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Transition-Moment Directions of Protonated 1-Methylcytosine

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Abstract: Polarized reflection spectra from the (010) and (101) faces of single crystals of 1-methylcytosine hyrobromide have been measured. Corresponding absorption spectra obtained by Kramers–Kronig analysis of the reflection data are interpreted within the framework of the oriented gas model in order to assign the transition-moment directions of the first two in-plane electronic transitions of protonated 1-methylcytosine. In-plane angles, θ, are positive toward N_3 from the N_1–C_4 reference axis. The results are as follows: transition I at 35 600 cm^{-1} (281 nm), $\theta = 15°$ or $-8°$ (both $\pm 2°$); and transition II at 47 000 cm^{-1} (213 nm), $\theta = -50°$ or $+57°$ (both $\pm 10°$). An alternative interpretation of the spectra is presented in which the direction of transition I is uniquely polarized at about $+4°$. Band contour differences are accounted for by exciton mixing calculations.

The optical properties (hypochromism, linear dichroism, circular dichroism, fluorescence polarization, etc.) of polynucleotides in solution have served as indicators of the structure and conformation of such polymers. Confidence in conformational deductions that are derived from optical information is, however, not great at the present time.[1] The underlying basis of all such approaches involves the calculation of the polymer properties from the spectral parameters of the purine and pyrimidine monomer units for various conformational choices of the polymer. After two decades, knowledge of the needed parameters of the bases continues to be somewhat meager. Even the number of transitions present in various spectral regions of the different bases is still not agreed on.[1,2] The present work represents a renewed effort to establish experimentally the necessary spectral information for the monomers so that definitive testing of the theoretical apparati that translate monomer properties into polymer properties can be carried through.

Cytosine is an attractive case for such an investigation, for it not only forms a variety of double-stranded polymers involving its complementary forms[3] (guanosine and inosine) but it also forms double-stranded or stacked polymers with itself under various conditions. For example, poly(C) occurs as a random coil at neutral pH, whereas at pH 4 a semiprotonated double-stranded poly(C)–poly(C^+) occurs.[4] The unusual dimer CppC shows strong excimer fluorescence in neutral solution that returns to monomer type emission under slightly acidic conditions.[4] On the other hand, the dinucleotide CpC is apparently completely stacked in low-temperature ethylene glycol–water glasses.[5] The large number of forms involving just C and C^+ may constitute the best case for testing the theories that derive properties of aggregates from the characteristics of the monomers involved.

The monomer information required includes the energy, the oscillator strength, and the transition moment direction or polarization of each transition. Information regarding the electronic transitions of the cytosine molecule is now available in the literature;[6] however, no investigation of any protonated cytosine species has been presented. In this paper we report the results of an examination of protonated 1-methylcytosine. It is hoped that these results together with those for cytosine will form a satisfactory basis for definitive calculations of the various aggregates that form.

The experimental approach first involves the measurement of the reflection spectra polarized along the principal directions of different faces of single crystals of 1-methylcytosine·HBr (or 1-MC·HBr). Corresponding absorption spectra are then obtained from the reflection data via numerical analysis with use of the Kramers–Kronig transformation. Finally, the absorption spectra are interpreted within the framework of the oriented gas model in an effort to define the polarization directions of the first two electronic transitions of the 1-methylcytosine cation.

Experimental Procedures

Single crystals of 1-methylcytosine·HBr were grown by slow evaporation from aqueous, acidic (HBr) solutions. Plate-like crystals with well developed (010) and (101) faces were selected for measurement. The crystal faces were identified by morphologic examination. Polarized reflection spectra between 360 and 183 nm were recorded with a microspectrophotometer that has been previously described.[7]

The Kramers–Kronig transformation involves a numerical integration of the reflectivity over the entire frequency domain. Since only a portion of the spectrum is experimentally accessible an approximate procedure involving trial reflectivities for the unmeasured regions is employed. The reflectivities in the trial regions are systematically altered until the computed absorbtivity is zero throughout the known region of transparency. The absorption coefficients so obtained are usually quite accurate and independent of the details put into the trial regions as long as the band in question is well removed from the trial region. The uncertainty increases, in general, the nearer the band is to the guessed regions (vide infra).

Crystal Structure

The crystal structure of 1-MC·HBr has been reported by Bryan and Tomita as orthorhombic (space group *Pnma*) with four molecules per cell.[8] The cations and bromide ions are arranged in planes precisely parallel to the *ac* crystal plane. Spectra taken from the (010) face (i.e., polarized parallel to the *a* and *c* axes) will thus represent the full in-plane absorption intensity, whereas the *b* polarized spectrum of (101) represents absorption polarized exactly normal to the molecular planes. The projection of the unit cell onto the *ac* plane is given in Figure 1. 1-Methylcytosine is protonated at the N_3 position.

Spectra

The aqueous solution spectrum of 1-methylcytosine in dilute HCl (pH ~2) is given in Figure 2 along with that of a neutral solution (pH ~6) for comparison. A large change in the spectrum is clearly apparent upon protonation. HCl was chosen for the measurement of the solution spectrum since the onset of strong absorption in aqueous HBr solutions obscures measurements below about 230 nm while HCl solutions are transparent farther into the ultraviolet (~190 nm). The relative changes exhibited by the lowest energy band upon protonation are of course identical regardless of whether HCl or HBr is used. The two bands of the protonated form at 281 nm (band I) and 213 nm (band II) are the subjects of the present study.

The reflection spectra polarized along the *a* and *c* axes of the (010) face and the $\parallel b$ and $\perp b$ axes of the (101) face are shown

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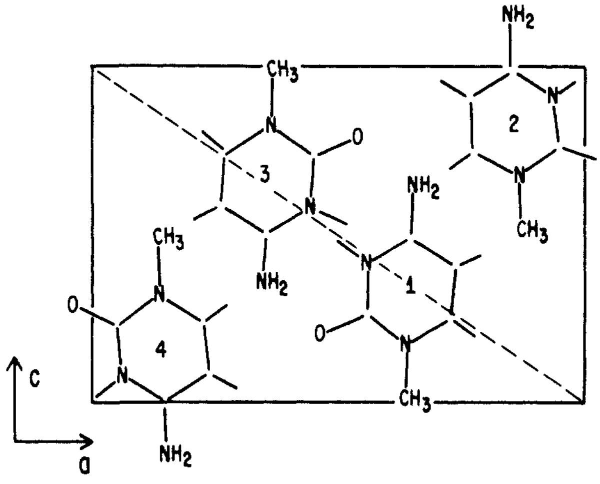

Figure 1. Projection of the unit cell onto the (010) crystal plane. The site numbers correspond to the designations used in the lattice sums. The dashed diagonal line is the intersection of the (101) crystal plane with the *ac* plane.

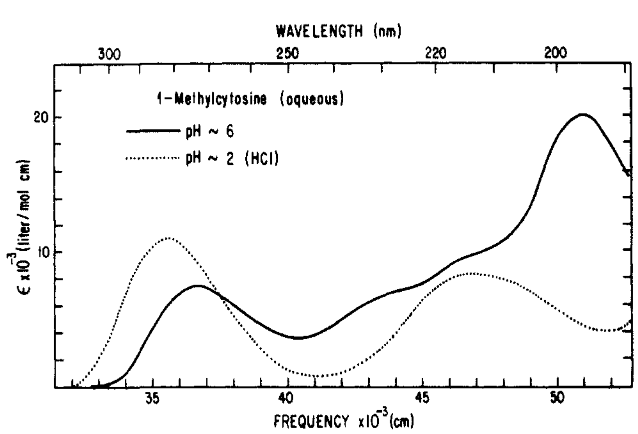

Figure 2. Aqueous solution spectra of neutral and protonated 1-methylcytosine.

Table I. Solution and Crystal Spectral Data for Protonated 1-Methylcytosine

	solution		crystal			
	f	ν (cm^{-1})	f_a	f_b	f_c	$f_{\perp b}$
band I	0.21	35 600	0.02	0.005	0.48	0.13
band II	0.24	47 000	0.18	0.02	0.10	0.20

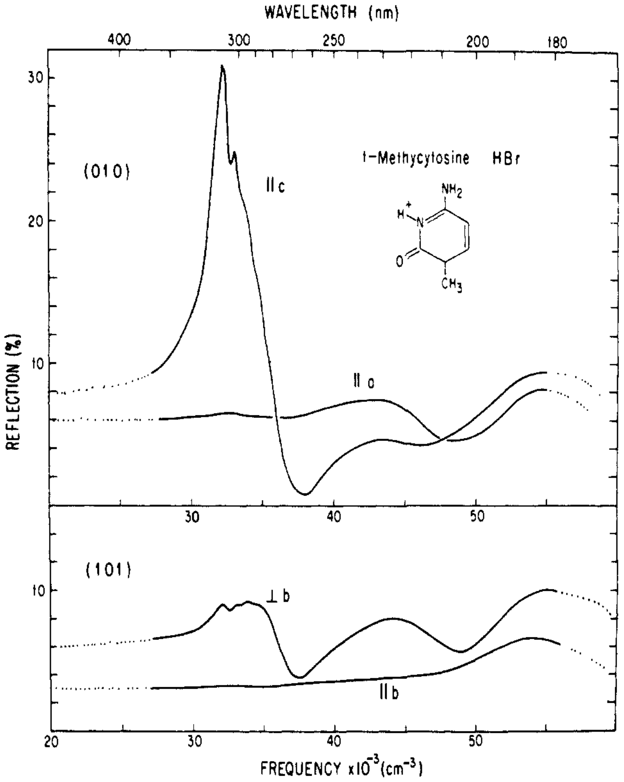

Figure 3. Normal incidence polarized reflection spectra of the (010) top and (101) bottom crystal planes. The dotted portions correspond to the unmeasured, trial reflectivities employed in the Kramers–Kronig transformations.

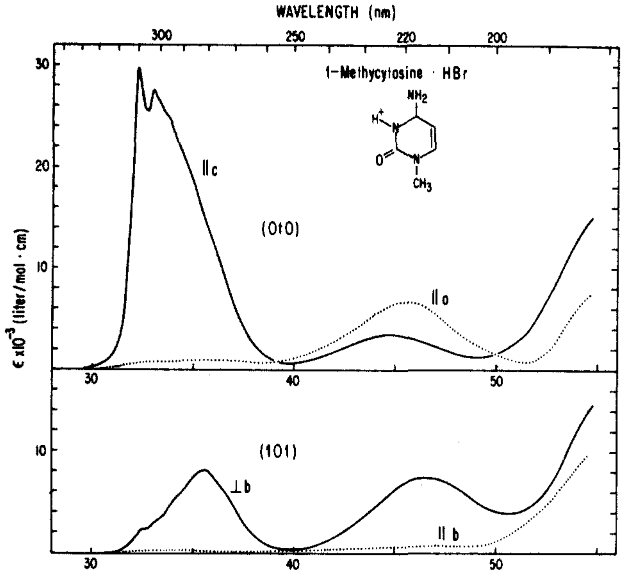

Figure 4. Absorption spectra of the (010) and (101) crystal faces derived from reflection data.

in Figure 3. Qualitative inspection of the spectra shows that both bands I and II are polarized nearly in the molecular plane since the spectrum polarized perpendicularly to the molecular plane (‖*b*) is essentially flat throughout this region. A general rise below 200 nm occurs in all the curves and may represent the onset of a more nearly isotropic transition possibly involving the bromide ion and is probably not to be associated with an independent cation.

The fact that this high energy reflection band is but partly included in the measured region leads to considerable uncertainty in the computed modest absorption coefficients in the vicinty of band II ±2000 extinction). In contrast those coefficients for the more removed band I components are much less uncertain (±200 extinction). The corresponding absorption spectra are shown in Figure 4, while pertinent numerical values are given in Table I.

Oriented Gas Analysis

Except for some later band shape considerations, the analysis of the absorption spectra in order to obtain polarization directions will follow the oriented gas model in which intermolecular interactions along with the concomitant intensity mixing are ignored. The observed oscillator strengths along the different axes are used to define dichroic ratios from which transition-moment directions can be identified. Except in special cases the dichroic ratio for a transition obtained from any face will be consistent with two possible in-plane transition-moment directions.[9] Resolution of this common ambiguity in the interpretation of crystal spectra cannot be made without other data from similar molecules with other crystal structures, from stretched film results, etc.

Transition I. The first band is strongly polarized along the *c* axis. The dichroic ratio f_c/f_a is 22:1 and translates into the two possible choices for a transition moment direction of −8° and +15° (pitched at ±12° from the *c* axis). The small out-of-plane intensity

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along *b* (~1% that along *c*) corresponds to an average out-of-plane cant of about 6° and could arise from departure from coplanarity of the cations with the *ac* crystal plane because of crystal imperfections or thermal motions and from vibronic mixing. Along this same line it is possible that the absorption intensity observed along the *a* axis is entirely of the same sort as that observed normal to the plane. In such a case the transition moment might nomially be polarized nearly parallel to the *c* crystal axis (+3.6° in the molecule). Thus depending on the interpretation one chooses to invoke, transition I is represented either by (1) a uniquely polarized vector along either the +15° or −8° directions or (2) a set of vibronic component vectors the directions of which cluster around an average in-plane angle of +3.6°. The latter interpretation gives the relative absorption coefficients along *c*:*a*:*b* as 100:4:1.

It has been suggested by a referee that the use of convergent light for the reflection measurements might lead to spurious structure along the *a* and *b* axes. Although the geometry of the incident beam is sharply tailored to minimize such an effect, in fact a very small longitudinally polarized component is present, and this component will "sample" longitudinally polarized crystal states. In the present study there is virtually no longitudinally polarized (i.e., polarized normal to the (010) face) crystal oscillator strength in the region of transition I. The structure observed along the *a* axis therefore cannot plausibly arise from the use of convergent radiation. The *b* axis of (101) is maximally susceptible to this effect, so that the very weak, observed structure ($\Delta\%R \simeq 0.1\%$) may entirely arise from the use of convergent light. In any event the magnitudes involved are equivalent to the experimental uncertainty in the measured reflection values and the Kramers–Kronig derived absorption coefficients.

The isotropic oscillator strength, $^1/_3(f_a + f_b + f_c)$, derived from the crystal spectra is 0.17 and is to be compared with the solution value of 0.21. The component polarized along $\perp b$ of (101) is expected to show an oscillator strength of 0.15 (i.e., 32% that observed along the *c* axis) and can be compared to the observed value of 0.13.

Transition II. The bands near 45 000 cm^{-1} also appear to be derived from an in-plane transition owing to the weakness of absorption along the *b* axis. The dichroic ratio f_a/f_c is 1.8, and the corresponding in-plane transition moment directions consistent with this value are −50° and +57°. The present data are insufficient for making a choice in the two values given. The uncertainty in the absorption coefficients derived from the Kramers–Kronig procedure of these bands owing to the nearness of the incompletely measured higher energy band leads to an estimated uncertainty of ±10° in these values. The isotropic oscillator strength has a value of 0.10 and is but 42% of the solution spectrum value. This sharp reduction presumably signals the transfer of oscillator strength to higher energy states through crystal interactions.

Band Shapes and Crystal Interactions

The contours of transition I are different along the *c* axis (010) and the $\perp b$ axis of (101). Such a result is not uncommon in crystal spectra and has led in some instances to the mistaken conclusion that additional transitions are present. The present case is clearcut, for the spectra along the three orthogonal axes *a*,*b*, and *c* show unambiguously that little intensity is polarized along any direction other than the *c* axis. Another allowed electronic transition polarized in a different direction would, if present, necessarily show up strongly along the *a* or *b* axes. Such is not the case. The dramatic difference in the band shapes long *c* and $\perp b$ must find an explanation in crystal field effects.

Exciton mixing calculations have been carried through in an attempt to quantitatively appraise such changes in band contours. For calculational purposes we assume that transition I is composed of nine equally spaced (800 cm^{-1}) vibronic components with relative intensities to match the solution spectrum band contour and all polarized at +3.6° in the molecular plane. We ignore higher energy bands and treat the nine vibronic state problem with perturbation theory in the dipole approximation.[9] Matrix elements are evalauted by forming the appropriate inner products of the dipole transition moments with lattice sums of dipole–dipole interactions. These lattice sums are dependent on the direction of the wave vector, **k**, so that different secular equations occur not only for the two principal axes of each crystal face but also for different crystal faces.[10,11] The result is that the mixing coefficients among the series of vibronic components can be very different (even in sign) from axis to axis and from crystal face to crystal face. Along one axis intensity might shift always toward the lower energy members of the series while the reverse might occur for some other crystal axis. The calculations support such a conclusion of 1-MC·HBr crystals.

Table II. Inner Dipolar Lattice Sums t_{ij} for Unit Vectors Directed along the Various Crystallographic Axes[a,b]

	site combinations			
	1,1	1,2	1,3	1,4
aa	455	58	−872	−2175
bb	−1761	−507	−477	130
cc	−566	−1424	−524	172
ac	0	0	635	0
ab	0	0	0	0
bc	0	0	0	0

[a] The dipole position is taken to be the midpoint of the N_1–C_4 segment. [b] The other site combinations are related to those given as follows: 1,1 = 2,2 = 3,3 = 4,4; 1,2 = 2,1 = 3,4 = 4,3; 1,3 = 3,1 = 2,4 = 4,2; 1,4 = 4,1 = 2,3 = 3,2. The only exception is $t_{2a,4c} = -t_{1a,3c}$.

Lattice sums, $T_{i,j}$ are evaluated by the Ewald–Kornfeld procedure[12] and as discussed in prior publications[7,11] are given as

$$T_{i,j} = d_i d_j t_{i,j} + \frac{4\pi}{v_0}(d_i\cdot\hat{\mathbf{k}})(d_j\cdot\hat{\mathbf{k}})$$

Here the *d*'s are the dipole transition moments for transitions *i* and *j*, v_0 is the volume of the unit cell, $\hat{\mathbf{k}}$ is the unit wave vector (or normal of the crystal face), and $t_{i,j}$ are unit dipole inner sums. For computational purposes we have evaluated the inner sums for unit vectors directed along the *a*, *b*, and *c* crystal axes.[6,11] These numbers are given in Table II and can be used to evaluate the $t_{i,j}$ for any two arbitrarily directed unit vectors.

The calculations reported here are straightforward since the polarization direction of each vibronic member is assumed to be parallel to the *c* axis. The $\hat{\mathbf{k}}$ dependent term in the lattice sum expression vanishes for the (010) face but not for the $\perp b$ axis of (101). The results of the calculations are presented graphically in Figure 5. Although the calculations overestimate the effects somewhat, the observed hand shapes are reasonably well reproduced by the calculations and support the general analysis given here. The energy difference of the lowest vibronic member along the *c* and $\perp b$ axes, i.e., E_c–E_b, can be estimated to be about +300 cm^{-1} from the derived spectra and compares with a calculated value of +295 cm^{-1}. The intensity pattern observed here for 1-MC·HBr is very similar to those reported for single crystals of 1-methyluracil.[13] The interpretation is the same.

Discussion

Pyrimidine base spectra are, in general, diffuse with little more than a suggestion of vibronic structure. Transition-moment directions are deduced from dichroic ratios obtained by using the areas under the entire band envelopes and are not necessarily equivalent to those of the pure electronic transition moments (i.e., for the 0–0). There are two major factors complicating the interpretation of such crystal spectra. On the one hand, the polarizations of the different vibronic components of electronic transitions are not all alike and can vary from one vibronic component to the next owing to Herzberg–Teller mixing. This situation occurs in the free molecule so that the polarization of the band may be inherently mixed. On the other hand, mixing of

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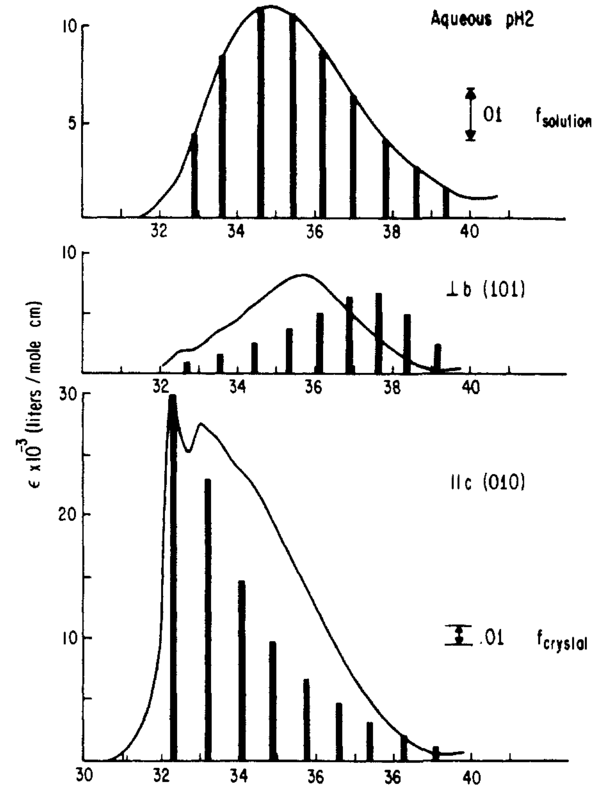

Figure 5. The effect of the **k** dependence of the exciton mixing on the band shapes of transition I. (Top) Aqueous solution spectrum decomposed into nine vibronic transitions. (Middle and bottom) The distribution of intensity after exciton mixing along $\perp b$ (101) and $\| c$ (010). The relative oscillator strengths are shown.

different electronic states due to intermolecular interactions in the crystal can cause serious changes in the dichroic ratios relative to those for an oriented gas model. The magnitudes of the resulting ambiguities have not been generally appraised.

The impurity of polarization inherent in an electronic transition in certain circumstances can be appreciable. For example, the first excited singlet of anthracene exhibits about 33% long axis polarized, vibronically induced intensity in the nominally short axis polarized transition.[14] Such a magnitude, if operative in the type of system studied here, could lead to errors in directions of 30° or more. Although the outcome is probably exaggerated in the linear polyacenes owing to the presence of a strong, nearby, oppositely polarized state, it is in fact a general problem. The low symmetry of the 1-methylcytosine cation (effectively planar, point group C_s) will permit the transition moment direction of each vibronic component to change by various amounts to one side or the other of the pure electronic 0–0 direction. Instead of a unique vector direction characteristics of the entire transition, we should expect to have a large cluster of individual vibronic component vectors possibly clustering around some general direction.

The data presented here can only be used to place a rough upper limit on such inherent depolarization, for exciton mixing effects need to be adequately separated first. We can choose to ignore the latter mixing effects and seek crystal systems in which the observed absorption intensity is strongly polarized along some particular crystal axis. If no intensity is observed in orthogonal directions, then the vibronic transition moments are all parallel. The present results of 100:4:1 for f_c:f_a:f_b correspond to the largest dichroic ratios ever found with use of integrated, whole band areas. However, it should be mentioned that crystals of 1-methyluracil exhibit a nearly equivalent purity of polarization for the lowest energy transition.[15] Even so, a dichroic ratio of 100:1 corresponds to an average transition moment angle of 6° away from the main direction. The ratios of 100:4:1 (out of plane) indicate that such mixed polarization is at most not large. The angular differences from the principal axes correspond to ±12° (in plane) and ±6° (out of plane) and do not, however, seem so small.

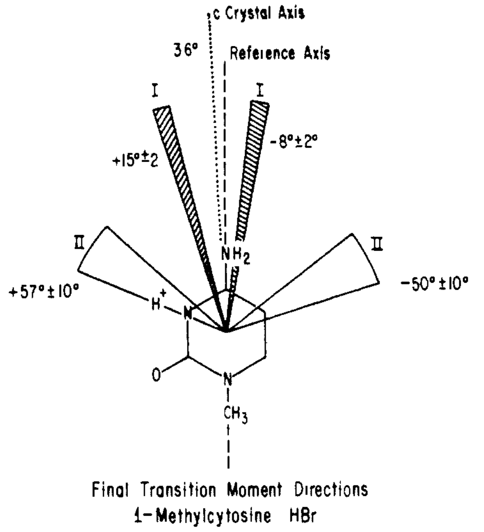

Figure 6. Final transition moment directions of protonated 1-methylcytosine. The two possible directions consistent with the observed dichroic ratio for each transition are shown with their corresponding uncertainty arcs. The alternate, unique choice for I is shown as the dotted line parallel to the c crystal axis.

Intermolecular interactions in the crystal cause two types of mixing of states. As discussed in the previous section, intraband mixing between vibronic members of a given electronic state causes band shape changes and corresponding dichroic ratio changes along the band envelope. For example, the dichroic ratio of band I, $f_{c(010)}/f_{\perp b(101)}$ changes from 30:1 to 1:1 along the band contour corresponding to an apparent angular change in θ in excess of 53°. On the other hand, by employing oscillator strengths for the entire band envelope, intraband mixing effects should be eliminated. More serious, possibly, are the changes in dichroic ratios arising from interband exciton mixing effects. The early work on adenine hydrochloride and the recent work on cytosine appear to be the only published attempts at assessing such magnitudes. In those papers the range of uncertainty of ±10° was given as a rough upper limit for changes in transition moment directions of purine and pyrimidine-type systems caused by interband mixing.[6,11] Since the data presented here include but two absorption bands, it is felt that an attempt at treating interband mixing would not be useful since unknown higher energy transitions no doubt dominate the effects. The results of the present oriented gas work are summarized in Figure 6.

Hug and Tinoco[16] have suggested that the spectrum of cytosine cation should resemble that of uracil, and it is of interest to compare the present results to the available transition-moment directions of 1-methyluracil.[15,17] The polarization of the first band of the latter (267 nm) is $\theta = 0 \pm 1°$ or $+7 \pm 1°$. These directions are close to the present result when we assign the moment as roughly parallel to the c-crystal axis (i.e., $\theta \simeq 4°$). The second band of 1-methyluracil (206 nm) has been assigned a direction $\theta = -53 \pm 2°$.[17] This value is near the $-50 \pm 1°0$ choice found for the cation. No additional evidence is presently available to corroborate further this suggestion. No theoretical analysis has been published with which to correlate the bands of C and C$^+$ so as to interpret the large changes that occur upon protonation (see Figure 2). Curiously, the transition-moment directions of bands I and II are very nearly the same for the two systems: C (+6°, −53°), C$^+$ (+4°, −50° or +57°). No speculation of what happens to bands III and IV of cytosine upon protonation is advanced here. There is no compelling evidence for perpendi-

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cularly polarized nπ^* in the $\|b$ spectrum.

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Registry No. 1-MC·HBr, 58052-67-8.

Zero-Field NMR of Small-Amplitude Motions in a Polycrystalline Solid

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Abstract: The librational motions of the water molecules in polycrystalline barium chlorate monohydrate have been studied by using proton and deuterium zero-field NMR. In contrast to high-field NMR, subtle molecular motions produce readily observable changes in the zero-field spectrum. Computer simulations and application of a novel-pulsed zero-field technique confirm that the splitting observed in the zero-field spectrum of the hydrate results from the motionally induced asymmetry of the magnetic dipole–dipole coupling tensor.

NMR has been an excellent tool for the study of motion in condensed matter since one observes a time average over the motion resulting in an average chemical shift, quadrupolar coupling, or dipolar interaction. Because powder patterns[1] are insensitive to the relatively small perturbations of these motions one often resorts to single-crystal measurements[2] or oriented liquid crystal measurements.[3] Zero-field NMR offers an approach to this problem which is useful for polycrystalline or otherwise disordered materials since it has been demonstrated to provide sharp dipolar[4–6] and quadrupolar information[7–9] from such systems down to very low frequencies. Zero-field NMR should be sensitive to small amplitude motions which result in splittings or extra lines in the frequency spectrum. Such motions typically do not result in observable changes in the high-field NMR spectrum. In this report we present the first experimental results for the study of libration in a polycrystalline hydrate using proton and deuterium zero-field experiments.

The proton zero-field spectrum of a static water molecule would consist of lines at zero frequency and at $\pm\nu_d = 3\gamma^2 h/8\pi^2 r^3$, where r is the internuclear distance of the two protons.[4] The characteristic motion of the waters in a typical hydrate are rapid 180° flips about their C_2 axes[10] and librations about three axes.[11,12] To a good approximation the librational modes correspond to rotations about the x, y, and z axes[12] of the molecular coordinate system shown in Figure 1 and are commonly referred to as rocking, waving, and twisting, respectively. The influence of the motion on the proton zero-field spectrum is treated by calculation of its effect on the dipolar Hamiltonian, $\mathcal{H}_d$, which is responsible for the zero-field spectrum. The rapid 180° flips have no effect since they merely exchange the two protons. Waving has no effect since it leaves the orientation of the internuclear vector r invariant. The dipolar Hamiltonian is therefore motionally averaged by only two of the librational modes. The resulting motionally averaged Hamiltonian, $\mathcal{H}_d'$, is given in the molecular frame by

$$\mathcal{H}_d' = \langle R_z(\theta_z)R_x(\theta_x)\mathcal{H}_d R_x(\theta_x)^{-1}R_z(\theta_z)^{-1}\rangle = \vec{I}_1\langle R_z(\theta_z)R_x(\theta_x)\mathrm{D}R_x(\theta_x)^{-1}R_z(\theta_z)^{-1}\rangle\vec{I}_2 \equiv \vec{I}_1\mathrm{D}'\vec{I}_2 \quad (1)$$

where θ_x and θ_z are the librational angles about the x and z axes, respectively, and the brackets signify a time average over the librational motion. To second order in the angles θ_i characterizing the libration, we can write the motionally averaged tensor, $\mathbf{D}'$, in angular frequency units as[11,13]

$$\mathrm{D}' = d\begin{bmatrix} 1 - 3\langle\theta_z^2\rangle & 0 & 0 \\ 0 & -2 + 3\langle\theta_z^2\rangle + 3\langle\theta_x^2\rangle & 0 \\ 0 & 0 & 1 - 3\langle\theta_x^2\rangle \end{bmatrix} \quad (2)$$

where $d = \gamma^2 h/2\pi r^3$. Application of the rotations in the reverse order of eq 1 produces the same expression for $\mathbf{D}'$ to this order of approximation. *An unequal intensity in the amplitudes of the two librational modes produces a nonaxially symmetric average dipolar tensor.* This is made more clear by defining $\Delta = \mathbf{D}'_{22}$ and $\eta = (\mathbf{D}'_{11} - \mathbf{D}'_{33})/\mathbf{D}'_{22}$ and rewriting eq 2 as

$$\mathrm{D}' = \begin{bmatrix} -\Delta(1-\eta)/2 & 0 & 0 \\ 0 & \Delta & 0 \\ 0 & 0 & -\Delta(1+\eta)/2 \end{bmatrix} \quad (3)$$

Calculation of the sudden experiment zero-field spectrum for this case proceeds in a manner analogous to that described pre-

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