial gas at room temperature, and the statistical weights are correspondingly corrected.

6. Concluding remarks

The orientational behavior of a dipolar asymmetric top molecule in an electric field is in general markedly different from that of the symmetric top equivalent. This is mainly due to the effect of avoided crossings of states with different K-values, which are allowed crossings for symmetric top molecules. From a computational point of view it is desirable that avoided crossings are either all traversed adiabatically, since then the order of the energy levels that correspond with a given set of parent states is independent of the field strength, or all traversed diabatically. The latter is likely to be the case for iodobenzene by virtue of its weak asymmetry. In such a case the assumption of avoided crossings, apart from being unduly time-consuming, may lead to erratic results, in particular if the rotational constants are large and thus the number of populated states small. Iodobenzene has small rotational constants and therefore many populated states, even at relatively low rotational temperatures. Here the assumption of avoided crossings appears to lead to self-compensating errors as far as the calculation of the average orientation is concerned. Clearly, in such a case the assumption of a symmetric top is indicated.

The situation is contrastingly different in the case of water. Here application of a field of 25 kV/cm is a very modest perturbation, and the term brute force is not appropriate here. The orientation of about 1.4% that can still be attained at a rotational temperature of 15 K is largely a consequence of this low temperature, where only the few lowest rotational states of water are populated.

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