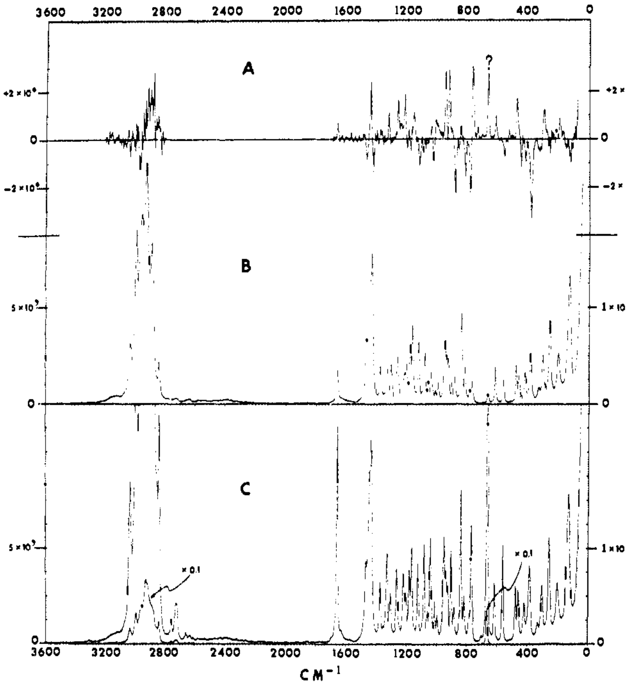


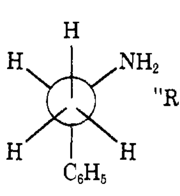
**Figure 3.** Difference and sum spectra for (−)-$\alpha$-pinene in photon counts: (A) ($I_r^{\parallel} - I_l^{\parallel}$), (B) ($I_r^{\parallel} + I_l^{\parallel}$), (C) ($I_r^{\perp} + I_l^{\perp}$). The peak in (A) at 665 cm$^{-1}$ is doubtful. See error discussion.

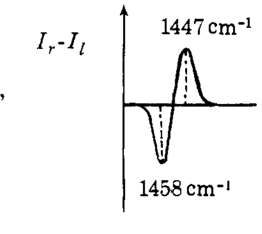
Table I. Raman CID's of *d*-(+)-$\alpha$-Phenylethylamine and (−)-$\alpha$-Pinene

| *d*-(+)-$\alpha$-Phenylethylamine | | (−)-$\alpha$-Pinene | | | |
|---|---|---|---|---|---|
| $\tilde{\nu}$(cm$^{-1}$) | $\Delta_{\parallel} \times 10^3$ | $\tilde{\nu}$(cm$^{-1}$) | $\Delta_{\parallel} \times 10^3$ | $\tilde{\nu}$(cm$^{-1}$) | $\Delta_{\parallel} \times 10^3$ |
| 315 | −0.85 | 300 | +0.50 | 951 | +0.85 |
| 364 | +0.35 | 330 | −0.45 | 1015 | +1.10 |
| 402 | −0.90 | 386 | −1.15 | 1034 | −1.25 |
| 479 | +0.70 | 423 | −0.45 | 1045 | +0.30 |
| 622 | −0.20 | 480 | +0.80 | 1127 | −0.35 |
| 850 | −0.40 | 562 | −0.65 | 1164 | +0.65 |
| 915 | −0.30 | 620 | +0.50 | 1222 | +1.25 |
| 1080 | +0.30 | 771 | +2.50 | 1246 | +0.90 |
| 1105 | −0.50 | 789 | −2.60 | 1268 | +0.70 |
| 1447 | +0.60 | 821 | −0.70 | 1328 | +0.65 |
| 1458 | −0.80 | 888 | −1.50 | 1430 | −0.25 |
| | | 910 | +0.65 | 1446 | +0.35 |
| | | 928 | +1.15 | 1476 | −0.30 |
| | | 942 | (−0.05) | | |

"safe". We estimate that absolute errors for the CID's are below $2 \times 10^{-4}$, and relative errors between 10 and 40%.

We reserve a detailed discussion of our data for a subsequent paper.[13] Clearly, the wealth of chiral information in Figures 2 and 3 is striking. Negligible CID's were found in the CH stretch region and below 250 cm$^{-1}$. As stated previously,[14] the degenerate antisymmetric CH$_3$ deformation mode centered at 1450 cm$^{-1}$ has important potential for probing the local chiral environment of methyl groups. In $\alpha$-phenylethylamine the local degeneracy of the methyl group is removed by the asymmetric environment, and a sizable CID couplet is found.





As more experimental data become available, the splitting and sign can doubtlessly be correlated with the nature of various substituents, and a more general sector rule established. In our present case, we would expect no sign change by, e.g., replacing the phenyl group with a substituted phenyl group. In $\alpha$-pinene the spectral region is complicated by overlapping bands from three methyl groups. For complex molecules this might limit the usefulness of this sector rule.

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## MINDO/3 Study of $^{14}$N Nuclear Quadrupole Coupling Constants

*Sir:*

Attempts to calculate NQ (nuclear quadrupole) coupling constants for polyatomic molecules have not as yet been too successful.[2] While satisfactory results have been obtained from detailed ab initio SCF calculations, these are limited to fairly small molecules, and attempts to use semiempirical methods such as CNDO have not proved too satisfactory. We wish to report some calculations of $^{14}$N coupling constants by MINDO/3[3] which seem to suggest that it may provide a solution to this problem.

In the LCAO MO approximation, the electronic contribution to the field gradient tensor for nucleus $\alpha$ is given[2] by:

$$\langle q^{\alpha}{}_{e} \rangle = -e \sum_{i\alpha} \sum_{j\alpha} P_{i\alpha,j\alpha} q^{\alpha}{}_{i\alpha,j\alpha} - 2e \sum_{i\alpha} \sum_{j\beta} P_{i\alpha,j\beta} q^{\alpha}{}_{i\alpha,j\beta} - e \sum_{i\beta} \sum_{j\gamma} P_{i\beta,j\gamma} q^{\alpha}{}_{i\beta,j\gamma} \quad (1)$$

Table I. Calculated $^{14}N$ Nuclear Quadrupole Coupling Constants

| Molecule | Field gradient (au) | | | $e^2Qq/h$ (MHz) | |
|---|---|---|---|---|---|
| | $q_{elec}$ | $q_{nuc}$ | $q_{total}$ | Calcd[a] | Obsd |
| $N_2$ | −2.45 | 1.12 | −1.33 | −6.18 | −5.55[b] |
| $NH_3$ | −0.87 | −0.20 | −1.07 | −4.98 | −4.08[c] |
| HCN | −1.61 | 0.80 | −0.81 | −3.77 | −4.58[d] |
| $CH_3CN$ | −1.67 | 0.85 | −0.82 | −3.81 | −4.21[e] |
| $(CH_3)_3CCN$ | −1.68 | 0.91 | −0.77 | −3.58 | −3.85[f] |
| NC—CN | −1.76 | 0.86 | −0.90 | −4.19 | −4.27[g] |
| $HC\equiv C-CN$ | −1.72 | 0.85 | −0.87 | −4.04 | −4.20[h] |
| $CH_3C\equiv C-CN$ | −1.65 | 0.86 | −0.79 | −3.67 | −4.40[i] |
| $CH_3NC$ | −1.35 | 1.26 | −0.09 | −0.41 | +0.50[e] |
| $H\overset{*}{N}=\overset{+}{N}=N^-$ | −0.28 | 0.95 | 0.67 | +3.11 | +4.85[j] |
| $HN=\overset{+}{N}=\overset{*}{N}^-$ | −1.36 | 1.23 | −0.13 | −0.60 | −1.35[j] |
| Pyridine | −1.01 | 0.01 | −1.00 | −4.65 | −4.86[k] |
| Pyrazine | −1.14 | 0.04 | −1.10 | −5.11 | −4.85[l] |
| Benzonitrile | −1.70 | 0.90 | −0.80 | −3.72 | −3.64[m] |

[a] With $Q(N) = 1.98 \times 10^{-26}$ cm² and geometries found by minimizing the energy with respect to all geometrical variables; see R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 97, 1285 (1975). [b] F. W. Terman and T. A. Scott, *Bull. Am. Phys. Soc.*, 3, 23 (1968). [c] G. R. Günther-Mohr, R. L. White, A. L. Schawlow, W. E. Good, and D. K. Coles, *Phys. Rev.*, 94, 1184 (1954). [d] J. W. Simmons, W. E. Anderson, and W. Gordy, *Phys. Rev.*, 77, 77 (1950). [e] M. K. Kemp, J. M. Pachan, and W. H. Flygare, *J. Phys. Chem.*, 71, 765 (1967). [f] J. Sheridan and A. Turner, *Proc. Chem. Soc.*, 21 (1960). [g] P. J. Haigh and L. Guibé, *C.R. Acad. Sci.*, 261, 2338 (1965). [h] A. A. Westerley and E. B. Wilson, *J. Am. Chem. Soc.*, 72, 199 (1950). [i] A. Colligiani, L. Guibé, P. J. Haigh, and E. A. C. Lucken, *Mol. Phys.*, 14, 89 (1968). [j] R. Kewley, K. V. L. N. Sasty, and M. Winnewisser, *J. Mol. Spectrosc.*, 12, 387 (1964). [k] G. O. Sorensen, *J. Mol. Spectrosc.*, 22, 325 (1967). [l] L. Guibé and E. A. C. Lucken. *Mol. Phys.*, 10, 273 (1966). [m] A. Colligiani, R. Ambrosetti, and L. Guibé, *J. Chem. Phys.*, 54, 2105 (1971).

Table II. One-, Two-, and Three-Center Contributions to Calculated Electric Field Gradients

| Molecule | One-center contributions[a] | Two-center contributions[a] | Three-center contributions[a] | $q_{el}$[a,b] | $q_{cor}$[a,c] | $a_{total}$[a,d] |
|---|---|---|---|---|---|---|
| $NH_3$[e] | −1.44 | 0.58 | −0.01 | −0.87 | −0.20 | −1.07 |
| $NH_3$[f] | −1.18 | 0.14 | 0.01 | −0.79 | −0.25 | −1.05 |
| HCN[e] | 0.29 | −1.84 | −0.06 | −1.60 | 0.80 | −0.81 |
| HCN[f] | −0.81 | −1.23 | −0.01 | −2.05 | 1.19 | −0.86 |

[a] In atomic units. [b] Total electronic contribution to the field gradient at nitrogen. [c] Total contribution to the field gradient at nitrogen by the cores[e] all nuclei[f]. [d] Total field gradient at nitrogen. [e] This work. [f] Reference 9.

Here Roman subscripts refer to AO's and the Greek ones to atoms, the $P$ are bond order matrix elements, and

$$q^{\alpha}{}_{j\beta,k\gamma} = \langle \phi_{j\beta} | (3\mathbf{r}_\alpha\mathbf{r}_\alpha - r_\alpha{}^2\mathbf{l}) r_\alpha{}^{-5} | \phi_{k\beta} \rangle \tag{2}$$

where $r_\alpha$ is the scalar distance of an electron from nucleus $\alpha$ and $\mathbf{r}_\alpha$ is the corresponding vector. The first (one-center) term in eq 1 represents contributions by electrons in AO's of atom $\alpha$, the second term represents contributions by electrons in overlap clouds between AO's of atom $\alpha$ and AO's of other atoms, and the third term represents contributions by electrons in AO's of other atoms and overlap clouds between them.

All the elements in the first term vanish except diagonal elements involving 2p AO's.[4] It can be shown that the $z$ components are given by

$$q^{\alpha(z)}{}_{z\alpha,z\alpha} = {}^4\!/\!_5 \langle r^{-3} \rangle = -2q^{\alpha(z)}{}_{z\alpha,z\alpha} = -2q^{\alpha(y)}{}_{z\alpha,z\alpha} \tag{3}$$

with corresponding expressions for the $x$ and $y$ components. We used for $\langle r^{-3} \rangle$ the value 2.47 computed for nitrogen using Slater AO's.[2]

The contributions by the two-center diagonal terms $q^{\alpha}{}_{j\beta,j\beta}$ are treated as though they arose from corresponding point charges $eP_{j\beta,j\beta}$. The two-center off-diagonal terms can be shown to be given by

$$q_{i\alpha,j\beta} = {}^1\!/\!_2 \left\{ \sum_{k\alpha} S_{k\alpha,j\beta}\, q^{\alpha}{}_{i\alpha,k\alpha} + \sum_{k\beta} S_{j\beta,k\beta} q^{\alpha}{}_{j\beta,k\beta} \right\} = {}^1\!/\!_2\, S_{i\alpha,j\beta} \{ q^{\alpha}{}_{i\alpha,i\alpha} + q^{\alpha}{}_{j\beta,j\beta} \} \tag{4}$$

since the other terms in the sums vanish. In view of this result we approximated the off-diagonal three-center matrix elements by a similar Mulliken-type expression:

$$q^{\alpha}{}_{j\beta,k\gamma} \simeq {}^1\!/\!_2 S_{j\beta,k\gamma} \{ q^{\alpha}{}_{j\beta,j\beta} + q^{\alpha}{}_{k\gamma,k\gamma} \} \tag{5}$$

The terms in eq 4 and 5 should logically be omitted in an INDO-type approximation since they involve bicentric overlap; however, we found it necessary to include them. Including them makes it necessary to renormalize the eigenvectors, including overlap; thus the normalizing condition for the coefficients $a_{pi}$ of AO's $\phi_i$ in the MO $\Psi_p$ becomes:

$$\sum_i \sum_j a_{pi} a_{pj} S_{ij} = 1 \tag{6}$$

Calculations were carried out in this way for the field gradients of nitrogen for a number of nitrogen compounds (Table I). These are related[2] to the observed NQ coupling constants ($K$) by

$$K = eQh^{-1} q^{\alpha}{}_{total} \tag{7}$$

where $q^{\alpha}{}_{total}$ is the total field gradient (core + electrons) at the nucleus of atom $\alpha$ and $eQ$ is its nuclear quadrupole moment. Our treatment neglects contributions by polarization of the inner (1s) electrons (Sternheimer effect). However, this should be small and should lead only to a constant multiplicative correction to $eQ$ in eq (7).

The value of $Q$ for $^{14}N$ is not known. Most recent estimates have been derived from the observed $^{14}N$ NQR coupling constant in $NH_3$ by using field gradients calculated by various SCF MO methods. Values found in this way range from 1.56[5] to 2.16[6] au, whereas our field gradient for $NH_3$ leads to $Q$ = 1.78 au. The agreement is clearly reasonable, especially in view of our neglect of 1s polarization (which is consequently absorbed into our value for $Q$). Our calculated field gradients for $NH_3$, HCN, and $CH_3CN$ are also in quite good agreement with those of Snyder and Basch,[7] i.e., $NH_3$, −1.06; HCN, −0.81; $CH_3CN$, −0.70 au. In the case of $CH_3NC$, their value is (correctly) positive (+0.26 au) while ours, although small, is negative (−0.09 au); however, the errors in the corresponding NQR coupling constants are similar (ours, −0.66 MHz; theirs, +0.86 MHz), using in each case a value of $Q$ derived from $NH_3$.

Table I compares observed $^{14}N$ coupling constants with our MINDO/3 values, the latter being calculated with $Q$ = 1.98 au.[8] The agreement is quite good, especially in view of the fact that several of the experimental values are derived from NQR spectra of solids and are therefore subject to crystal field effects of uncertain magnitude.

Table II compares the various contributions to $q^{\alpha}{}_{total}$ calculated for $NH_3$ and HCN by MINDO/3 and by an ab initio SCF procedure.[9] While the individual contributions vary considerably, both methods gave similar estimates of the overall field gradients. The MINDO/3 calculations naturally took only a fraction of the time required for the ab initio ones.

These results suggest that MINDO/3 may prove generally effective for calculating NQ coupling constants. Apart from their value in NQR spectroscopy, such calculations may prove useful in other connections. For example comparisons of calculated with observed NQ coupling constants may enable MINDO parameters to be determined for elements in cases where thermochemical data are lacking.

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## Proton Affinity and the Frontier Orbital Concept. Predictions and Pitfalls

*Sir:*

Application of the frontier orbital concept[1] to the problem of proton attack was implicit in the work of Hieber[2] in which he considered the proton in metal hydrides to be "buried" in the metal electron density. Pitzer[3] rationalized the structure of diborane by considering its formation as resulting from a double proton attack on the $\pi$ orbital of the hypothetical $B_2H_4{}^{2-}$ to give the bridged structure.

In this communication we wish to predict the site of proton attack on $CH_3X$ (X = OH, Cl, Br, and I), $NF_3$, HOF, and $Fe(CO)_5$ by making use of the fundamental relationship between the first ionization potential (IP) of a molecule and the proton affinity (PA).

For an electron donor B the following thermochemical cycle is valid

$$BH^+ \rightarrow B + H^+ \quad \Delta H = PA(B) \tag{1}$$

$$BH^+ \rightarrow B^+ + H \quad \Delta H = D(B^+\text{-}H) \tag{2}$$

$$PA(B) = IP(H) - IP(B) + D(B^+\text{-}H) \tag{3}$$

where IP(H) = 13.598 eV and IP(B) is the first IP of B. The PA may arbitrarily be divided into two hypothetical steps. In the first one, the proton attacks the highest occupied molecular orbital (HOMO) and one electron is transferred from B to $H^+$. It is this orbital which is ionized in the IP(B) term of eq 3. If no bond were to be formed we would obtain PA(B) = IP(H) − IP(B). In the second step, the separated atoms $B^+$ and H unite to form $BH^+$ with a bond strength $D(B^+\text{-}H)$. In this simple analysis, the final position of proton attachment will correspond to the initial site of attack. Subtle electronic energy effects may cause proton migration, however, particularly if there is a large amount of charge rearrangement in $B^+$ compared to B.

According to Fukui's first postulate,[1] the initial point of attack by an electrophile (in this case the proton) will occur at the position of highest electron density in the HOMO. The localization of the HOMO may be determined by a judicious interpretation of ultraviolet photoelectron spectroscopy (UPS) data. For instance, the UPS of the following molecules has been obtained: $CH_3\mathit{O}H$,[4] $CH_3\mathit{Cl}$,[5] $CH_3\mathit{Br}$,[5] $CH_3\mathit{I}$,[5] $\mathit{N}F_3$,[6] $H\mathit{O}F$,[7] and $\mathit{Fe}(CO)_5$.[8] In each case, the first band in the UPS corresponds to electron ejection from an orbital largely localized on the atom which is in italic. This is the position for which proton attack is predicted. Consideration of the symmetry properties of the HOMO allows one to predict the direction of attack, but this information is usually not directly available from UPS. However, utilizing simple MO concepts we would predict, for example, that proton attack on $CH_3Cl$ would occur along a line perpendicular to the C–Cl axis. Likewise, attack on HOF would occur along a line perpendicular to the plane of the molecule.

For $CH_3OH$ and HOF, these predicted results agree with the results of ab initio calculations[9] regarding the position of proton attachment. For $CH_3X$ (X = Cl, Br, I) the result is what one would expect intuitively, namely, attack at the lone pair on the halogen. For $Fe(CO)_5$[10] and $NF_3$[11] the prediction is in agreement with experimental results, albeit the studies on $Fe(CO)_5$ were carried out in solution whereas our prediction strictly holds only in the gas phase.

There are two molecules for which predictions are not so straightforward. The first is $CH_3F$ where a cursory examination of the photoelectron spectrum would assign the first band as arising predominantly from the $CH_3$ group since it occurs near the first IP of $CH_4$. However, the adiabatic (and vertical) IP of $CH_3F$ is *less* than that for $CH_4$.[12] This is contrary to what one would expect on the basis of inductive effects but can be rationalized by a considerable mesomeric effect[13] of fluorine with the $CH_3$ group. Further evidence for the strong mixing of $CH_3$ and F orbitals in the 1e and 2e molecular orbitals is provided by the fact that the UPS exhibits no sharp band due to the fluorine lone pairs in the region of 15.8 eV, such as is observed in HF.[14] We conclude that in $CH_3F$ there is substantial delocalization of the HOMO and hence no prediction can be made regarding the position of proton attack.

The ab initio calculation[12] on $CH_3F$ indicates that the HOMO (2e), although containing a sizeable C–H bonding component, is considerably C–F antibonding. This is a result of delocalization. Calculations utilizing the semiempirical CNDO/2 and INDO molecular orbital methods[15] also indicate that the HOMO is nearly equally divided between the $CH_3$ and F moieties, just as in the isoelectronic $F_2$ molecule. The structure of protonated $CH_3F$ is not known, but ab initio calculations[9] indicate that it has a structure similar to that of the isoelectronic $CH_3OH$ molecule.

A second example which illustrates the cautions which must be observed in this application of the frontier orbital concept is provided by ferrocene. The first two peaks in the UPS have been assigned to ${}^2E_{2g}$ and ${}^2A_{1g}$ ionic states, corresponding to electron ejection out of orbitals predominantly of Fe 3d character.[16] However, the molecular ground state calculation indicates the HOMO's to be ligand $\pi$ nonbonding, $e_{1g}$ and $e_{1u}$.[17] In such a case, when the order of one-electron orbital energies is different from the order of corresponding ionic states in the UPS, a breakdown in Koopmans' theorem is indicated.[17] Consequently, the concept of HOMO is meaningless and no prediction as to the position of proton attack can be made. Experimentally, ferrocene has been shown to protonate both at the iron atom and at the ring.[18]

Finally, we wish to show the utility of the frontier orbital concept in predicting the structure of products resulting from electrophilic attack in a more general system. Such an example is provided by the reaction[19] (in solution) of "$Cl^+$" with ClF to product $ClClF^+$; that is, the "$Cl^+$" attacks the chlorine atom and not the fluorine atom. The HOMO in ClF is of $\pi$ character mainly localized on chlorine.[20] We can therefore also rationalize the fact that $ClClF^+$ is a bent