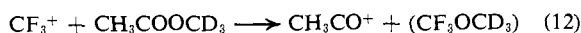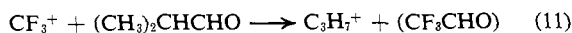of Su and Bowers.[7] The measured rate constants for reactions of CF_3^+ or $C_2F_5^+$ with acetone $(CH_3)_2CH-COCH_3$ and CH_3COOCD_3 are very close to the estimated collision rate constants. If we accept these values for the collision rate constants, we must conclude that these reactions of CF_3^+ and $C_2F_5^+$ are very efficient, while the CCl_3^+ ion has a relatively low probability that a collision with these molecules will lead to reaction.

For all the ion–molecule reaction pairs listed above, with the exception of CF_3^+–$(CH_3)_2CHCOCH_3$, other reaction channels constituted 5% or less of the total reaction. However, not all carbonyl compounds undergo reactions involving cleavage of the $C{=}O$ bond to the exclusion of other reaction channels with these ions. When the carbonyl compound contains a weak bond, displacement reactions compete effectively. For instance, at least 95% of the reaction between CF_3^+ and $(CH_3)_2CHCHO$ or CH_3COOCD_3 proceeds as follows.

$$CF_3^+ + (CH_3)_2CHCHO \longrightarrow C_3H_7^+ + (CF_3CHO) \quad (11)$$

$$CF_3^+ + CH_3COOCD_3 \longrightarrow CH_3CO^+ + (CF_3OCD_3) \quad (12)$$

A similar reaction mechanism occurs between CF_3^+ and $(CH_3)_2CHCOCH_3$ where about 20% of the product ions are $C_3H_7^+$.

In reactions of $C_2F_5^+$ with higher ketones, CF_3CO^+ was an important product ion.

In every mixture, product ions further reacted with the carbonyl compound to form the protonated ketone or aldehyde as the final ionic product (Figure 1).

(7) T. Su and M. T. Bowers, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 347 (1973).

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Structural Implication in Metalloporphyrins of the 1590-cm^{-1} Anomalously Polarized Resonance Raman Line[1]

Sir:

A number of studies[2–6] have demonstrated the utility of resonance Raman spectroscopy as a structural probe of the chromophore in hemeproteins. Correlations between both the frequencies and the intensities of the fundamental vibrations seen in the resonance spectrum and the spin or oxidation state of the iron have been noted. By examining a series of metalloporphyrins, we have observed that the appearance of an anomalously polarized line in the 1582–1609-cm^{-1} spectral region reliably indicates that the metal resides in-plane with the porphyrin moiety. For this line, neither the metal oxidation nor its spin state is of primary im-

(1) This work was supported by grants from the National Institutes of Health (AM-14344 and GM-18894), the National Science Foundation (GP-17061), and the Research Corporation.

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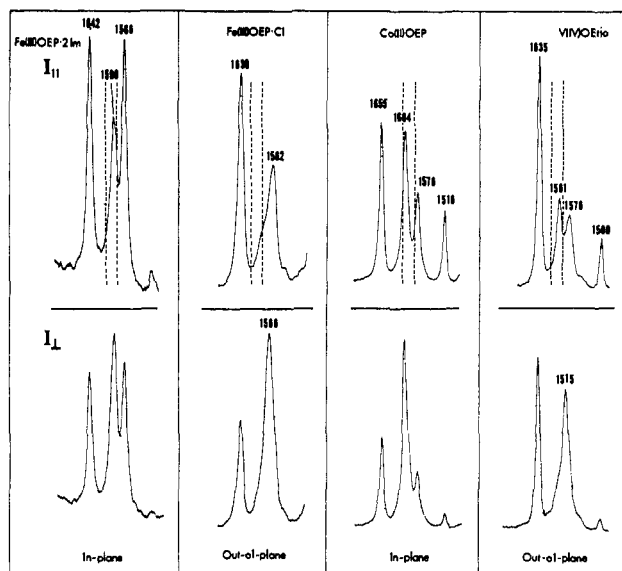(6) T. M. Loehr and J. S. Loehr, *Biochem. Biophys. Res. Commun.*, **55**, 218 (1973).

Figure 1. Parallel and perpendicular components of the resonance Raman spectra of metalloporphyrins in KBr (excited with 514.5-nm radiation). Orientation of the pellet is 10° from the incident beam. Accidental degeneracy is manifested in the frequency shift observed between $I_{||}$ and $I_\perp$ in FeOEPCl and VOEtio.

portance. An independent observation[7] that the resonance Raman spectrum contains geometrical information recently has been advanced by Spiro and Strekas.

Synthetic metallooctaethylporphyrin (MOEP) or -etioporphyrin I (MEtio) were chosen because of the similarity of their resonance Raman spectra to those of the hemeproteins. Spectra were obtained with 0.5–1 mM solutions of the porphyrin dissolved in CH_2Cl_2, in KBr pellets (1 mg porphyrin/200 mg KBr),[8] or as a crystalline powder affixed to transparent tape. A rotating cell or platform was used to prevent photodecomposition of the chromophore during laser irradiation. Exciting wavelengths were 457.9, 488.0, and 514.5 nm (argon ion laser) and 560.0, 570.0, and 580.0 nm (tunable dye laser).

The differences observed between the solid and solution sample spectra were limited to anomalous polarization ratios $(\rho = I_\perp/I_{||} > 0.75)$ that were two to three times smaller in the solid samples. This effect was not found for the polarized or depolarized bands, nor was there an appreciable shift in the vibrational frequencies for any of the lines when spectra of the solid and solution samples were compared.

Upon irradiation at 514.5 nm an anomalously polarized line (ap) was found (group I) at 1609 cm^{-1} in Ni^{II}Etio, 1604 cm^{-1} in Co^{II}OEP, 1598 cm^{-1} in Co^{III}OEP·Imid(OH), 1590 cm^{-1} in Fe^{III}OEP·2Imid, and 1587 cm^{-1} in Cu^{II}OEP. With the same experimental conditions a polarized line $(\rho < 0.75)$ was seen (group II) at 1592 cm^{-1} in iron(III) protoporphyrin IX dimethyl ester, 1591 cm^{-1} in (Fe^{III}OEP)$_2$O, 1591 cm^{-1} in V^{IV}OEtio, 1591 cm^{-1} in Zn^{II}OEP, 1584 cm^{-1} (shoulder) in Fe^{III}OEPCl, and 1583 cm^{-1} in Mg^{II}OEP. Representative spectra are shown in Figure 1. Comparison of the members of group I with those of group II demonstrates that neither spin nor valence state of the metal correlates with the appearance of the anomalously

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polarized (ap) line; rather the property distinguishing the two sets is the in-plane metal in group I and the out-of-plane metal in group II. Estimates of the metal displacement from the basal plane is obtained from structural determinations:[9] Zn, 0.33, 0.35;[10] Mg, 0.27; VO, 0.48; and Fe(III), 0.48 Å.

In agreement with previous studies[4,5] on hemeproteins, ap lines possessed a maximum ρ when the exciting light was absorbed by the visible bands, while the relative intensity of the polarized lines increased as shorter exciting wavelengths were employed.

Current interpretations[2,4,5] of heme resonance Raman spectra assign the polarized bands ($\rho < {}^3/_4$) to a_{1g} in-plane porphyrin skeletal vibrations and inverse polarized lines ($\rho = \infty$) to a_{2g} vibrations. The dependence of the apparent value of ρ for the ap line upon exciting wavelength is consistent with a_{2g} vibronic coupling between the Q (visible) and B (Soret) electronic states. Increasing intensity of the polarized bands as the B band is approached by the exciting line is indicative of an a_{1g} vibration. The data reported here support a recent conclusion[7] that accidental degeneracy between the a_{2g} vibration and an a_{1g} mode rather than lowering of molecular symmetry is responsible for an appreciable parallel component to the ap lines at 1590 cm^{-1} (group I) and 1574–1568 cm^{-1} (group II). An ap line near 1313 cm^{-1} also shows a slight shift in the $I_{\parallel}$ maximum at 457.9 nm as compared with 514.5 nm. This, too, is consistent with accidently degenerate vibrations. The symmetry reductions from D_{4h} commonly encountered[9] in porphyrins are to D_{2d} or C_{4v} and could not account for the parallel ap components.

The present results emphasize the structural interpretation of hemeprotein ap and polarized bands found in the 1550–1600-cm^{-1} region. As long as the exciting wavelength is absorbed by the Q bands, resonant Raman spectra of metalloporphyrins displaying an ap line in the 1582–1609-cm^{-1} region indicate an in-plane metal, e.g., low-spin Fe(III). In contradistinction, upon excitation into the Q band, a polarized line in this region with the concurrent shift[11] of the ap band to 1552–1574 cm^{-1} is indicative of an out-of-plane metal.

The mechanism by which displacement of the metal from the porphyrin plane can cause this phenomenon is suggested[7] to be due to "doming" of the porphyrin skeleton and concomitant displacement of meso carbon atoms from the mean porphyrin plane. This explanation is attractive since it is independent[12] of the nature of the metal substituent, requiring only a distortion of the macrocycle. Verification of this mechanism must await studies on crystalline samples of metallotetraphenylporphyrins, where structural information is available for a wide class of metals.

A polarized line at ca. 1500 cm^{-1} evinces a less clearcut correlation with metalloporphyrin structure. For the in-plane metals this line is observed between 1509

and 1534 cm^{-1}, while it appears between 1480 and 1500 cm^{-1} for the out-of-plane cases. The depolarized line encountered at 1664–1609 cm^{-1} in our study has been proposed[3,7] as an "oxidation state marker" in the hemeproteins. Although this proposal may be correct for the hemeproteins, we find it does not apply to Co^{II}-OEP, 1651 cm^{-1}, as compared with Co^{III}OEPClO$_4$, 1651 cm^{-1} (CH$_2$Cl$_2$ solution).

Finally, as an application of the 1590-cm^{-1} ap band as a structural probe, we note that replacement of ClO$_4$$^-$ by the strongly coordinating Br$^-$ ion in Co^{III}OEP$^+$ alters the resonant Raman spectrum in a manner indicative of a cobalt atom now displaced from the porphyrin plane.[13]

(13) NOTE ADDED IN PROOF. Classification of a metal as in- or out-of-plane is ambiguous for *slight* displacement from the basal nitrogen plane. Thus, in CO^{II}Etio NO the resonant Raman spectrum displays an ap line at 1604 cm^{-1} which classifies it as in-plane; but a structural determination (W. R. Scheidt and J. L. Hoard, *J. Amer. Chem. Soc.*, 95, 8281 (1973)) on nitrosyltetraphenylporphinatocobalt(II) yields a 0.094 ± 0.05 Å displacement.

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The Bicyclo[3.3.2]decatrienyl Dianion[1]

Sir:

One's current appreciation of the pericyclic $4n + 2$ Hückel rule has been nourished by three preparative achievements: cyclopentadienide (1),[2] tropylium (2),[3] and the cyclooctatetraenide dianion (3).[4] The less exhaustively explored longicyclic topology now also has its characteristic rule.[5] A fully unsaturated bridged bicyclic ion is expected to be stabilized if any two of its three bridges differ in mode. Thus, if two each possess $4n$ π electrons (mode 0), the third must possess $4n + 2$ (mode 2) and *vice versa*.
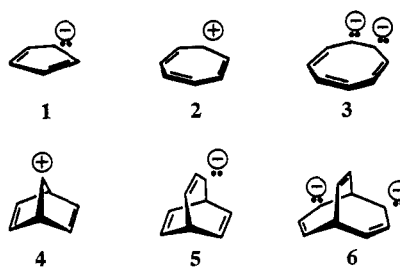
This topology now also has two ions whose roles recall those of 1 and 2. Like the cyclopentadienyl anion, the 7-norbornadienyl cation (4) was available as witness even before the rule was formulated.[6] Like the tropylium cation, the bicyclo[3.2.2]nonatrienyl

(9) Values are cited for *meso*-tetraphenylporphyrin complexes and a vanadyl deoxophylloerythroetioporphyrin. See J. L. Hoard, *Science*, 174, 1295 (1971); *Ann. N. Y. Acad. Sci.*, 206, 18 (1973); E. B. Fleischer, *Accounts Chem. Res.*, 3, 105 (1970).
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(11) MgOEP and ZnOEP did not display an ap line at 1565 cm^{-1} when the 514.5-nm exciting light was used. Attempts to employ longer wavelength excitation directly into the Q band were foiled by excessive fluorescence. At shorter wavelengths ρ became smaller which would indicate both a_{1g} and a_{2g} vibrations are present.
(12) An ap line at 1587 cm^{-1} was found for metal-free H$_2$OEP.

(1) Presented, in part, at the First Fall Organic Conference, Division of Organic Chemistry, American Chemical Society, Falmouth, Mass., Oct 3, 1973.
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