How Predictable Are IR Transition Moment Directions? Vibrational Transitions in Propene and Deuterated Propenes

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Abstract: Transition moment directions of mid-infrared transitions in four isotopomers of propene, $CH_2{=}CHCH_3$, $CH_2{=}CDCH_3$, $CD_2{=}CHCD_3$, and $CD_2{=}CDCD_3$, have been determined from linear dichroism spectra recorded in stretched polyethylene as solvent. The results were compared with expectations based on bond directions and with results of *ab initio* calculations at levels of approximations ranging up to CCSD/6-311G**. The former procedure is found to be unreliable, even for high frequency vibrations. With rare exceptions, the highest levels of ab initio theory agree with the experimental directions to within about ±20°, and for intense transitions, to within the experimental uncertainty of about ±(5−10)°.

Introduction

Accurate knowledge of IR transition moment directions in molecules is important in spectral assignment and in many applications, such as interpretation of vibrational circular dichroism (VCD) and studies of alignment in organized molecular assemblies.[1] In highly symmetric molecules, these directions are frequently obvious from the nature of the vibration. In low-symmetry molecules, it is tempting to use local symmetry to estimate the polarization directions of those characteristic vibrations that are believed to be sufficiently localized to carry specific labels. In effect, this amounts to assuming transferability for these vectorial quantities. For instance, the symmetric CH stretching vibration of a terminal methyl group on an alkane chain in a monolayer is often assumed to lie in the direction of the $C{-}CH_3$ bond. How justified is such an assumption?

Little is known about this at present with certainty, although the issue is clearly important. An answer may be sought in experiments or calculations. For some time, *ab initio* calculations of vibrational spectra of small organic molecules have been able to predict relative frequencies and intensities of vibrational transitions with a useful accuracy.[2] However, transition moment directions in molecules of low symmetry are much more sensitive to computational details, and it is not yet clear which one of the usually employed levels of theory is sufficient to predict them reliably, or whether the commonly used harmonic approximation is capable of predicting them reliably at all. The experimentally determined directions also provide a useful test for the ability of computational methods to describe molecular force fields and charge distribution.

At this point, experimental data are therefore definitely needed, but few are available.[3−5] Once a procedure for a reliable calculation of transition moment directions in low-symmetry molecules has been clearly established, it will be possible to learn more about the degree of transferability of IR polarization directions by computational means.

The best molecules for answering our question experimentally, and also for testing calculational procedures, are those whose symmetry (e.g., C_2 or C_s) permits an unlimited number, but not all, transition moment directions. In higher symmetry molecules, all transition moments are constrained to lie in one of a small number of directions, e.g., for the point groups C_{2v}, D_{2h}, or D_2, in one of the three molecular axes x, y, or z. Although the knowledge of these transition moment directions is very useful for state symmetry assignment, they rarely provide a demanding test of the methods of calculation used. If the molecule has no symmetry at all (C_1), experimental determination of transition moment directions tends to be very difficult. For the present study, we have chosen the C_s symmetry molecule, propene $CH_2{=}CHCH_3$ (**1**), and its isotopomers $CH_2{=}CDCH_3$ (**2**), $CD_2{=}CHCD_3$ (**3**), and $CD_2{=}CDCD_3$ (**4**). The symmetry plane is defined by the three carbon atoms, and possible complications due to the rotation of the methyl group are ignored. In earlier studies[6−11] of the vibrational spectra of **1**, **2**, and **4**, many of the fundamentals were assigned correctly, but some reassignments will be proposed below.

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Experimental determination of transition moment directions is possible by several methods.[1] Perhaps simplest of these is the use of an aligned sample for measurement of linear dichroism (LD), defined as the difference in absorbance for linearly polarized light with the electric vector along the unique sample axis Z and perpendicular to it, along Y. Although such measurements can be performed on single crystals if their structure is suitable,[12] they are then rather tedious. Another procedure is to analyze intensities in the rotational structure in a gas-phase spectrum.

The procedure employed presently is to use a thin sheet of stretched polyethylene (PE) as the aligning solvent.[13] PE easily dissolves large amounts of many nonpolar solutes. When stretched 400−500%, it provides a sufficient degree of alignment for most of them, and strong base-line absorption is limited to a few narrow regions in the infrared. By also performing the measurements in perdeuterated polyethylene (PE-d_4), the latter regions may be shifted, thereby making studies of the whole infrared region possible.

Alignment in a thin sheet of PE is uniaxial, and the stretching direction is the unique alignment axis Z. The uniaxial nature of the alignment means that only limited information on IR polarizations can be obtained, and the nature of the alignment is much less well known than in a crystal. The great ease with which the measurements can be performed provides a compensation for these shortcomings. For nonpolar molecules, alignment is dictated by molecular shape, in that the longest molecular axis (perpendicular to the smallest molecular cross-section) tends to align along Z, the shortest perpendicular to it. The alignment mechanism has been the subject of considerable study.[14]

Experimental Section

Unlabeled propene (**1**, 99%) was purchased from Matheson, and the deuterated (>98%) propenes **2**−**4** were purchased from Merck Co. They were used without purification. Sheets of ordinary polyethylene (Du Pont Co.) and perdeuterated polyethylene (Merck Co.) were stretched to 500% and mounted one about 15 mm above the other in a copper holder attached to the cold finger of an Air Products (Displex 202-E) closed-cycle helium refrigerator. After evacuation of the vacuum shroud, the sample was placed in the FTIR instrument and cooled to 12 K, and base lines for two perpendicular directions of an IR polarizer were determined for the ordinary polyethylene sheet. The position of the cryostat was firmly locked in the FTIR instrument, in order to preserve the base-line absorption. Later, propene was introduced into the vacuum shroud and the sample was warmed to room temperature. After 4−6 h, the polymer was saturated with propene. It was cooled to 10−20 K above the melting point of propene (88 K), and the vacuum shroud was evacuated. Finally, the stretched sheet, now containing propene, was cooled again to 12 K and two polarized spectra of propene oriented in ordinary polyethylene were obtained. Then, the cryostat position was unlocked and the cryostat was lifted approximately 15 mm, thereby placing the perdeuterated polyethylene sample in the infrared light path. After measurement of two linear dichroism spectra in PE-d_4 the cryostat was warmed again to room temperature and the propene was completely removed to a liquid nitrogen trap. The cryostat was then cooled to 12 K, and the two sets of polarized base lines were determined. The same procedures were performed with the deuterated propenes. The FTIR instrument (Nicolet 60-SXR) was equipped with IGP-225 (KRS-5) or IGP-227 (CaF_2) wire grid polarizers purchased from Cambridge Physical Sciences, Ltd. The spectral resolution was set to 1 cm^{-1}.

Computational Details

Infrared spectra were calculated in the double harmonic approximation at geometries constrained to C_s symmetry but otherwise fully optimized (the methyl group is oriented with one of its CH bonds eclipsed with the C=C double bond). At the HF and MP2 levels, we used the Gaussian 92[15] set of programs and at the coupled cluster (CCSD) level, the ACES[16] set. The basis sets used in HF calculations were 3-21G,[17] 6-31G,[18] 6-31G*,[18] 6-31G**,[18] 6-31+G**,[18,19] and 6-311+G**.[19,20] The last named set was also used for MP2 calculations. The CCSD calculations were performed with a 6-311G**[20] basis set.

The absolute value of the largest of the six frequencies that correspond to rotation and translation was always below 2 cm^{-1}, except in the HF calculation with the 6-311+G** basis set, in which the geometry optimization was only rough and these frequencies ran up to 20 cm^{-1}. With this basis set, an accurate optimization was performed only at the MP2 level. None of the 21 vibrational frequencies were imaginary.

Data Evaluation Method[1]

Alignment in Laboratory Frame. The orientational information on a uniaxially aligned sample accessible from an absorption experiment is limited to the squares of the cosines of the angles between the observed transition moments and the unique sample axis, averaged over the molecules in the sample. Neglecting the effect of solvent birefrigence on the spectral properties of the solute, one obtains for absorbance E_Z (E_Y) measured with the electric vector parallel (perpendicular) to the unique sample axis Z

$$E_Z = \sum \langle \cos^2(Z,\boldsymbol{M}_i)\rangle A_i \qquad (1)$$

$$E_Y = (1/2)\sum [1 - \langle \cos^2(Y,\boldsymbol{M}_i)\rangle] A_i \qquad (2)$$

where the sum is over all transitions i, $\boldsymbol{M}_i$ is the transition moment of transition i, assumed to be firmly anchored in the molecular framework, $(Z,\boldsymbol{M}_i)$ is the angle it forms with sample axis Z, and A_i describes the intrinsic absorbance contribution from transition i (three times its contribution to the absorbance of an isotropic sample of the same concentration and optical path). Here and elsewhere, the pointed brackets indicate averaging over all observed molecules.

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We define the orientation factor K_i of the i-th transition as $K_i = \langle \cos^2(Z,\boldsymbol{M}_i)\rangle$. In the absence of overlap between transitions, K_i can be determined from the absorbances $E_Z(i)$ and $E_Y(i)$ measured for the i-th transition:

$$K_i = E_Z(i)/[E_Z(i) + 2E_Y(i)] \tag{3}$$

Alignment in the Molecular Frame. The relation between the average alignment of a transition moment $\boldsymbol{M}_i$ with respect to the laboratory frame, described by K_i, and its direction in the molecular frame, described by direction cosines in the molecular x, y, z frame, is

$$K_i = \boldsymbol{c}_i^{\dagger}\mathbf{K}\boldsymbol{c}_i \tag{4}$$

where $\boldsymbol{c}_i$ is the column vector of direction cosines ($\cos \phi_x^{\,i}$, $\cos \phi_y^{\,i}$, $\cos \phi_z^{\,i}$) and

$$\mathbf{K} = \langle \cos u \cos v\rangle, \quad u, v = x, y, z \tag{5}$$

is the molecular orientation tensor. We diagonalize $\mathbf{K}$ by choosing the molecular axes x, y, and z to be its principal axes. The orientation factors of the molecular axes (the principal orientation factors) are the principal values of $\mathbf{K}$: $K_x \equiv K_{xx} = \langle \cos^2\underline{x}\rangle$, $K_y \equiv K_{yy} = \langle \cos^2\underline{y}\rangle$, and $K_z \equiv K_{zz} = \langle \cos^2\underline{z}\rangle$, respectively, where $\underline{u}$ is the angle of axis u with Z. The labels of the axes are chosen such that $K_z \geq K_y \geq K_x$; i.e., the direction of the axis z in the molecular framework is defined as the one that is aligned the best with Z and corresponds to the highest possible value of K. It is called the effective orientation axis. The axis x is the one whose average alignement with Z is the worst.

For the moment, we leave aside the issue of direction cosine sign ambiguities that result from the fact that only the second powers of these quantities enter the fundamental expressions used. Then, the desired information on the directions of the transition moments $\boldsymbol{M}_i$ in the molecular frame requires, first, the knowledge of five items that are common to all transitions and characterize the orientation tensor, and second, two additional pieces of data for each transition i, which will define the orientation of its transition moment $\boldsymbol{M}_i$ in the principal axes system x, y, z. The five common items are the three rotation angles that define the positions of the three principal axes of $\mathbf{K}$ relative to some arbitrarily chosen initial axes and two of the principal values of $\mathbf{K}$. The third principal value (orientation factor) is determined by the relation

$$K_x + K_y + K_z = 1 \tag{6}$$

In the general case, the number of unknowns is excessive. However, in many molecules, symmetry dictates all three directions of the principal axes and confines all of the transition moments directions to these axes. Then, the labels on the axes and the values of the orientation factors are the only unknowns. A solution of the labeling problem is usually facile, since numerous comparisons with absolute polarization directions obtained from other sources have amply demonstrated that the alignment of planar nonpolar molecules in PE is such that the directions of the principal axes are dictated by molecular shape. In particular, the position of the molecular "long axis" z in the molecule can usually be estimated, and for planar unsaturated and aromatic molecules the "short axis" x is perpendicular to the molecular plane. The problem of finding the two unknown orientation factors is then typically overdetermined. Clear relations between molecular shape and their values have been found and permit predictions of values to be expected for molecules of related shape.

The most interesting case is that of molecules such as propene whose symmetry dictates only one of the principal axis directions (in C_s propene, the out-of-plane direction, x), and constrains the transition moment directions to lie either in x or perpendicular to x. Two of the elements of $\mathbf{K}$ then vanish by symmetry and one diagonal element is equal to the orientation factor of x, easily determined from the dichroism of any of the transitions polarized along x, for all of which, $K_i = K_x$. The remaining two unknowns can be chosen to be K_z and the angle ω that defines the location of the orientation axis z in the yz plane relative to some arbitrarily chosen direction in the molecular framework (say, relative to the C=C direction in propene). If both of these two unknowns can be found somehow, the transition moment determination problem becomes soluble in absolute terms not only for the x-polarized transitions but also for those polarized in the yz plane. There will be one observed value K_i for each such transition, $K_y \leq K_i \leq K_z$, and one unknown direction cosine, defining the angle $\phi_z^{\,i}$ between $\boldsymbol{M}_i$ and the orientation axis z. Their relation is

$$\tan^2 \phi_z^{\,i} = (K_z - K_i)/(K_i - K_y) \tag{7}$$

As long as the value of the orientation factor K_z can be determined, useful information is obtained. Even though the angle ω, i.e., the absolute direction of the orientation axis z, cannot be estimated accurately from molecular shape, at least the transition moment directions relative to the unknown direction of the orientation axis can be derived. If several solutes differing only by isotopic substitution and thus nearly identical shapes are studied, their orientation tensors are virtually identical,[4,21] and relative directions of transition moments in the isotopomeric series are obtained. Often, however, it appears that ω can be estimated from molecular shape to within $\pm(10-20)°$.

In the absence of any other information, such as orientation factors of symmetrical molecules of related shape, limits for K_z can usually be derived from the condition that it must be larger than any actually observed K_i, and from the condition that $K_y = 1 - K_x - K_z$ must be smaller than any K_i actually observed for a transition polarized in the yz plane. Often, only a narrow range of admissible K_i values results.

Finally, we return to the issue of sign ambiguity. In the specific case of molecules of symmetry such as C_s it merely permits the determination of the absolute value $|\phi_z|$, and not its sign, $sgn\ \phi_z$. As a result, unless ϕ_z equals 0° or 90°, the experiment produces two possible directions for each transition moment in the molecular frame

$$\alpha = |\phi_z|\ sgn\ \phi_z - \omega \tag{8}$$

one for $sgn\ \phi_z = 1$ and one for $sgn\ \phi_z = -1$. An experimental decision between them is sometimes possible, e.g., from comparison of a series of molecules of related shape or from comparison with results of polarized emission measurements.

We have used this type of treatment for several molecules of C_s symmetry in the past.[22-24] In the following, we apply it to propene and its isotopomers.

Results

Illustrative LD spectra (**1** and **2**) are shown in Figures 1 and 2. Experimental and computational results are compared in

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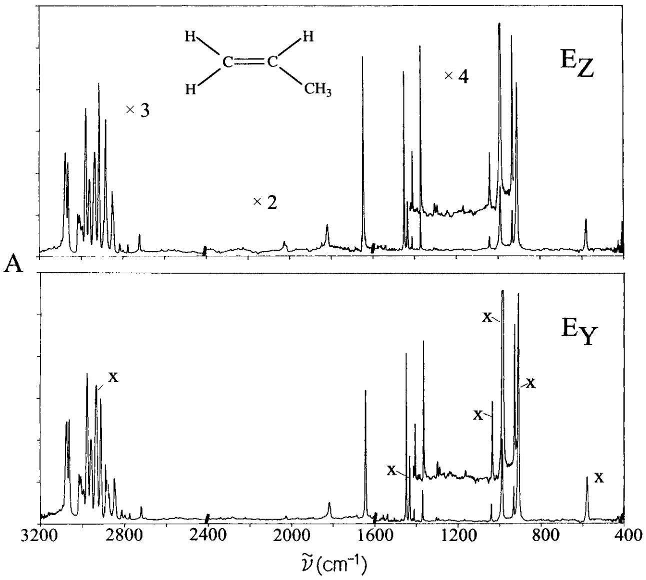

Figure 1. Polarized infrared absorption spectra of $CH_2{=}CHCH_3$ (**1**) dissolved in a polyethylene matrix at 12 K. Absorbance measured with the electric vector of the light oriented parallel (top) and perpendicular (bottom) to the stretching direction *Z*. Out-of-plane transitions are marked with *x*. The regions between 2400 and 1500 cm^{-1} and 1300 and 400 cm^{-1} were measured in PE, and the remainder of the spectrum in PE-d_4.

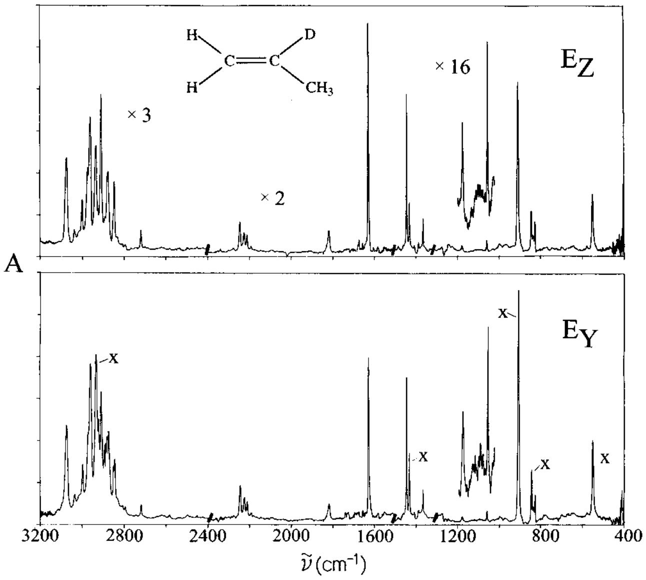

Figure 2. Polarized infrared absorption spectra of $CH_2{=}CDCH_3$ (**2**) dissolved in a polyethylene matrix at 12 K. Absorbance measured with the electric vector of the light oriented parallel (top) and perpendicular (bottom) to the stretching direction *Z*. Out-of-plane transitions are marked with *x*. The regions between 2400 and 1600 cm^{-1} and 1300 and 400 cm^{-1} were measured in PE, and the remainder of the spectrum in PE-d_4.

Tables 1−4. Table 5 shows the experimental transition moment directions obtained for similar vibrational modes in different isotopomers (**1**−**4**) and compares them with simple-minded expectations based on the nature of the vibrational motions involved. The descriptive labels for the normal modes of vibration were derived by visual inspection[25] of the normal modes calculated at the MP2/6-311+G** level and remained the same at other levels of calculation.

Orientation Factors. Figure 3 shows a plot of the orientation factors K_i in PE for all observed transitions. Those expected to be associated with out-of-plane polarized vibrations are grouped closely around a low value (0.24−0.27), which clearly needs to be identified as K_x. The rest are spread out in a separate region at higher values (0.29−0.43), and they clearly must lie between K_y and K_z. The spread of the values observed for K_x exceeds the statistical error of measurement, which affects only the third decimal place, and we believe it to be partly due to perturbations of the transition moment directions by the effects of the environment. Whatever its origin, it ultimately limits the accuracy with which the transition moments can be determined from the data available.

The values of the orientation factors differ very slightly between PE and PE-d_4. This is a convenient coincidence. In general, every batch of PE produces slightly different solute alignment, even if stretched to the same degree.

Considering the four propene isotopomers as a group, and assuming that they all orient in the same way,[4,21] the following orientation factor values were obtained for PE [PE-d_4]: (i) the average K_x was 0.262 [0.259] for out-of-plane polarized transitions, (ii) the smallest value for an in-plane polarized transition was 0.303 [0.310], and (iii) the highest value for an in-plane polarized transition was 0.428 [0.428]. It is probably not a coincidence that for both ordinary and perdeuterated polyethylene these three values add up to one (in **1** alone the sum is 0.995 both in PE and in PE-d_4). With 52 observed in-plane transition moments, it is statistically very likely that at least one will lie within experimental error of the orientation axis *z* and another within experimental error of the axis *y*. We therefore adopt the following sets of principal orientation factors for the determination of transition moment directions in PE [PE-d_4]: $(K_x, K_y, K_z) = (0.262, 0.303, 0.428)$ and [0.259, 0.310, 0.428], and assume that the uncertainties in these values are due to the uncertainty in the determination of K_x.

In principle, it could happen that a range of angles close to the *z* axis and a similar range very close to the *y* axis are accidentally not represented among the 52 observed transition moment directions. Then, K_z would be larger than 0.428 [0.428] and K_y would be smaller than 0.303 [0.310] by the same amount. Since the orientation factor of the out-of-plane axis, K_x, has always been found to be the smallest of the three in the well over 100 planar molecules investigated so far, in agreement with the mechanism believed to be responsible for the orientation,[14] the minimum acceptable value for K_y is 0.262 [0.259], yielding for K_z a maximum acceptable value of 0.469 [0.479]. In this extremely unlikely case, the transition moment that is the closest to the *z* axis would form an angle of 26° with it, and the one that is the closest to the *y* axis would form an angle of 26° with it. All other transition moments, presently calculated to be spread at 0 to 90° away from *z*, would then be compressed into a range 26−64° away from *z*, but their relative positions would not be affected. This would make the agreement with the calculated values worse but would not change any of the conclusions reached concerning the lack of applicability of the simple model. This type of uncertainty would be removed if the direction of a single transition moment were known reliably from theory or another experiment, such as a gas-phase analysis of rotational structure. As we shall see below, the highest level of theory used presently predicts the transition moment directions for intense transitions with a root mean square (rms) error of only about 6°, reassuring us that the K_y and K_z values adopted presently are correct.

Relative Transition Moment Directions. The experimental absolute values of angles $|\phi_z^i|$ of deviation of the in-plane

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Table 1. Propene, $CH_2{=}CHCH_3$ (**1**). Calculated and Experimental Infrared Spectrum[a]

			calcd (CCSD/6-311G**)			exptl					
ν	sym	assignment	$\tilde{\nu}$	I[b]	α[c]	$\tilde{\nu}$	I[c]	K^H	K^D	$\lvert\phi_z\rvert$	α[c]
1	a'	CH_2 as st	3249[f]	20.3	−88	3075	23	0.344	0.342	56 ± 7	86 ± 7
2		CH st	3169	12.1	76	3008	6	0.307	0.317	83 ± 9	59 ± 9
3		CH_2 s st + CH st	3157	23.0	37	2977	26		0.339	60 ± 6	22 ± 6
4		CH_3 as st + CH st	3135[f]	12.3	35	2958	13		0.327	68 ± 7	30 ± 7
5		CH_3 s st	3051	24.9	−42	2912	27		0.407	25 ± 5	−63 ± 5
6		C=C st + CH_2 sc	1731	7.8	−25	1645	35	0.428	0.415	3 ± 9	−35 ± 9
7		CH_3 as d + CH_2 sc	1519	11.0	30	1449	62		0.343	58 ± 7	20 ± 7
8		CH_2 sc + CH b + CH_3 sd	1476	1.1	75	1411	4	0.353	0.351	53 ± 9	89 ± 9
9		CH_3 s d + CH_2 sc	1433	1.1	81	1370	10	0.394	0.371	38 ± 12	−76 ± 12
10		CH b + CH_2 b[e]	1335	0.2	−13	1293	2	0.329	0.322	67 ± 12	29 ± 12
11		CH_2 r + CH_3 r	1207	0.2	−40	1169	1	0.361		47 ± 10	−85 ± 10
12		CH_3 r + CH b + CH_2 r	957[f]	2.9	7	932	10	0.361	0.363	47 ± 6	9 ± 6
13		C-C st + CH_2 r	943[f]	1.1	6	916	1	0.365		45 ± 11	7 ± 11
14		C=C-C b	426	0.8	−33						
15	a''	CH_3 as st	3111	25.0	90	2933	22		0.271	90 ± 6	
16		CH_3 as d	1503	6.1	90	1433	15	0.271	0.267	90 ± 7	
17		CH_3 r	1082	3.1	90	1040	4	0.241	0.248	90 ± 11	
18		CH b + CH_2 tw	1022	14.9	90	988	38	0.255	0.266	90 ± 5	
19		CH_2 w	921	38.0	90	908	100	0.263	0.266	90 ± 4	
20		C-CH_2 tw	584	10.1	90	578	21	0.263	0.262	90 ± 6	
21		C-CH_3 tr	193	0.3	90						

[a] In polyethylene; orientation factors K^H (ordinary) and K^D (perdeurated); $\tilde{\nu}$ in cm^{-1}; as = asymmetric, d = deformation, r = rock, s = symmetric, sc = scissors, st = stretch, tr = torsion, tw = twist, w = wag. [b] Intensity, in km/mol. [c] Angles in degrees. [d] Relative integrated isotropic intensity ($E_Z + 2E_Y$). [e] Only the CH bond closer to the methyl group is bending, and its motion is out of phase with the bending of the CH bond of the CH group. [f] Transition is included in the "reliable" set during fitting.

Table 2. Propene-2-*d*, $CH_2{=}CDCH_3$ (**2**). Calculated and Experimental Infrared Spectrum[a]

			calcd (CCSD/6-311G**)				exptl						
ν	sym	assignment	$\tilde{\nu}$	Δ[b]	I[c]	α[d]	$\tilde{\nu}$	Δ[b]	I[e]	K^H	K^D	$\lvert\phi_z\rvert$	α[d]
1	a'	CH_2 as s	3248[f]	1	16.3	−85	3073	2	22	0.344	0.344	56 ± 8	86 ± 8
2		CD st	2340[f]	829	10.4	69	2244	764	4	0.310		76 ± 11	66 ± 11
3		CH_2 s st	3160	−3	8.1	14	2971	6	5	0.340	0.331	61 ± 10	23 ± 10
4		CH_3 as st	3137[f]	−2	23.7	41	2960	−2	16		0.315	78 ± 9	40 ± 9
5		CH_3 s st	3051[f]	0	24.6	−41	2908	4	19		0.428	0 ± 7	−38 ± 7
6		C=C st + CH_2 sc	1712[f]	19	8.2	−27	1628	17	18	0.410	0.422	18 ± 7	−20 ± 7
7		CH_3 as d	1519	0	10.7	30	1445	4	31		0.346	56 ± 8	18 ± 8
8		CH_2 sc	1468	8	1.5	73	1407	4	2	0.342	0.340	58 ± 5	84 ± 5
9		CH_3 s d	1431	2	0.8	81	1366	4	6		0.403	27 ± 7	−65 ± 7
10		CH_3 r + CD b + CH_2 r	1095[f]	240	1.4	2	1058	235	3	0.355	0.359	50 ± 5	12 ± 5
11		CH_2 r + CH_3 r	1212	−5	0.5	−18	1178	−9	1	0.355	0.394	41 ± 12	3 ± 12
12		CD b + CH_3 r + CH_2 r	845	112	1.6	13	826	106	9	0.365	0.394	39 ± 10	1 ± 10
13		C-C s + CH_2 r	940	3	0.8	8	914	2	1		0.381	39 ± 11	1 ± 11
14		C=C-C b	422	4	0.8	−32							
15	a''	CH_3 as st	3111	0	25.0	90	2933	0	15		0.265	90 ± 8	
16		CH_3 as d	1503	0	5.7	90	1431	2	14		0.251	90 ± 7	
17		CH_3 r	1077	5	0.5	90	1037	3	1		0.245	90 ± 12	
18		CD b + CH_2 t	870	152	3.5	90	844	144	13	0.260	0.253	90 ± 7	
19		CH_2 w	922	−1	43.0	90	908	0	100	0.263	0.252	90 ± 4	
20		C-CH_2 tw	554	30	11.4	90	550	28	27	0.262	0.263	90 ± 6	
21		C-CH_3 tr	189	4	0.3	90							

[a] In polyethylene; orientation factors K^H (ordinary) and K^D (perdeuterated); $\tilde{\nu}$ in cm^{-1}; as = asymmetric, d = deformation, r = rock, s = symmetric, sc = scissors, st = stretch, tr = torsion, tw = twist, w = wag. [b] Isotopic shift relative to **1**. [c] Intensity, in km/mol. [d] Angles in degrees. [e] Relative integrated isotropic intensity ($E_Z + 2E_Y$). [f] Transition is included in the reliable set during fitting.

transition moments from the orientation axis z were derived using the above assumptions separately for propene molecules oriented in PE and in PE-d_4. In each case, the uncertainties in the values of the principal orientation factors produced a range of possible values for $|\phi_z^i|$. The results from PE and PE-d_4 agreed very well, even though the two polymers differed in the degree of crystallinity. The final values of these relative polarizations given in Tables 1−4 were taken to be the averages of those obtained in the two polymers, and their error bars were dictated by the overlaps of the error ranges obtained from the uncertainties in the K_x values in the two polymers.

Absolute Transition Moment Directions. The remaining task is to use eq 8 to convert the absolute values of the in-plane transition moment directions $|\phi_z^i|$ expressed relative to the effective orientation axis z into absolute transition moment directions α_i in the molecular framework (Figure 4). The angles α_i ($-90° < \alpha \leq 90°$) and ω are measured counterclockwise from the direction of the double bond in the C=CMe moiety (i.e., a positive value implies an inclination away from the C−Me bond). The use of eq 8 requires the knowledge of ω, the direction of z with respect to the C=C bond, and of the sign $sgn\ \phi_z^i$ of each angle ϕ_z^i.

This information is not accessible from our experimental data, and we take it from a limit of a converged series of increasingly better quality *ab initio* calculations for the 16 most intense observed transitions that also have calculated intensities in

Table 3. Propene-1,1,3,3,3,-d$_5$, CD$_2$═CHCD$_3$ (3). Calculated and Experimental Infared Spectrum[a]

			calcd (CCSD/6-311G**)				exptl						
ν	sym	assignment	$\tilde{\nu}$	Δ^b	I^c	α^d	$\tilde{\nu}$	Δ^b	I^e	K^H	K^D	$\|\phi_z\|$	α^d
1	a'	CD$_2$ as st	2419	830	7.9	−89	2335	740	9	0.327	0.328	66 ± 6	76 ± 6
2		CH st	3166^f	3	20.7	70	3001	7	41	0.340	0.329	62 ± 5	80 ± 5
3		CD$_2$ s st	2314	843	2.5	23	2193	784	10	0.342	0.359	53 ± 6	15 ± 6
4		CD$_3$ as st	2325	810	11.4	38	2221	737	27	0.303		90 ± 5	52 ± 5
5		CD$_3$ s st	2194	857	10.9	−45	2104	808	9	0.412		21 ± 7	−59 ± 7
6		C═C st + C-C st	1675	56	8.2	−26	1600	45	42	0.405	0.427	13 ± 8	−25 ± 8
7		CD$_3$ as d	1093	426	5.2	25	1047	402	12	0.359	0.355	49 ± 6	11 ± 6
8		CD$_2$ sc	1068	408	0.6	−8	1032	379	48	0.381	0.359	41 ± 5	3 ± 5
9		CD$_3$ s d + C-C st	1195	238	1.6	−87	1147	223	2	0.342	0.339	58 ± 9	84 ± 9
10		CH b	1331	4	0.5	65	1290	3	7	0.363	0.359	48 ± 7	−86 ± 7
11		CD$_2$ r + CD$_3$ s d	1027	180	0.6	19	997	172	4	0.333	0.318	74 ± 13	36 ± 13
12		CD$_3$ r + CD$_2$ r	740	217	0.9	1	727	205	23	0.336	0.335	61 ± 6	23 ± 6
13		C-C st	801	142	1.8	21	788	128	1	0.365		45 ± 7	7 ± 7
14		C═C-C b	353	73	0.5	−32							
15	a''	CD$_3$ as st	2303	808	13.6	90	2203	730	21	0.262		90 ± 8	
16		CD$_3$ as d	1086	417	4.6	90	1043	390	37	0.259	0.242	90 ± 8	
17		CD$_3$ r + CD$_2$ r	838	244	2.3	90	812	228	31	0.270	0.255	90 ± 7	
18		CH b	979	43	13.6	90	954	34	38	0.270	0.251	90 ± 7	
19		C-CD$_2$ w	731	190	23.7	90	722	186	100		0.255	90 ± 5	
20		C-CD$_2$ tw	445	139	5.5	90	440	138	28	0.270	0.268	90 ± 9	
21		C-CD$_3$ tr	146	47	0.2	90							

[a] In polyethylene; orientation factors K^H (ordinary) and K^D (perdeuterated); $\tilde{\nu}$ in cm^{-1}; as = asymmetric, d = deformation, r = rock, s = symmetric, sc = scissors, st = stretch, tr = torsion, tw = twist, w = wag. [b] Isotopic shift relative to **1**. [c] Intensity, in km/mol. [d] Angles in degrees. [e] Relative integrated isotropic intensity ($E_Z + 2E_Y$). [f] Transition is included in the reliable set during fitting.

Table 4. Propene-d_6, CD$_2$═CDCD$_3$ (4). Calculated and Experimental Infrared Spectrum[a]

			calcd (CCSD/6-311G**)				exptl						
ν	sym	assignment	$\tilde{\nu}$	Δ^b	I^c	α^d	$\tilde{\nu}$	Δ^b	I^e	K^H	K^D	$\|\phi_z\|$	α^d
1	a'	CD$_2$ as st	2420	829	10.1	89	2328	747	8	0.320	0.324	69 ± 5	73 ± 5
2		CD st	2352^f	817	5.9	73	2252	756	4	0.331		62 ± 7	80 ± 7
3		CD$_2$ s st + CD st	2301^f	856	5.7	46	2191	786	5	0.303		90 ± 5	52 ± 5
4		CD$_3$ as st	2324	811	11.3	35	2223	735	23	0.315		72 ± 6	34 ± 6
5		CD$_3$ s st	2194	857	11.1	−46	2116	796	8	0.412		21 ± 7	−59 ± 7
6		C═C st + CD$_2$ sc	1655	76	8.6	−28	1583	62	24	0.422	0.422	13 ± 5	−25 ± 5
7		CD$_3$ as d	1094	425	4.7	28	1054	395	3	0.303	0.310	90 ± 7	52 ± 7
8		CD$_2$ sc+CD$_3$ s d+CD b	1209^f	268	1.7	88	1163	248	8	0.330	0.338	61 ± 5	81 ± 5
9		CD$_3$ s d + CD$_2$ sc	1089	344	0.5	−3	1048	322	15	0.403	0.381	33 ± 8	−5 ± 8
10		CD b + CD$_3$ a d	956	379	0.0	−61	928	365	1	0.354	0.354	51 ± 5	−89 ± 5
11		CD$_2$ r + CD$_3$ s d	1043	164	1.3	8	1012	157	7	0.333		61 ± 6	23 ± 6
12		CD$_3$ r + CD b + CD$_2$ r	709^f	248	1.1	7	693	239	6	0.359	0.351	51 ± 6	13 ± 6
13		C-C st + CD$_2$ r	796^f	147	1.4	25	777	139	5	0.333	0.338	60 ± 7	22 ± 7
14		C═C-C b	350	76	0.5	−32	(329)						
15	a''	CD$_3$ as st	2303	808	13.6	90	2206	727	9	0.240		90 ± 8	
16		CD$_3$ as d	1084	419	3.1	90	1041	392	22	0.291	0.263	90 ± 12	
17		CD$_3$ r	890	192	2.0	90	869	171	3	0.267	0.267	90 ± 9	
18		CD b + CD$_2$ tw	742	280	0.2	90	730	258	14		0.263	90 ± 7	
19		CD$_2$ w	726	195	30.1	90	708	200	100		0.261	90 ± 4	
20		C-CD$_2$ tw	440	144	6.2	90	435	143	17	0.251	0.254	90 ± 11	
21		C-CD$_3$ tr	143	50	0.2	90							

[a] In polyethylene; orientation factors K^H (ordinary) and K^D (perdeuterated); $\tilde{\nu}$ in cm^{-1}; as = asymmetric, d = deformation, r = rock, s = symmetric, sc = scissors, st = stretch, tr = torsion, tw = twist, w = wag. [b] Isotopic shift relative to **1**. [c] Intensity, in km/mol. [d] Angles in degrees. [e] Relative integrated isotropic intensity ($E_Z + 2E_Y$). [f] Transition is included in the reliable set during fitting.

excess of 1 km/mol. For these transitions, we have reasonable confidence in both the calculated α and the measured $|\phi_Z|$.

In order to find the optimal choice of ω and of the set of signs $sgn\ \phi_z^i$, referred to collectively by the symbol C, we use conventional numerical methods to minimize the function

$$S_C(\omega) = [(1/N)\textstyle\sum_i[\alpha_i - (|\phi_z^{\,i}|\ sgn\ \phi_z^{\,i} - \omega)]^2]^{1/2} \qquad (9)$$

for each of the 65 536 combinations C of the 16 signs $sgn\ \phi_z^i$ with respect to the value of ω. For the combination C that gives the smallest value of S, we discard any transitions i for which the calculated and the observed α_i disagree by more than 10° and replace them with the next most intense observed transitions with calculated intensities in excess of 1 km/mol. We repeat the process until the angles α_i for all members of this set of 16 “reliable” transitions differ from their calculated values by less than 10°. The rms deviation $S_C(\omega)$ of this set is 5.81°, and the ω so determined is −38.0°. It is used throughout in the following. For each of the remaining 36 in-plane polarized transitions, $sgn\ \phi_z^i$ is chosen so as to minimize the deviation for that transition only. The final rms deviation for all 52 transitions is 16.0°.

In order to detect any systematic biases in the procedure, we have performed two tests. First, a reoptimization of the value of ω to minimize the rms deviation of all the observed transitions rather than just the most intense 16 gave the result $\omega = -38.5°$, with a rms deviation of 16.0°. Clearly, the directions of the weaker transitions are calculated less well than those of the

Table 5. Polarization Directions for In-Plane Vibrations

		1		2		3		4		anticipated	
ν	assignment	$\tilde{\nu}$	$\lvert\phi_z\rvert$	$\tilde{\nu}$	$\lvert\phi_z\rvert$	$\tilde{\nu}$	$\lvert\phi_z\rvert$	$\tilde{\nu}$	$\lvert\phi_z\rvert$	α	$\phi_z{}^a$
1	CH_2 (CD_2) as st	3075	56 ± 7	3073	56 ± 8	2335	66 ± 6	2328	69 ± 5	90	52
2	CH (CD) st	3008	83 ± 9	2244	76 ± 11	3001	62 ± 5	2252	62 ± 7	60	82
3	CH_2 (CD_2) s st	2977	60 ± 6	2971	61 ± 10	2193	53 ± 6	2191	90 ± 5	0	−38
4	CH_3 (CD_3) as st	2958	68 ± 7	2960	78 ± 9	2221	90 ± 5	2223	72 ± 6	30	−68
5	CH_3 (CD_3) s st	2912	25 ± 5	2908	0 ± 7	2104	21 ± 7	2116	21 ± 7	−60	22
6	C=C st	1645	3 ± 9	1628	18 ± 7	1600	13 ± 8	1583	13 ± 5	0	−38
7	CH_3 (CD_3) as d	1449	58 ± 7	1445	56 ± 8	1047	49 ± 6	1054	90 ± 7	30	−68
8	CH_2 (CD_2) sc	1411	53 ± 9	1407	58 ± 5	1032	41 ± 5	1048	33 ± 8	0	−38
9	CH_3 (CD_3) s d	1370	38 ± 12	1366	27 ± 7	1147	58 ± 9	1163	61 ± 5	−60	22
10	CH (CD) b	1293	67 ± 12	1058	50 ± 5	1290	48 ± 7	928	51 ± 5	−30	−8
11	CH_2 (CD_2) r	1169	47 ± 10	1178	41 ± 12	997	74 ± 13	1012	61 ± 6	90	52
12	CH_3 (CD_3) r	932	47 ± 6	826	39 ± 10	727	61 ± 6	693	51 ± 6	30	−68
13	C-C st	916	45 ± 11	914	39 ± 11	788	45 ± 7	777	60 ± 7	−60	22

[a] Assuming $\omega = -38°$.

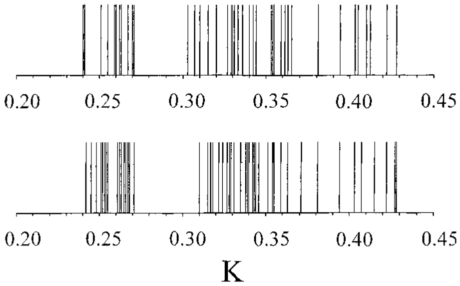

Figure 3. Distribution of the observed orientation factors for **1**−**4** in PE (top) and PE-d_4(bottom).

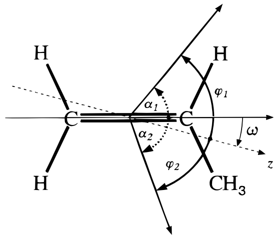

Figure 4. Definition of the angles used to specify directions of in-plane transition moments. All angles are measured counterclockwise.

strong ones, but the error is randomly distributed in both directions. Second, we have repeated the optimization procedure for each molecule separately, using all of its observed transitions. This produced the following results (rms error in parentheses): **1**, $\omega = -34.3°$ (20.6°), **2**, $\omega = -41.9°$ (12.9°), **3**, $\omega = -40.3°$ (15.0°), and **4**, $\omega = -37.3°$ (13.1°). These values are distributed symmetrically around the average, $\omega = -38.5° \pm 4°$, and show no indication of intrinsic bias. Thus, we believe that the above best value, $\omega = -38° \pm 6°$, is quite reliable.

The final absolute directions α_i of the transition moments derived from the observations with this method are collected in Tables 1−4, which also give the α_i values calculated at the highest level of approximation, CCSD/6-311G** (Figure 5). The error bars given for the experimental results do not contain the uncertainty in ω (±6°), which affects all absolute polarization directions equally.

The convergence of the calculated transition moment directions with the improving level of calculation is illustrated in Figure 6 for the case of **1**.

Discussion

Spectral Reassignments. CH_2=$CHCH_3$ (1). The orignal assignments[6,7] for the lower frequency part of the spectrum, ν_6−ν_9 and ν_{12}−ν_{13} of a' symmetry and ν_{16}−ν_{21} of a'' symmetry, are found to be correct. The ν_{14} and ν_{21} vibrations were outside the range of our instrument. The vibrations observed in polyethylene at 1293 and 1169 cm^{-1} can now be assigned to the ν_{10} and ν_{11} fundamentals. Other components of the multiplets observed earlier were not present in our spectra.

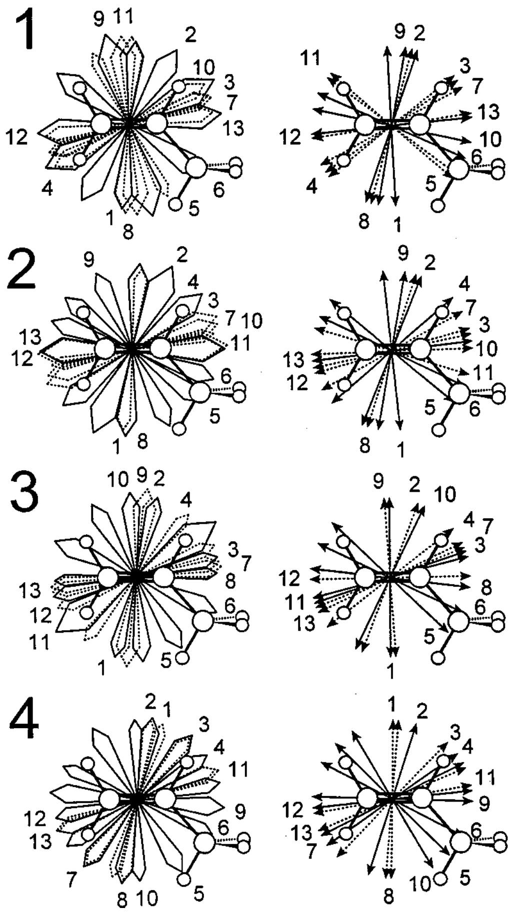

Figure 5. Comparison of observed (left) and calculated (right, CCSD/6-311G**) mid-IR in-plane transition moment directions in propene and its isotopomers in the molecular frame (bottom). The methyl group was positioned symmetrically with regard to the molecular plane but is shown slightly rotated for the sake of clarity. Some of the arrows have been rotated by 1−2° to avoid overlap. Solid and dotted lines are used merely to guide the eye.

The assignment of various CH stretching fundamentals is more equivocal, due to Fermi resonances with combination and overtone bands. However, in low-temperature polyethylene spectra assignments are simplified by the absence of heavily overlapping rotational envelopes, present in room-temperature gas-phase spectra in this region. The ν_{15} mode at 2933 cm^{-1}

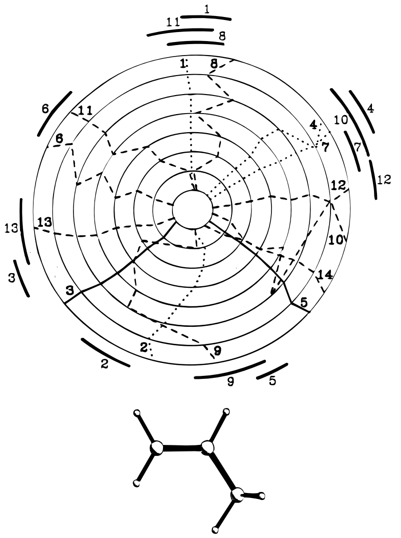

Figure 6. In-plane moment directions of in-plane (a' symmetry) IR transitions in propene (**1**) relative to the framework shown, computed at various levels of approximation. From the center outwards: HF/3-21G, HF/6-31G, HF/6-31G*, HF/6-31G**, HF/6-31+G**, HF/6-311G**, MP2/6-311+G**, CCSD/6-311G**. Solid lines: transitions with observed integrated intensity of at least 20%; dashed lines: 10−20%; dotted lines: less than 10% of the integrated intensity of ν_{19}.

is clearly of a'' symmetry, and not of a' symmetry as previously proposed.[7] Since it is the only such vibration in the 3000 cm^{-1} region, it can be safely assigned as a CH$_3$ asymmetric stretch. The vibration at 2958 cm^{-1} is observed to have a' symmetry, and we assign it as the ν_4 fundamental. The previous assignments of the remaining vibrations agree with our results. According to our calculations, both CH$_3$ stretches are highly decoupled from other motions, while the CH$_2$ and CH stretches couple somewhat with each other. The new assignments are summarized in Table 1.

CH$_2$═CDCH$_3$ (2). The assignments for propene-*2-d* were also reported in ref 7. The vibration reported at 2930 cm^{-1} and assigned as a CH$_3$ symmetric stretch (a') is found in polyethylene at 2933 cm^{-1}. It is now reassigned to a CH$_3$ asymmetric stretch of a'' symmetry. The best candidate for the CH$_3$ symmetric stretch is found at 2908 cm^{-1}, almost the same frequency as in **1**. These reassignments are strongly supported by the computational results (see Table 2). The band observed in ref 7 at 913 cm^{-1} and assigned as a'' symmetry vibration is now reassigned to a C−C stretch of a' symmetry. Other minor clarifications of earlier assignments are collected in Table 2.

CD$_2$═CHCD$_3$ (3). We have not found any assignments for this compound in the literature. Our results are summarized in Table 3.

CD$_2$═CDCD$_3$ (4). Perdeuterated propene (**4**) was studied previously in the gas phase.[6] The following reassignments are made (Table 4): Previously, two a' vibrations were reported at 868 and 872 cm^{-1}. The former was assigned as a "CD$_3$ wagging" and the latter as "CD$_2$ wagging". We only observe one vibration in this region. It is of a'' symmetry, is located at 869 cm^{-1}, and is assigned as the out-of-plane CD$_3$ rocking mode. Previously, it was believed that this rocking mode overlaps with the C−C stretching vibration observed in the gas phase at 788 cm^{-1} and now in polyethylene at 777 cm^{-1}. We propose that an "a' symmetry CD$_2$ wagging" does not exist, as the two in-plane bending motions of the CD$_2$ group are called rocking (at 1012 cm^{-1}, observed at the same position previously and labeled CD$_2$ bending) and scissoring (at 1163 cm^{-1}, previously unobserved). For the a' symmetry "CD$_3$ wagging" peak previously believed to be located at 868 cm^{-1}, in polyethylene we observe a peak at 693 cm^{-1}, not observed in the gas-phase work, and attribute it to a predominantly CD$_3$ in-plane rocking motion. The symmetric CD$_3$ bending previously assigned to a peak at 1022 cm^{-1} is now called symmetric CD$_3$ deformation and is found at 1048 cm^{-1}. The peak previously reported at 1033 cm^{-1}, and attributed to the CD bending vibration, is not observed in polyethylene. This mode is now assigned to a previously unobserved peak at 928 cm^{-1}. Our results also suggest that earlier assignments of CD$_3$ asymmetric stretch and CD$_2$ symmetric stretch were reversed.

As in the case of **1**, ν_5 and ν_7 are calculated to be highly decoupled from other motions. The agreement between observed and calculated isotopic shifts relative to **1** strongly supports the presently proposed assignments for **4**.

Transition Moments: Anticipated and Observed. The simplest way in which IR transition moment directions can be predicted is based on the assumption that all vibrations are perfectly localized, unless otherwise demanded by local symmetry. Then, one-bond stretching vibrations would be polarized along the direction of the bond, and one-bond bending vibrations would be polarized in the bending plane, perpendicular to the direction of the bond. Vibrations involving several bonds related by local symmetry would be polarized along the direction of the vectorial sum of the local moments determined by the bond directions as above and entering with signs dictated by the relative phases of the motion. Thus, a symmetric methyl group deformation would be polarized along the 3-fold axis of the CH$_3$ group, and an asymmetric methyl vibration perpendicular to it, etc. This procedure is commonly used, for instance, in studies of alkane chain orientation.

An attempt to use this simple procedure immediately runs into problems if local vibrations of similar frequencies mix extensively. According to the *ab initio* calculations performed in this study, all of the vibrations with frequencies below 1000 cm^{-1} and most of those with frequencies in the range 1000−1400 cm^{-1}, as well as some of the CH and CD stretching vibrations, are mixed strongly and cause difficulties in the application of the procedure, which depends on the use of the simplest normal mode labels to describe the nature of vibrations.

If one wishes to proceed anyway in order to test the procedure, it is necessary to make some nearly arbitrary decisions concerning a few mode labels in the low frequency region. We used mode frequencies as a rough guide when the calculations suggested that the modes were strongly mixed. In particular, the labels used for the 826 and 1058 cm^{-1} vibrations of **2** could be also be reversed, and so could those on the 1048 and 1163 vibrations of **4**. This is however of little consequence for the conclusions reached.

Once a set of assignments (labels) is accepted, two predictions can be made: (i) One expects no change in a transition moment $|\phi_z{}^i|$ upon deuteration that preserves local symmetry. (ii) One expects the transition moments α_i to lie in directions dictated by bond directions (Table 5).

The verification of the first expectation is independent of the errors possibly introduced in the derivation of the location of the principal orientation axis in the molecule, i.e., of the value of ω, and of the errors conceivably introduced in estimating the values of K_y and K_z. Thus, it represents a very reliable test of the simple model. Table 5 shows that the expectations are fulfilled within about 20° for the high frequency vibrations, with the exception of a 40° variation in the case of the CD$_2$ symmetric stretch in **4**. Among lower frequency vibrations, CH (CD) bend, CH$_3$ (CD$_3$) rock, and C−C stretch keep their transition moment direction constant within 20° or so, while the others vary over a larger range. We conclude that if a polarization direction is to be deduced from a vibration label, it should be done for a high frequency vibration, and that an error of at least ±10° will be common.

The test of the second expectation is critical, in that it ties the transition moment directions to the molecular framework. The test can be performed in two steps. Initially, without relying on the accuracy of our determination of ω, and of our estimate of K_y and K_z, we can check whether transition moments expected to lie in the same direction indeed are parallel. One such pair are the CH_2 (CD_2) asymmetric stretch and the CH_2 (CD_2) rock, both expected to be polarized perpendicular to the C=C bond. Their transition moments are parallel within experimental error. Another set is the CH_2 (CD_2) symmetric stretch, the C=C stretch, and the CH_2 (CD_2) scissoring mode, all expected to be polarized along the C=C bond. Their transition moments are not parallel at all. The directions of the first and the third of these moments tend to agree, except in **4**, where they differ by 60°, but the direction of the second one differs by at least 40° in all four compounds, and actually is nearly perpendicular to that of the first one in **4**. Another set of three are the CH_3 (CD_3) asymmetric stretch, asymmetric deformation, and rocking vibrations, all expected to be polarized perpendicular to the C−C bond. Instead of being parallel, the three moment directions differ by 20−60° in the four compounds. The last set of three moments anticipated to be parallel are those of the CH_3 (CD_3) symmetric stretch and symmetric deformation and C−C stretch, all expected to lie in the C−C bond direction. Once again, the three directions are far from similar in any one of the four compounds.

This poor performance could be blamed on the inclusion of at least one relatively low-frequency vibration in each group, and hope might be held for high-frequency vibrations alone, but even the comparison of the polarizations of the CH_2 (CD_2) symmetric stretching and C=C stretching vibrations is discouraging. In view of this, it is not surprising that the next step, a comparison of the expected direction in the molecular frame with the absolute directions derived from the measurements using $\omega = -38°$, gives disappointing results. Even for the most favorable choice of $sgn\, \phi_z^i$, the rms deviation is 38.3°. Although for most of the high frequency vibrations, CH_2 (CD_2) scissor mode and higher, the observed angle does not differ from the expected one by more than 20°, for two of them it does [CH_2 (CD_2) symmetric stretch in **4** and C=C stretch in **1**, **3**, and **4**]. For all of the lower frequency vibrations except the CH_2 (CD_2) rock, the deviation exceeds 20° in at least one of the four isotopomers.

Although the simple model did not hold much promise for low-frequency vibrations to start with, we are forced to conclude that its erratic performance renders it problematic for high frequency vibrations as well. Our results suggest that it should be used only for CH stretching vibrations and that errors on the order of ±20° are to be expected.

Transition Moments Computed and Observed. Since the simplest way of estimating transition moment directions from molecular structure was found to be very unreliable, it becomes necessary to rely on computations. It is then particularly important to determine at which level of theory reliable answers can be obtained. Figure 6 shows the gradual convergence of the computed transition moment directions in **1** as the basis set and treatment of electron correlation are improved. For the most intense and even the medium intensity transitions, the correct prediction is made already at a rather low level of calculation, but the transition moment directions of transitions calculated to be weak are converged only at the highest levels of theory employed presently. Clearly, a reasonably large basis set and some treatment of electron correlation are necessary if agreement is to be obtained for all vibrations. Results for the other isotopomers are similar.

Since the MP2/6-311+G** results and the CCSD/6-311G** results resemble each other very much, we assume that further improvements of the basis set and electron correlation treatment are not likely to introduce significant changes. The agreement of the results obtained with either one of these methods with the experimental values is quite respectable. The largest discrepancies are on the order of 20° or so, but most of them are much smaller. Tables 1−4 show the comparison for the CCSD results, for which the rms deviation is 16.0°. Two vibrations for which the agreement is poorer are ν_{10} in **4** (CD b + CD_3 ad), with an error of 30°, and ν_{11} in **1** (CH_2 r + CH_3 r), with an error of 45°.

Sources of Computational Error. Considering the amount of computational effort involved, the fairly frequent 20° discrepancies are still disappointingly large, being two to three times the experimental error. Still, in some applications, this level of accuracy may be perfectly acceptable. For example, in VCD, a rotation of an electric dipole transition moment by 20° will only rarely change the sign of its projection into the magnetic dipole transition moment and thus the VCD sign, and only for weakly optically active vibrations. The apparently randomly occurring occasional even larger errors are very disturbing, since they undermine confidence in the utility of the calculations for applications in structural work. Apparently, an even larger degree of effort is required before one can have absolute confidence in the results, even just to within 20°. For much larger molecules, this appears prohibitive, given the present state of computational technology.

Perhaps the size of the errors is not surprising, given the comparison of measured and calculated relative intensities (Tables 1−4). While the measured relative values cannot be considered highly accurate, there is no doubt that the correlation with the calculated intensities is rather poor. Although in general the transitions calculated to be more intense tend to be more intense experimentally, many of the observed values are off the regression line by factor of several fold.

As far as transition moment directions are concerned, the worst aspect of the situation is that the best theory level employed here is apparently already converged and yet rather unsatisfactory. If this surmise is correct and further improvement of basis set and electron correlation treatment do not change the results, the inescapable conclusion will be that (i) either environmental effects have to be considered in the computation, (ii) or the standard double harmonic approximation is inadequate, (iii) or, most likely, both statements apply.

The existence of environmental effects on transition moment directions is indicated by the slight variations in the dichroic ratios observed for out-of-plane polarized transitions. Significant twisting of weak electronic transition moments (by as much as 40°) due to hydrocarbon solvent, such as polyethylene, is well established,[26] and there is no reason why it should not occur for weak vibrational transition moments as well. Simple models for solvent-induced mixing of normal modes can be envisaged, but we are not aware of quantitative attempts to calculate solvent-induced twisting of vibrational transition moment directions.

In a similar vein, it appears certain that the harmonic approximation does not adequately describe the coupling of the motions of different parts of the molecule. Anharmonic effects

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(26) Langkilde, F. W.; Thulstrup, E. W.; Michl, J. *J. Chem. Phys.* **1983**, *78*, 3372. Langkilde, F. W.; Gisin, M.; Thulstrup, E. W.; Michl, J. *J. Phys. Chem.* **1983**, *87*, 2901.

such as Fermi coupling are clearly present. For example, Figure 2 shows three CD stretching bands in the spectrum of **2**, which contains only one CD bond. Even for molecules of the size of propene, full anharmonic treatment nowadays represents a formidable computational challenge.

Conclusions. IR transition moment directions in the molecular frame are needed for use in VCD studies, as well as in supramolecular structural work, in which molecular orientations in aligned assemblies are deduced from linear dichroism of IR transitions, and elsewhere. Their determination or calculation are straightforward if the molecule has high enough symmetry for each of its axes (x, y, z) to transform according to a different irreducible representation. However, many of the molecules of interest have lower symmetry. If the results obtained here for propene have general validity for low-symmetry molecules, IR transition moment directions in such molecules cannot be deduced reliably from molecular structure by inspection, not even for high-frequency vibrations, with the exception of CH stretches, where the typical uncertainty is about ±20°. They can be computed at the MP2/6-311+G** or better level with an error that commonly ranges up to 20° and occasionally is even much higher, in a presently somewhat unpredictable fashion. It is suggested that the residual error is primarily due to the neglect of solvent and anharmonic effects. However, it appears that for high-frequency modes the error does not exceed ±20°, and for the most intense transitions, it is substantially smaller, comparable to the present experimental error of about ±10°.

It would therefore appear highly advisable to base conclusions concerning orientation of low-symmetry molecules in assemblies on observations of the linear dichroism of two or more intense IR transitions in the same molecule, using experimentally determined transition moment directions in the molecular frame whenever possible. When experimental directions cannot be obtained, and computed directions need to be used, they should be obtained on at least the MP2/6-311+G** level of theory, or, reluctantly, by inspection of molecular geometry in the case of CH stretches.

Finally, little is known about the potentially important issue of IR transition moment perturbation by the condensed phase environment. The variation of dichroic ratios observed for the out-plane polarized vibrations in the present study suggests that the phenomenon is real. It would be useful to compare the present results for propene and deuterated propenes with results of future measurements in the gas phase.

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