cm^{-1}. It is important to note that the integrated intensity of the 14,183-cm^{-1} band definitely does not decrease on going from 300 to 5°K, eliminating transition assignments which require vibronic intensity giving mechanisms. Furthermore, no A term is present in the MCD spectrum[8] in this region of absorption. Thus the observed temperature dependence of the absorption and the MCD results strongly suggest that an allowed transition to a nondegenerate excited state is responsible for the 14,183-cm^{-1} band.

Conclusive evidence for the assignment of the low energy absorption system in quadruply bonded, binuclear Re(III) complexes to the $\delta \rightarrow \delta^*$ transition comes from 5°K polarized crystal spectral measurements on the C_{2h} $Re_2Cl_6[P(C_2H_5)_3]_2$ complex.[9-11] Upon lowering the symmetry from D_{4h} to C_{2h}, ${}^1A_{1g} \rightarrow {}^1A_{2u}$ becomes ${}^1A_g \rightarrow {}^1B_u$, which is xz allowed (with $C_2 \equiv y$). For $Re_2Cl_6[P(C_2H_5)_3]_2$, in which the Re–Re vector is virtually perpendicular to the a crystallographic axis, the origin of the low energy band occurs at 13,785 cm^{-1}. Strong xz ($\perp a$) polarization is observed, exactly as predicted for a $\delta \rightarrow \delta^*$ transition. The $\delta \rightarrow \sigma_n$ assignment is eliminated as a possibility, because in C_{2h} the ${}^1A_g \rightarrow {}^1A_u$ transition is allowed only in the direction (y) where essentially no absorption is found.

The electronic origin of the $\delta \rightarrow \delta^*$ band in $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$[12] at 5°K is found at 13,597 cm^{-1}, upon which is built a progression in the $a_{1g}(\nu_1)$ metal–metal stretch (average spacing 255 cm^{-1}, ground state[7] 277 cm^{-1}). Additional 255-cm^{-1} progressions develop from peaks at 13,694 and 13,765 cm^{-1}, which allow us to assign excited-state values of 98 and 168 cm^{-1} to the $a_{1g}(\nu_3)$ ReReBr bending (ground state not observed, calcd[7] 65 cm^{-1}) and $a_{1g}(\nu_2)$ Re–Br stretching (ground state[7] 184 cm^{-1}) vibrations, respectively. Undoubtedly there is substantial mixing of the three excited-state a_{1g} modes for both $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, as there is in the ground state.[7]

The Raman spectra of compounds containing the quadruply bonded $Mo_2Cl_8^{4-}$ [13] exhibit[14,15] a band at *ca.* 350 cm^{-1} which is resonance enhanced upon irradiation at 4800 Å.[15] Our 5°K electronic absorption spectrum of K_4MoCl_8[16] reveals that a richly structured system (origin 17,897 cm^{-1}; vibrational spacing *ca.* 351 cm^{-1}) attributable to $\delta \rightarrow \delta^*$ falls in that region. The fact that the ground- and excited-state vibrational frequencies are approximately equal is intriguing, but an interpretation in terms of bonding changes is not possible in the absence of quantitative information concerning the extent of mixing of Mo–Mo and Mo–Cl stretching modes. Low-temperature electronic absorption spectral studies of several binuclear Mo(II) complexes are now being investigated in an attempt to clarify this point.

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[8] The MCD spectrum of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ was measured in acetonitrile solution. We thank Professor P. J. Stephens of the University of Southern California for allowing us access to his equipment and for assistance with the measurements.

[9] The compound $Re_2Cl_6[P(C_2H_5)_3]_2$ was prepared by addition of $P(C_2H_5)_3$ to a slightly acidified methanol solution of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, as described in more detail for the analogous $P(C_6H_5)_3$ derivative.[10] Crystals of the compound are monoclinic, space group $P2_1/n$, with lattice constants a = 7.644, b = 10.985, and c = 14.206 Å, β = 96.5° (two molecules per unit cell).[11] The crystals grow as prisms elongated on a. The normal to the well-developed face makes an angle of 52.1° with the c^* axis, confirming assignment as (011). The crystals are strongly dichroic (blue $\perp a$, yellow $\| a$). Thin single crystals for spectral measurements were grown from chloroform solution.

[10] F. A. Cotton, N. F. Curtis, and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

[11] F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, 7, 2135 (1968).

[12] Thin crystals of $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$[10] for spectral work were grown from acetonitrile solution.

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A Breakdown of the Hammett Acidity Function Concept

Sir:

The Hammett acidity function concept[1-3] requires that pK_{HA}, for all the acids correlated, in any one of the solvent mixtures involved, be a linear function of $pK_{HA}{}^0$, the corresponding quantity in a reference solvent (usually water) *with unit slope.* For the acid, HA (which is usually an indicator acid in the present context) $pK_{HA}{}^S$ is given by eq 1. Parker's notation[4] is

$$pK_{HA}{}^S = \log \frac{(HA)}{(H^+)(A^-)} + \log \frac{{}^S\gamma^{S'}{}_{HA}}{{}^S\gamma^{S'}{}_{A^-}{}^S\gamma^{S'}{}_{H^+}} \qquad (1)$$

used for activity coefficients. S′ is the solution in which the concentrations are actually determined. S is a convenient reference solution. Quantities in parentheses are concentrations. If S is an ideal aqueous solution it is denoted by 0. Then $pK_{HA}{}^S$ is $pK_{HA}{}^0$ and is given by an equation analogous to eq 1. Similar equations can also be written for a standard indicator acid, HA_0. By an appropriate combination of these equations, eq 2 is obtained.

$$pK_{HA}{}^S - pK_{HA_0}{}^S = pK_{HA}{}^0 - pK_{HA_0}{}^0 + \log \frac{{}^0\gamma^S{}_{A^-}{}^0\gamma^S{}_{HA_0}}{{}^0\gamma^S{}_{A^-_0}{}^0\gamma^S{}_{HA}} \qquad (2)$$

The basic hypothesis of Hammett acidity functions[1,2] holds that activity coefficient ratios such as ${}^0\gamma^S{}_{A^-}/{}^0\gamma^S{}_{HA}$ are independent of $pK_{HA}{}^0$; that is that ${}^0\gamma^S{}_{A^-}{}^0\gamma^S{}_{HA_0}/{}^0\gamma^S{}_{A^-_0}{}^0\gamma^S{}_{HA}$ should be unity if the acids are of the same structural type. Thus $pK_{HA}{}^S$ should be a linear function of $pK_{HA}{}^0$ with unit slope. This has always been recognized as an approximation.[1-3] It is the purpose of the present communication to point out a systematic failure of this approximation.

It has been known for some time that, for acids of related structural type, $pK_{HA}{}^S$ is a linear function of

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[3] (a) R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **42**, 1681 (1964); (b) A. Albagli, A. Buckley, A. M. Last, and R. Stewart, *J. Amer. Chem. Soc.*, **95**, 4711 (1973).

[4] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

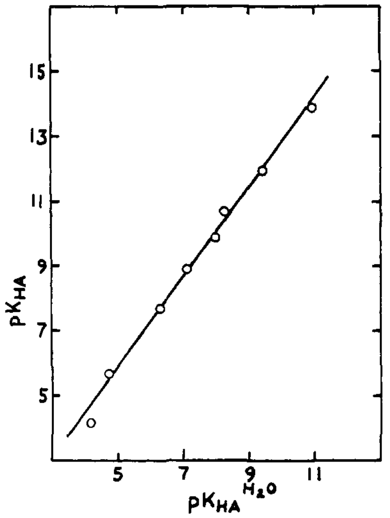

Figure 1. pK_{HA}^S for phenolic substances in 80% DMSO as a function of pK_{HA}^0 for the same substances, taken from ref 5. The slope of the correlation line is 1.4.

pK_{HA}^0 but with slope that is often greater than unity.[5] Recent further results strengthen this conclusion. For a wide variety of phenolic acids pK_{HA}^S in 80% DMSO–water is a linear function of pK_{HA}^0 with slope of 1.4 (Figure 1).[6] For carboxylic acids in anhydrous DMSO, pK_{HA}^S is a linear function of pK_{HA}^0 with slope of 2.7 (Figure 2)![7] For phenols (and trifluoroethanol) in DMSO containing 1.0 *M* water, the slope is 2.2.[8] As a consequence of these results it appears that ${}^0\gamma^S{}_{A^-}/{}^0\gamma^S{}_{HA}$ is usually a function of the acid strength as well as the solvent composition and the structural type. Since the acidity function, H_- (or H_0 if the equations are rewritten for a positively charged acid, HA^+) is defined by eq 3, its numerical value usually

$$-H_- = \log ({}^0\gamma^S{}_{A^-}/{}^0\gamma^S{}_{HA}) + \log (H^+){}^0\gamma^S{}_{H^+} \quad (3)$$

depends on the indicator used to determine it. To illustrate the magnitude of the error potentially introduced, we may consider the case of benzoic and 2,6-dihydroxybenzoic acids. In DMSO they give pK_{HA}^S values of 11.1 and 3.1, respectively. The pK_{HA}^0 of benzoic acid is 4.2.[9] If the activity coefficient ratio in eq 2 is unity, as assumed in constructing acidity functions, then 2,6-dihydroxylbenzoic acid should have pK_{HA}^0 of -3.8. In fact, it is 1.2.[9]

The foregoing results show that no Hammett acidity function exists for phenols or carboxylic acids in mixtures of water and DMSO made basic by addition of small, constant, concentrations of strong base. It seems unlikely that the widely used acidity function of that description based on aromatic nitrogen acids[3] gives accurate pK_{HA}^0 values so that it can be safely used for acids of pK_{HA} widely variant from those of the indicators used to set up the function. These conclusions seem to differ from Stewart's most recent conclusions[3b] mainly in emphasis.

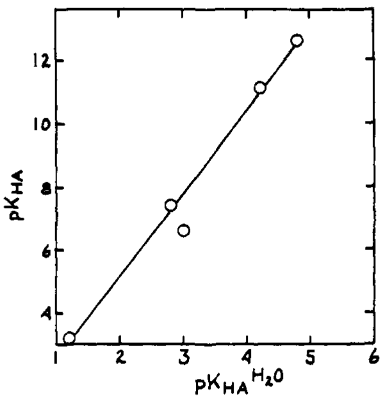

Figure 2. pK_{HA}^S for carboxylic acids in anhydrous DMSO as a function of pK_{HA}^0 for the same substances, taken from ref 6. The slope of the correlation line is 2.7.

Mixtures of mineral acids with water, or with water and some fixed fraction of an organic solvent are not different in principle from other mixtures. The requirements for an acidity function are the same, and the usual method of constructing acidity functions, by the method of overlapping indicators,[1,2] does not test the requirement that ${}^0\gamma^S{}_{A^-}{}^0\gamma^S{}_{HA_0}/{}^0\gamma^S{}_{A^-_0}{}^0\gamma^S{}_{HA}$ be unity when the strength of the acids is quite different. Usually only indicators of similar pK_{HA} are directly compared. However, somewhat indirect evidence[10] for H_2O–H_2SO_4 mixtures appears to support the position that ${}^0\gamma^S{}_{A^-}{}^0\gamma^S{}_{HA_0}/{}^0\gamma^S{}_{A^-_0}{}^0\gamma^S{}_{HA}$ is close to unity. The same may be true for ternary mixtures of water, an organic solvent, and a mineral acid, when the binary mixture of water and the organic solvent is used as the reference solvent.[11]

Acknowledgment. We are pleased to acknowledge the support of the National Science Foundation through Grant GP-31360X.

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Two-Photon Excitation Spectra. A New and Versatile Spectroscopic Tool[1]

Sir:

We have recently developed a technique for studying the two-photon absorption spectra of molecules that is as versatile and as straightforward to use as is ordinary ultraviolet spectroscopy. The information obtained from two-photon spectra is complementary to conventional one-photon ultraviolet data but it will usually be different enough that a completely new classification of ultraviolet spectral characteristics can be expected for organic chromophores. In addition the present technique extends the readily usable effective wavelength range to about 1750 Å without the requirement of even quartz optics.

The output from a nitrogen laser pumped dye laser is

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