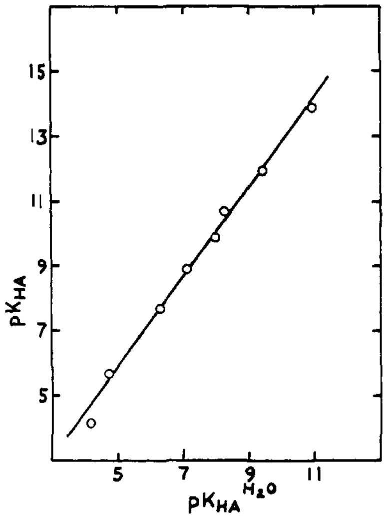

Figure 1. $pK_{HA}{}^{S}$ for phenolic substances in 80% DMSO as a function of $pK_{HA}{}^{0}$ for the same substances, taken from ref 5. The slope of the correlation line is 1.4.

$pK_{HA}{}^{0}$ 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.

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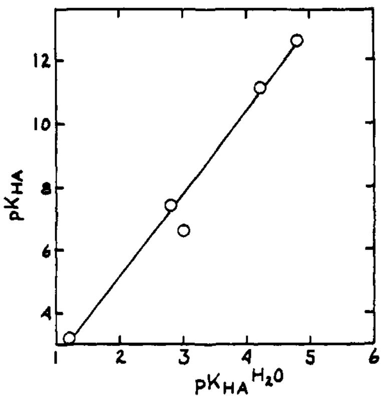

Figure 2. $pK_{HA}{}^{S}$ for carboxylic acids in anhydrous DMSO as a function of $pK_{HA}{}^{0}$ for the same substances, taken from ref 6. The slope of the correlation line is 2.7.

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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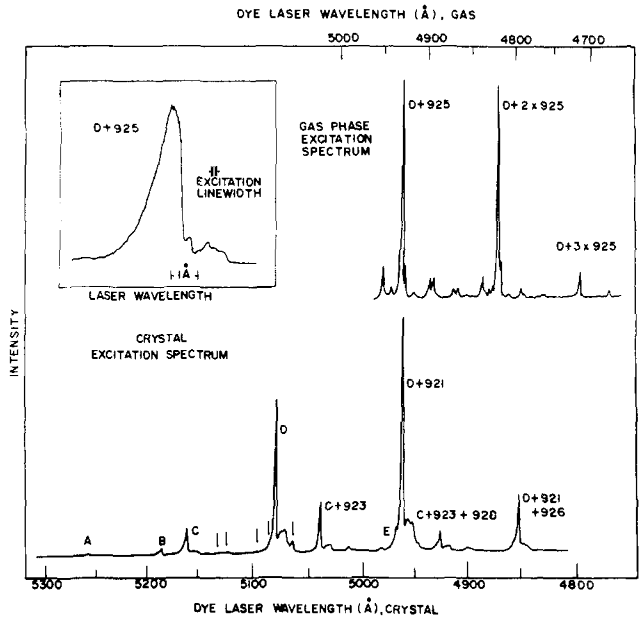

Figure 1. Two-photon spectra of benzene in the crystal and in the vapor: lower, the crystal excitation spectrum, the bands marked A through D are fundamentals of 177, 740, 922, and 1545 cm^{-1} respectively, and the progression forming mode is $a_g(1)$ at *ca.* 923 cm^{-1}; upper right, the vapor excitation spectrum at 70 Torr; upper left, a higher resolution spectrum of the vapor showing the asymmetry of the band caused by unresolved rotational structure.

focused into a cell containing the sample, and the sample luminescence detected by a sensitive photomultiplier is used to monitor the absorption. If the sample does not luminesce a signal can be generated by causing the sample excitation to be transferred (by collision or Förster transfer or energy migration in the solid) to a known energy acceptor which then luminesces. The dye-laser is constructed according to the Hänsch[2] design and is continuously tunable by means of a mechanical drive that rotates the diffraction grating which forms the rear reflector of the laser cavity. The laser line width which is controlled by the choice of cavity elements determines the spectral resolution. In the experiments we report here the laser line width was chosen to be *ca.* 2 cm^{-1} by placing a 10:1 beam expander in the cavity.

The method is useful for the study of liquids, dilute solutions, solids (*e.g.*, organic crystals), and gases. We previously reported[3] the two-photon allowed spectrum of the first singlet–singlet g $\rightarrow$ g transition of the biphenyl crystal, and this was the first high-resolution two-photon spectrum to be recorded. Using red to blue laser dyes we have now obtained high-resolution spectra of naphthalene (h_8 and d_8), naphthalene in durene, and benzene (h_6 and d_6) all at 2°K in single crystals. The benzene and naphthalene spectra refer to the lowest energy excited singlet states of these materials and they arise because of vibronic coupling through ungerade modes of the excited state since the overall selection rule for two-photon absorption (in the dipole–dipole approximation) is g $\rightleftarrows$ g, and these lowest excited states have u electronic symmetry. For the case of benzene we have observed an additional eight out of a total of ten ungerade fundamentals of the $^1B_{2u}$ state. The spectra of naphthalene and naphthalene in durene mixed crystals have been obtained with polarized light, and it is apparent that b_{1u} and b_{2u} (in-plane) vibrations of the first excited state are clearly distinguished as expected from a π-electron theory of two-photon absorption. It appears as if the two-photon spectrum of benzene is also consistent with a model in which the π electrons dominate the interactions of the molecule with the radiation. This technique has provided sufficient information to assign definitively a large number of excited state *u* vibrations for the first time.

We also wish to report our observation of two-photon absorption to vibronic levels of the $^1B_{2u}$ state of benzene vapor. The results, shown in Figure 1, open up the possibility of high-resolution gas-phase studies of molecules, exposing an entirely new set of upper states that have not been previously studied. The detailed rotational selection rules for these two-photon processes can be quite different from the conventional rules, even for diatomics, since among other things the angular momentum associated with the two-photons must be conserved. The benzene spectrum is two-photon forbidden (g $\rightarrow$ u) and requires a vibronic coupling, so we anticipate that allowed two-photon transitions should be readily observed in gases at low enough pressure to permit vibrational and rotational analyses, and single vibronic level excitation experiments.

Previous two-photon absorption studies involving a significant wavelength scan were done point by point at low resolution using high-powered single shot pulsed lasers to provide one of the photons[4–6] or have involved a single shot dye laser.[7]

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Crystal Structure of an Acetylene Sorption Complex of Partially Manganese(II)-Exchanged Zeolite A

Sir:

The catalytic and selective sorption properties of transition metal ion-exchanged zeolites are well known.[1] In such zeolites, it is observed that the amount and nature of the sorbate can greatly affect the coordination geometries about the transition metal ions. Using partially exchanged Co(II) and Ni(II) forms of the synthetic sieve zeolite 4A,[2] Klier has spectroscopically observed the formation of three-, four-, and six-coordinate Ni(II) and Co(II) complexes.[3,4] Recent X-ray diffraction studies have corroborated the existence of the

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