expected range (950–970 cm^{-1}) for this vibration.[12] In substituted ethylenes, this HOOP frequency can be significantly lowered by the inductive effect of groups covalently linked to the double-bonded carbons (e.g., 926 cm^{-1} in $HClC{=}CHCH_3$).[13] Our preliminary calculations show that this frequency can also be lowered by placing a negatively charged opsin residue near $C_{11}{=}C_{12}$ to reduce its bond order. A similar perturbation was recently suggested by Honig et al.[14] to explain the absorption spectra of rhodopsin analogues.

Whereas the frequencies of RR lines depend only on the ground-state conformation of the chromophore, their intensities also depend on the resonant excited-state geometry. The observed HOOP mode enhancement is a function of the displacement of the hydrogen equilibrium positions between the ground and excited states.[4,15] Thus, the fact that the 922-cm^{-1} batho line is enhanced means that the excited-state twist about the 11,12 double bond is different from that of the ground state, as intuitively expected for a cis → trans photoisomerization. The intensities of the 854- and 875-cm^{-1} HOOP modes can similarly be used to model relative twists about specific chain bonds in bathorhodopsin. This analysis should elucidate key features of the cis → trans isomerization trajectory in visual excitation.

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(12) The out-of-plane vibrations of hydrogens trans to a C=C double bond are coupled to form normal modes of approximately A_u and B_g local symmetry (C_{2h}). The higher frequency (A_u) vibration gives a reproducible IR group frequency between 950 and 970 cm^{-1} for a wide variety of model compounds, although it is normally silent in Raman spectra. Cf. ref 13. Even for the highly conjugated *all-trans*-retinal *n*-butylamine protonated Schiff base, the A_u HOOPs are found in the 950–970-cm^{-1} range (e.g., IR 967 cm^{-1}).

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Direct Measurement of the Electron Susceptibility Anisotropy in Paramagnetic Complexes Using High-Field Deuterium NMR

Sir:

A well-defined separation of the individual contact and pseudocontact contributions to the ^1H NMR chemical shifts of paramagnetic complexes requires an accurate knowledge of the elements of the susceptibility tensor ($\mathbf{x}$). The total shift is expressed as a sum of contact and dipolar terms, where the equation for the dipolar shift[1] (eq 1) contains the χ_{ii} values.

$$(\Delta H/H)_D = -\frac{1}{3}\left[\chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy})\right]\langle(3\cos^2\theta' - 1)/R^3\rangle - \frac{1}{2}[\chi_{xx} - \chi_{yy}]\langle\sin^2\theta' \cos 2\varphi'/R^3\rangle \quad (1)$$

We report a direct measurement of the χ_{ii} on the basis of the observation of line splittings in deuterium NMR spectra. This solution-state NMR measurement eliminates extrapolation from low-temperature,[2] solid-state,[3] measurements of $\mathbf{x}$.

Placing a molecule with an anisotropic magnetic susceptibility in a strong magnetic field causes a partial cancellation of the random Brownian motion, and a small net alignment results. This partial order produces a nonzero average of anisotropic interactions; the quadrupole coupling energy of nucleii with $I \geq 1$ does not average to zero and leads to a splitting of absorption lines.

Here, we present observations of alignment effects in the high-resolution deuterium NMR spectrum of the paramagnetic, trigonal bis[phenyl-d_5-tris(1-pyrazolyl)borato]cobalt(II) system,[1b,4] abbreviated as Co(PTPB-d_5)$_2$, and we will show how these measurements directly yield the χ_{ii} necessary to quantify the pseudocontact shifts in eq 1. Data for the corresponding *p*-tolyl-d_7 derivative, depicted as Co(TTPB-d_7)$_2$, are also presented.

The room-temperature deuterium NMR spectra of Co(PTPB-d_5)$_2$ at three different field strengths (Figure 1) exemplify the results. The 21.14-kG spectrum clearly shows the three expected resonances with the para resonance substantially broader than the ortho and meta positions. Higher field data, at 46.98 kG, show the para resonance split, and the highest field spectrum (84.6 kG) exhibits additional splitting of the meta resonance and broadening of the ortho line. The field dependence of the para-deuteron splitting is included in Figure 2 as well as the temperature dependence of the *p*-CD_3 splitting in Co(TTPB-d_7)$_2$. The observed splittings are independent of concentration.

The alignment of any molecule in a magnetic field can be described by two order parameters[5]

$$S_0 = \langle(3\cos^2\theta - 1)/2\rangle = [\chi_{zz} - (\chi_{xx} + \chi_{yy})/2]H_0^2/15kT \quad (2a)$$

$$S_1 = \langle\sin^2\theta\cos 2\varphi\rangle = [\chi_{xx} - \chi_{yy}]H_0^2/15kT \quad (2b)$$

where θ and φ are the polar angles describing the H_0 vector relative to the susceptibility axes (x, y, and z). Magnetic alignment of an $I = 1$ quadrupole with an axially symmetric field gradient produces a residual quadrupole splitting[6]

$$\Delta\nu_Q = [(e^2qQ/h)H_0^2/20kT]\{(3\cos^2\alpha - 1) \times [\chi_{zz} - (\chi_{xx} + \chi_{yy})/2] + [(3\sin^2\alpha\cos 2\beta)/2](\chi_{xx} - \chi_{yy})\} \quad (3)$$

where α and β are the polar angles describing the C–D director relative to the magnetic axes. Since the combinations of the χ_{ii} in eq 3 are precisely those needed in eq 1, measured splittings of deuterium resonances with known α and β directly yield the magnetic anisotropy information for evaluation of dipolar shifts.

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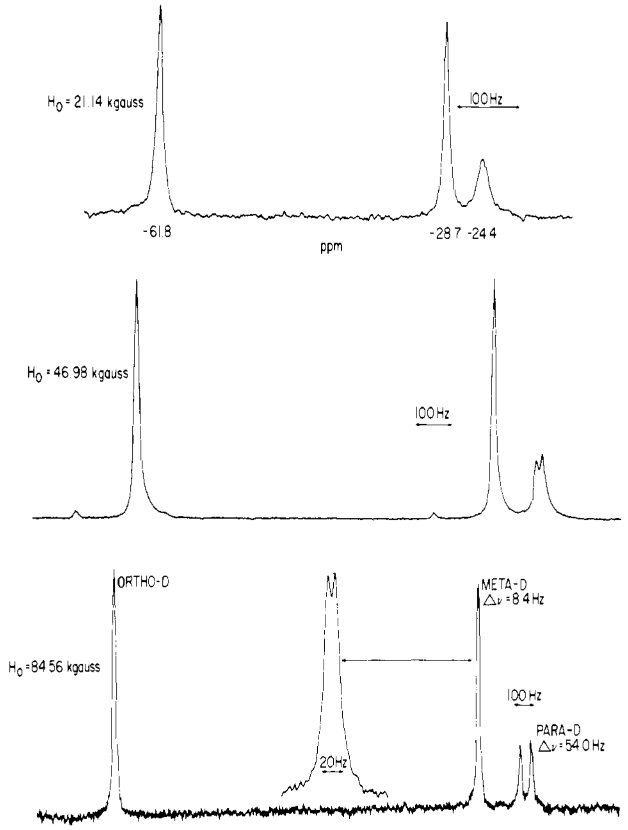

Figure 1. Field dependence of the ^2H NMR spectrum of a 0.08 M solution of Co(PTPB-d_5)$_2$ in chloroform at 295 K. HFX-90 spectrum (top), NT-200 spectrum (center), and WH-360 spectrum (bottom).

Measurement of the para-deuteron splitting in Co(PTPB-d_5)$_2$ ($\alpha = 0°$) yields the susceptibility anisotropy $[\chi_{zz} - (\chi_{xx} + \chi_{yy})/2] = \Delta\chi = 1.66 \times 10^{-26}$ cm^3 at 295 K.[7] Likewise, the splitting of the p-CD$_3$ resonance ($\alpha = 109.47°$) in Co(TTPB-d_7)$_2$ gives $\Delta\chi = 1.58 \times 10^{-26}$ cm^3. The small differences between these two independent results are explained by experimental uncertainties and by the assumed values for e^2qQ/h and α. Good agreement with the spin-isolation approach[8] ($\Delta\chi = 1.76 \times 10^{-26}$ cm^3) results; however, the quadrupolar method is less sensitive to molecular structure as there is no radial dependence.

Figure 2 verifies the quadratic field dependence of the ordering and illustrates the T^{-2} dependence resulting from a near T^{-1} dependence of $\Delta\chi$ and a further T^{-1} term in the order parameter. More precise data will define the temperature dependence of $\Delta\chi$.[9]

The above technique allows quick, accurate determination of the elements of **x** under NMR conditions, thus making unnecessary extrapolation from different phases, solvents, and temperatures. The method requires knowledge *only* of the angles of the C–D bonds to the magnetic axes; in molecules of C_{2v} symmetry or greater (where the inertial and magnetic axes are parallel), symmetry can define α and β. Unlike dipolar shifts, the splitting is independent of the distance from the paramagnetic center and is also independent of contact density. The technique is viable in cases where the assumption of isolated spin is inadequate and is applicable to molecules with nonmagnetic ground states where the ESR technique[2] fails.

All experimental restrictions hinge upon observation of an NMR spectrum with a quadrupolar splitting larger than the resonance line width. The many factors contributing to T_2 preclude a singular statement of the limitations. However, T_{1e} must be sufficiently rapid[1c] to produce a sharp (1–100 Hz) ^1H NMR spectrum, and the molecule must be small enough that rapid tumbling minimizes quadrupolar relaxation.[10]

The technique is not universally applicable, but given the importance of **x** in the interpretation of dipolar NMR shifts, it can be applied to such traditional areas of paramagnetic NMR[1c] as transition metal complexes, lanthanide and actinide complexes, metallocenes, and biological systems.

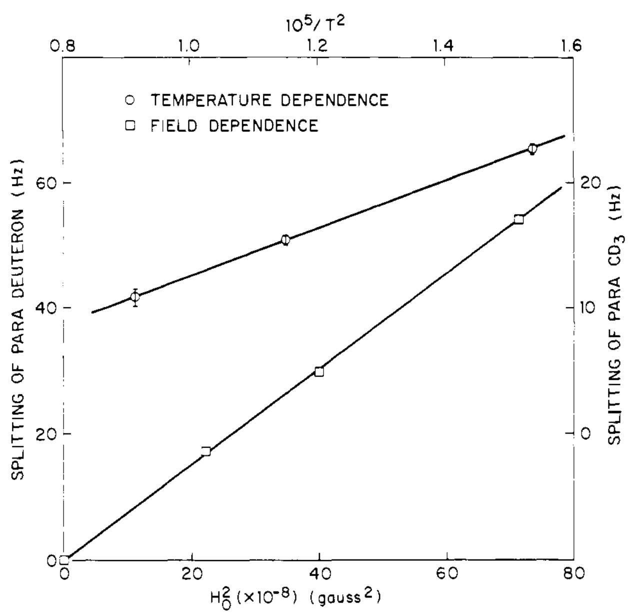

Figure 2. Field and temperature dependences of quadrupolar splitting. The field dependence uses the data of Figure 1 for Co(PTPB-d_5)$_2$. The temperature dependence of the p-CD$_3$ resonances in Co(TTPB-d_7)$_2$ in tetrahydrofuran is shown.

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(7) The quadrupole coupling constant in Co(PTPB-d_5)$_2$ was taken to be the same as in benzene-d_6 (185 ± 10 kHz) and that of -CD$_3$ in Co(TTPB-d_7)$_2$ the same as in toluene-d_3 (165 ± 10 kHz). See: Mantsch, H. M.; Saito, H.; Smith, I. C. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211–271.

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Carbon Monoxide Activation by f-Element Organometallics. An Unusually Distorted, Carbenelike Dihaptoacyl and CO Tetramerization

Sir:

The search for new modes of CO reactivity has recently led to studies with early transition-metal[1-4] and actinide organometallics.[5,6] The latter offered us the possibility of elucidating CO activation patterns at molecular sites which might have

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