Figure 1. Absorption energies and nearest neighbor metal-metal distances in tetracyanoplatinites and tetracyanopalladites.

carried out to assign the solution magnetic circular dichroism spectrum of $Pt(CN)_4^{2-}$ placed the A_{2u} state with predominant $^1A_{2u}$ parentage beneath the band envelope at 46,100 cm^{-1}, while a transition state calculation[9] of the $5a_{1g} \rightarrow 3a_{2u}$ ($^1A_{2u}$) excitation in the same ion by the $X\alpha$ scattered wave method predicted it at 50,600 cm^{-1}. Bearing in mind that the reference point of the Davydov calculation is the free ion in the gas phase, the agreement of these numbers with the extrapolated free ion excitation energy is satisfactory. Turning to the intensity in the simple point dipole approximation, the slope of the line in Figure 1 would be just $-2e^2|M|^2$; experimentally it is approximately $-0.008e^2A^2$, equivalent to a transition dipole length of about 1.9 Å. An estimate based on the area of the 46,100-cm^{-1} absorption band of $Pt(CN)_4^{2-}$ in solution was just under 0.8 Å. This discrepancy between the observed and predicted free ion dipole lengths is no doubt a measure of the approximation we have made by assuming only a point dipole–dipole interaction and not carrying out a summation over the whole lattice. Nevertheless, the discrepancy is not too great.

The success of this extremely simple approach to the tetracyanoplatinite crystal spectra leads us to suggest that the unusual optical properties of other crystals containing one-dimensional arrays of square planar d^8 complexes, such as the dimethylglyoxinates,[10] might be capable of a similar explanation, as we already tentatively suggested earlier.[11]

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Radical Ions of Benzene and Toluene in Nonpolar Solvents

Sir:

We report the preparation, through use of a crown ether, of the radical anions of benzene and toluene in nonpolar solvents. The simplest preparation is carried out by bringing a solution of dicyclohexyl-18-crown-6 in the parent hydrocarbon into contact with a potassium mirror. A reaction occurs, complete in a few hours at room temperature, after which the electron spin resonance spectrum of the anion is observed. The manipulations are carried out under high vacuum.

The benzene anion thus prepared in solution in benzene has a proton hyperfine coupling constant of 3.41 G. No deviation from equivalence of the six protons is observed. The spectrum is not as well resolved as in ethereal solvents at low temperature, being simulated by assignment of breadth 1.30 G between points of extreme slope to each of the seven lines. A Lorentzian shape, undistorted by unresolved hyperfine splitting, was used in the simulation.

The toluene anion is prepared just as is the benzene anion. The dominant feature of its spectrum is hyperfine splitting by four equivalent protons with a coupling constant of 4.5 G. There is a suggestion, most apparent on the component at lowest field, of further splitting of 0.7 G by coupling to the potassium counterion.

In both the benzene and toluene ions the proton hyperfine couplings are significantly smaller than in solution in ethers, about 10% in benzene and 20% in toluene.

The most surprising feature of the spectra is that in the pure parent hydrocarbon solvent the electron transfer between anion and solvent molecules does not wash out the hyperfine splitting. If the entire line breadth of the benzene anion arose from electron transfer, the second-order rate constant for the process could be no greater than 7×10^6 M^{-1} sec^{-1}.

Since the electron spin resonance spectra of the radical ions are almost completely resolved, the rate of electron transfer may be determined directly from the broadening of the proton magnetic resonance lines of the solvent. Determination of the rate constant requires knowledge of the concentration of radical anion. In one set of experiments we started with a solution of the crown ether at 1.5×10^{-2} M, presumably the stoichiometric maximum concentration of benzene anion which could be produced in that solution. The electron spin resonance of the resulting anion displays marked broadening owing to Heisenberg exchange. Since Heisenberg exchange rates are close to the encounter controlled limit,[1,2] we made an independent estimate of the radical concentration by matching the observed spectrum to one calculated for benzene anion undergoing Heisenberg exchange. Assumption that the Heisenberg exchange rate constant is 2×10^9 M^{-1} sec^{-1} leads to an estimated anion concentration of 0.7×10^{-2} M. Lacking an absolute spin count, we assume that the concentration of radical anion was between 0.7×10^{-2} M and the stoichiometric upper limit of 1.5×10^{-2} M. The proton magnetic resonance of the benzene in solution has full width at half maximum of 520 Hz. The rate constant for electron transfer, at the temperature at which the proton magnetic resonance was observed, is estimated to be between 1.0×10^5 and 2×10^5 M^{-1} sec^{-1}.

Similar results with a rate constant of the same order are obtained with toluene. As expected, the methyl proton lines are not as broad as those of the four-ring protons because their small hyperfine constants are of the same order as the reciprocal residence time of the electron spin on a toluene molecule. Consequently the simple strong pulse limit equa-

tion does not apply to the breadth of the methyl and para proton lines. The ring line is slightly asymmetric because the para proton line is not completely broadened and experiences a different contact shift from the ortho and meta proton lines.

The radical ions are undoubtedly associated with counterions. Eastman and collaborators[3] have shown that in the sodium salt of tetracyanethylene dissolved in benzene containing a crown ether the ion association is complete. Although our ESR spectra do not exhibit unambiguous symptoms of ion pairing, the slowness of the electron transfer process—some four orders of magnitude less than the encounter controlled limit observed in other solvents—is undoubtedly related to the ion pairing.

Since submission of this communication we have seen the recent article by Kaempf et al.,[4] which reports ESR observations identical with ours. The article reports neither NMR observations nor estimates of electron transfer rates.

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Stimulated Raman Scattering from H_2 Gas for Fast Heating in Laser-Temperature-Jump Chemical Relaxation Experiments

Sir:

We report the use of the stimulated Raman effect in hydrogen gas at 60–80 atm[1,13,15,16,17,18] in the construction of a versatile laser-temperature-jump spectrophotometer for very fast kinetic measurements with the chemical relaxation technique.[2] By the Raman effect in hydrogen gas, the original wavelength of 1.06 μ, obtained from a Q-switched Nd^{3+}-glass giant-pulse laser, is shifted to 1.89 μ. The infrared absorption of H_2O and of other compounds at this wavelength has already been studied extensively in aqueous,[3] nonaqueous,[4] organic, and mixed solvents[5] and in electrolyte[6] and nonelectrolyte[7] solutions.

The H_2 Raman-laser system has a definite advantage over the use of liquid N_2 (with a Raman shift to 1.41 μ) as reported by Sutin et al.,[8,12] because the H_2 Raman cell can be permanently installed outside the laser cavity and needs not to be refilled.

In our experiment a 2 J/20 nsec pulse from a Nd^{3+}-glass laser at 1.06 μ (beam diameter about 12 mm), which is Q-switched by a Pockels cell, is focused by a fused quartz lens (Spectrosil) of 50-cm focal length into a 1 m long pressure cell filled with H_2 at 80 atm. The distance between the lens and the pressure cell is about 10 cm. The light beam emerging from the pressure cell is collected by a second infrasil lens and is directed after filtering into a thin absorption cell

containing the sample, which it abruptly heats. The conversion of 1.06 to 1.89 μ is normally about 20% or more.[9] The conversion efficiency from 1.06 to 1.89 μ radiation after filtering off 1.06 μ with a BG18 filter was measured by a "Control Data Corporation's" Ballastic Thermopile Model 100 attached to Keithley Instrument Inc. Microvolt Ammeter Model 150 B.

Water has a big absorption band at 1.9 μ.[10] The converted energy produces vibrational heating of the solvent, which induces temperature-jump chemical relaxation effects of solute molecules. The 1.06 μ radiation is completely filtered off by a Schott's green glass BG18 filter placed between the pressure cell and the collecting lens. The BG18 filter has no transmittance between 1 and 1.2 μ but transmits about 62% radiation at 1.89 μ which is used for temperature-jump effects.

For aqueous solutions a double spacer absorption cell with three 2 mm thick infrasil windows is used. The front spacer thickness is 0.5 mm; the back spacer is 5 mm. The absorbing sample solution is in the front layer. The back layer contains pure water and is used as a filter, removing any remaining ir energy, and serves at the same time for thermostating purposes. A monochromatic observation beam traverses the spacer cell in about the same direction as the heating beam.

The H_2 Raman shifted pulse width is sharpened when compared with the original 1.06 μ unconverted pulse;[11] thus very rapid heating rise times can be produced, using the stimulated Raman effect of H_2 gas for temperature-jump spectrophotometry or for other fast reaction kinetic measurements. The observed half-width of the converted pulse (using an EG & G's SGD-100 type photodiode) was 12 nsec. The pulse width reduction of 1.06 to 1.89 μ in H_2 gas is a known phenomenon expected due to the nonlinear relation between exciting and stimulated wave field amplitudes. The power level in the converted pulse is correspondingly enhanced.

We have investigated the effect of using a second high pressure cell following the one previously described, which increases the net effective total focal volume for SRS, with the intention of obtaining a larger energy output from an additional conversion of the remaining 1.06 μ radiation. In this case more than 40% total conversion efficiency as measured by CDC Model 100 Ballastic Thermopile has been obtained, indicating that the second conversion is influenced by the modes of the 1.89 μ radiation already present in the beam. In these experiments the second pressure cell was only 500 mm long; the beam emerging from the first cell was refocused in this second cell by a set of infrasil lenses of 50 cm focal length, 10 cm apart; the distance of the focal point to the exit window of the second pressure cell was about 10 cm. As was already observed before,[9] the stability of the converted pulse energy is improved. This is important for obtaining reproducible amplitudes of the temperature change in T-jump experiments.

The extinction coefficient of H_2O at 1.89 μ is 128 cm^{-1}. There may be some advantage in frequency doubling the 1.89 μ radiation by suitable crystals, which would also make available the weaker absorption bands of H_2O at 0.97 μ.

For studies of the kinetics of association-reactions, this laser-temperature-jump-spectrophotometer is very suitable.