DOE/ER/13808-6

Dynamic Structural Effects and Ultrafast
Biomolecular Kinetics in Photoinduced
Charge Transfer Reactions

Three Year Progress Report: DE-FG02-87ER13808

for Period March 15, 1991 - May 14, 1994

J.T. Hupp

Northwestern University
2145 Sheridan Road
Evanston, IL

April 1994

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Prepared for

THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-87ER13808

MASTER

ch
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Three Year Progress Report: "Dynamic Structural Effects and Ultrafast Bimolecular Kinetics in Photoinduced Charge Transfer Reactions"

DOE Grant Number: DE-FG02-87ER13808

Principal Investigator: Joseph T. Hupp (Northwestern University)

The goals of this project were extensive, but were primarily electron-transfer-reactivity related. Some of the specifics were: (a) to obtain complete (multimode) experimental descriptions of vibrational (Franck-Condon) barriers to intramolecular electron transfer, and to explore the molecular generality of the approach (time-dependent scattering analysis), (b) to connect the information directly to measured rates of photoinduced ET (femtosecond, picosecond, nanosecond regime), (c) to obtain needed complementary information in the microsecond regime (longer-range thermal ET) via pulsed-accelerated-flow techniques, (d) to explore valence localization/delocalization phenomena via direct experimental characterization of vibronic coupling effects (resonance Raman in the extended near infrared) and via controlled, reversible *external* manipulation of internal electronic structure, and (e) to manipulate and accelerate bimolecular photoredox processes via exploitation of room-temperature supercritical fluids as reaction media.

4

1. Dynamic structural studies. Mode specific analyses or assessments of barriers in electron transfer reactions require a quantitative knowledge of coordinate displacements, together with force constant information. Prior to our studies, displacement information was usually inferred from redox-induced changes in bond lengths (local coordinates) determined by x-ray crystallography or EXAFS, or from a Franck-Condon analysis of structured luminescence spectra. Unfortunately, several limitations exist; among them are: 1) the need to prepare stable crystalline samples in multiple oxidation states (x-ray crystallography), 2) the need for measurable, structured photonic emissions from molecular excited states (Franck-Condon analysis), 3) severe constraints on the choice of reaction environment

(typically, low-temperature glasses or single crystals), 4) an inability to investigate chemically irreversible redox or photo-redox processes, and 5) for EXAFS, limitations on the choice of scattering center and an inability to detect structural changes remote from the scattering center.

Based on DOE support, we pioneered the experimental application of a fundamentally different approach – one which effectively circumvents all of the above difficulties. Our approach is based on a time-dependent analysis of Raman scattering between resonant electronic or redox states.¹⁶ The scattering strategy has proven exceedingly powerful and has provided an unprecedented level of detail and information regarding vibrational barriers.^{4,17,18}

Our efforts during the current grant period were aimed at expanding and chemically generalizing the scattering strategy.^{1,4,6,7,14} One of the more interesting systems (and one which was viewed with some reviewer skepticism at the proposal stage) is the weak outer-sphere charge transfer process shown below:

Scattering from this system provides dynamic structural information for the simple redox reaction shown in eq. 2. In any case, our studies⁷ revealed that a total of 14 vibrational modes are coupled to the 1-electron reduction of the cyano-N-methylpyridinium cation (where multiple control experiments, including excitation profile studies, confirmed that the observed scattering enhancement effects were indeed associated with ET). Further analysis ultimately provided a complete, quantitative description of the vibrational reorganization process, including *all* normal coordinate displacements, *all* pertinent vibrational frequencies, and *all* single-mode contributions to the overall reorganization energy. It is perhaps worth noting that the redox product species in eq.2 is chemically unstable (half life of less than a few seconds in most solvents); detailed dynamic structural information would be almost impossible to obtain, therefore, by methodologies other than time-dependent scattering.

We also initiated a study of symmetrical mixed-valence systems (localized systems). These systems typically display weak intervalence absorption bands in the near infrared. Raman studies in this spectral region, however, present severe technical difficulties. The difficulties arise, in part, because: (a) scattering efficiencies usually decrease as absolute frequency to the fourth power (making NIR scattering 100's of times less efficient than, say, near UV scattering), and (b) the best available NIR detectors are roughly 5 orders of magnitude poorer (in terms of signal-to-noise) than the best visible region detectors. Furthermore, since we were interested in low frequency metal-ligand vibrational displacements, we were unable to take routine advantage of Fourier transform processing – a common method for enhancing S/N ratios with solid-state detectors. Nevertheless, we regarded symmetrical mixed-valence systems as extremely attractive scattering targets because of extensive information already available concerning solvent reorganization, electronic coupling, electrochemical properties, etc. Two of the systems we examined (with 1064 nm excitation) were the following:

Based on these systems, we reported the first examples of resonance enhanced scattering in the near infrared. Unfortunately, in the initial studies, we were able to demonstrate enhancement only from visible-region MLCT transitions (i.e., preresonant scattering; unambiguous *intervalence*-enhanced scattering was not demonstrated).¹

We subsequently succeeded in observing intervalence-based scattering from the following localized system (unpublished):

The key here was to push the experiment still further into the infrared (1320 and 1337 nm excitation) and to take advantage of the slightly higher absorption (and scattering) cross section provided by the system. Among the most fascinating

findings was enhancement of a very large number of internal bipyridine and pyrazine (bridge) modes, in addition to the expected metal-ligand stretching modes. These results point to extensive back bonding induced structural changes that, nevertheless, have almost entirely escaped detection in related x-ray studies.

Finally, we have recently reported the first intervalence-enhanced scattering studies/dynamic structural studies for an electronically *delocalized* system.¹⁴ The specific system examined was the Creutz-Taube ion, $(\text{NH}_3)_5\text{Ru-pyrazine-Ru}(\text{NH}_3)_5^{5+}$ ($\lambda_{\text{max}} = 1640 \text{ nm}$). Here the most striking preliminary findings were the strong coupling of multiple symmetrical bridge modes (e.g. ν_{6a} and ν_1) to the "intervalence" excitation and the absence of coupling to the so-called antisymmetric metal-ammonia stretching motions. As described in considerably more detail elsewhere,¹⁴ these findings led us to the important conclusion that standard PKS-type models for valence delocalization are inapplicable to systems like the Creutz-Taube ion. Instead we found that delocalization could be understood only by including extensive, direct (i.e. *not* superexchange) bridge orbital participation in the process. Several related issues are developed in the accompanying proposal.

2. *Intramolecular ET kinetics.* Among our highest priorities for kinetic studies over the past grant period were cyanide-bridged metal-metal charge transfer reactions (e.g., eqs. 6 and 7) that had previously been fully Franck-Condon

characterized (in our lab) by time-dependent scattering methods.^{4,6,13} Initial studies with nanosecond transient absorbance instrumentation at Northwestern suggested extremely fast charge transfer kinetics. Collaborative femtosecond studies with the Barbara group at Minnesota eventually showed that reverse ET in reaction -- takes place in 10^{-12} - 10^{-13} seconds, in reasonable agreement with Franck-Condon

based reactivity predictions.⁶ (These studies, by the way, represented the first successful investigation of ET kinetics via direct intervalence pumping.) Followup studies with the Ru-Ru analog revealed that the picosecond component of the observed kinetic process was actually a thermochromic transient. This then placed the ET component of the decays for both systems in the <100 femtosecond regime,¹¹ i.e. among the very fastest ET reactions ever observed.

To examine intramolecular ET reactions over longer distances, with much smaller driving forces, and with much less electronic coupling, we devised reaction chemistry involving solvent-triggered redox isomerization^{3,9} (eq. 8) and showed that the kinetics could be followed by pulsed accelerated flow (PAF)

spectrophotometry.⁹ (PAF is a small volume, multiple velocity variant of continuous flow that is capable of resolving reaction half lives as short as a few microseconds,¹⁹ i.e. orders of magnitude faster than conventional flow methods.)

Although these proof-of-concept experiments were indeed successful, we soon realized that the selective solvation strategy implicit in eq. 8 necessarily involved a mix of solvate species — making exact reactant, intermediate and product energetic (and structural) characterization difficult. Consequently, we devised a much more well defined (and controllable) redox reaction strategy based on site-selective crown-ether binding (second-sphere binding).³ We have since applied the approach (unpublished work) to reaction 8, and to related reactions like those shown in eqs. 9 and 10, with excellent success.

As suggested by the accompanying figure, this unusual strategy – in contrast to the original selective solvation strategy – very cleanly separates binding kinetics (described by slopes) from electron transfer kinetics (described by intercepts). For the specific examples shown above, k_{binding} is ca. $10^7 \text{ M}^{-1}\text{s}^{-1}$. When combined with thermodynamic association data, these experiments also yield rates for *unbinding* (ca. 10^4 s^{-1}). Observed intramolecular ET rate constants (nitromethane as solvent) are $2 \times 10^5 \text{ s}^{-1}$ (eq. 9) and $5 \times 10^4 \text{ s}^{-1}$ (eq. 10).

We have additionally found that related (but somewhat faster) reactions, based on shorter bridges, can be followed by nanosecond intervalence-pump/visible-probe techniques (unpublished). Remarkably, the reaction kinetics can be monitored in *both* directions, over a range of ET driving forces, via systematic exploitation of crown binding techniques. For the specific examples shown below, k_{ET} values are $1.4 \times 10^7 \text{ s}^{-1}$ (eq. 11) and $6 \times 10^6 \text{ s}^{-1}$ (eq. 12; crown = dibenzo-30-crown-10).

With basic experimental feasibility work now fully complete, the next goals with the combined PAF and nanosecond pump/probe studies (described further in the accompanying proposal) are: 1) to elucidate the potentially exceptional reactivity of some very specific bridged redox assemblies, and 2) to assess and compare measured ET rates for multiple systems with rates estimated directly from optical data and contemporary theory. As suggested above, this has been a most elusive goal. With our demonstrated ability, however, to obtain intervalence

charge transfer kinetics parameters over an *eleven order of magnitude* range, we are highly optimistic that the goal can be reached.

3. *Medium and temperature effects.* Because of their profound effects upon photochemical reactivity we continued to be interested in medium and temperature effects, especially in relation to ET processes. One important segment of our work was a generalization² of our prior investigation²⁴ of "inert" salt effects upon optical ET barriers. Especially in low polarity solvents, these effects – as monitored by intervalence absorption spectroscopy – can be quite substantial (for example, optical barrier shifts of up to 2,000 cm⁻¹ for acetylene-bridged biferrocene monocation in methylene chloride as solvent). As suggested by the equation below,

we were able to provide a *quantitative* explanation for the effects, based on: 1) ion-pairing induced symmetry reduction, and 2) an assessment of the resulting incipient energetic cost of ET-coupled ion translation. (Multiple alternative explanations (most invoking fundamental breakdowns in conventional theory) had been offered in the existing literature.) In the extended work, we were further able: 1) to show the near universality of the effect, with regard to solvent identity, 2) to account, in a predictive, quantitative fashion, for the wide variability of the effect as a function of solvent identity, and 3) to confirm the basic validity of conventional medium reorganization theory (at least for this system).²

The observations made with the singly charged biferrocene species raised some significant questions regarding the basic validity of a number of prior studies (including studies from our own lab) of optical ET energetics in much more highly charged systems. Consequently, we reevaluated the classic mixed-valence system shown below by obtaining extensive new intervalence absorption data in the limit

of infinite dilution.¹³ We found agreement at a qualitative level – but disagreement at a quantitative level – when experimentally determined solvent reorganization energies and the predictions of the standard two-sphere Marcus theory were compared. (The extent of disagreement was large – approaching a factor of 3 in solvent barrier height – and, therefore, of obvious significance in the context of ET and photo-ET kinetics studies.) We were able, however, to account for the large discrepancies by making use of independently published intervalence Stark effect (i.e., electric field effect) data²⁰ and by employing a more appropriate (in this instance) cavity analysis of solvent reorganization.²¹ The details are presented in an accompanying article.¹³ The essence of the study, however, was the realization – forced upon us by the Stark-effect data – that effective intramolecular charge transfer distances can differ substantially from geometric metal-donor/metal-acceptor separation distances. We also discussed some possible secondary consequences relating to electronic coupling phenomena. We suggest that the observations – both reorganizational and electronic coupling parameters – may be more general, and indeed, might play a role in the majority of intramolecular ET reactions.

Initially in connection with studies described in the following section, we also examined medium effects upon a class III (delocalized) system.¹⁵ The unusual effects examined were those associated with double crown encapsulation. (The target compound (the Creutz-Taube ion; see below) contains a total of 30 ammine protons, each potentially capable of interacting (via hydrogen bonding) with a crown-ether oxygen.) Double encapsulation causes crown-size-dependent energy shifts in both the NIR (nominally intervalence) and visible (nominally MLCT) spectral regions. The effects are small; their significance, however, is in the light they shed on overall electronic structure and on the *mechanism* of electronic delocalization. We find that the effects can not be rationalized by standard PKS or related two-site delocalization theories. They can be very nicely understood, however, within the context of explicit metal-bridge-metal (i.e. three-site) theories.

Surprisingly, these studies, together with those described in section 1, are apparently the first to discriminate experimentally between these two very different delocalization theories.

Finally, we also reported one of the first systematic studies of *temperature* effects upon optical ET processes.¹⁰ The system chosen was $(\text{NC})_5\text{Fe}-\text{CN}-\text{Ru}(\text{NH}_3)_5^{1-}$ shown also in eq. 6, above. Part of our motivation was to gain additional insight into transient thermochromic effects uncovered in our collaborative femtosecond/picosecond studies of reaction 7. We were also interested, however, for more fundamental reasons. In the study we found a very substantial temperature dependence for the optical intervalence energy (see figure). A variety of control experiments with symmetrical mixed-valence analogs, together with variable-temperature electrochemical experiments, revealed that the effects are associated with a temperature-dependent initial-state/final-state separation energy.

Figure Intervalence absorption spectra for $(\text{NH}_3)_5\text{Ru}^{\text{III}}-\text{NC}-\text{Fe}^{\text{II}}(\text{CN})_5^-$ in water at (a) 31.8, (b) 40.4, and (c) 59.8 °C. Inset: E_{op} versus temperature.

Ultimately, these experiments provided perhaps the first compelling experimental support for the somewhat controversial assertion by Marcus and Sutin²² that energy gaps for ET processes – including light-induced ET processes – should be regarded as free energies, rather than T-independent internal energies.

4. Electronic coupling. For many systems, ET dynamics are ultimately controlled by initial-state/final-state electronic coupling strengths. For light-induced reactions, these strengths are most often estimated from oscillator strengths (integrated absorption intensities). In work described in more detail elsewhere,^{5,8} we carefully examined an alternative electrochemical approach²³ to determining

coupling energies. The specific systems (or series of systems) examined were Ru-phenanthroline (i.e. metal-ligand species) and Ru-NC-Fe (i.e metal-metal species). Surprisingly, we obtained (in both cases) much higher coupling strengths from the electrochemical experiments than from simple spectral measurements. The origin of the discrepancies is unclear; however, additional (independent) information from other experiments tended to favor the electrochemical findings. In any case, at least one of our hypotheses (relating to effective charge transfer distances for the spectral analysis) should finally be amenable to testing (in the proposed new grant period), based on newly acquired Stark-effect capabilities.

When coupling strengths are high, donor and acceptor orbitals will obviously mix and initially isolated redox sites can eventually become valence delocalized. Classic examples are the Creutz-Taube ion and its derivatives. During the preceding grant period, we made the remarkable discovery that valence localization/delocalization within these prototypical systems could be systematically, and reversibly, externally modulated. The approach was based on second-sphere crown-ether binding (eq. 15). The effect is qualitatively demonstrated in the figure below. Shown in the figure are intervalence absorption spectra. Localization (following crown binding) is indicated by spectral broadening and by a blue shift in the spectrum.

Since our initial report on this unusual phenomenon, we have also carried out resonance Raman studies (see section 1). We find that partial crown encapsulation leads to

Figure 1. Intervalence absorption spectra for $\text{L}(\text{NH}_3)_4\text{Ru-pz-Ru}(\text{NH}_3)_4\text{L}^{3+}$ ($\text{L}=\text{pyridine}$) in nitromethane- d_3 , ($b = 0.01 \text{ cm}$) with (a) no added crown, (b) 1 equiv of crown and (c) excess of crown.

a spectacular change in the overall pattern of scattering intensities and vibronic coupling effects. Specifically, we observe the loss of key symmetric bridge modes (associated with three center valence delocalization) and- the appearance of multiple new modes associated with two-center trapping. Elaboration and exploitation of these unprecedented effects are proposed in the renewal document.

5. Instrument construction. Experimental chemical and photochemical research necessarily entails physical measurements and data acquisition, often via a battery of spectroscopic and related techniques. Measurements, of course, are instrument based. While we recognize that new instrument construction is a task common to many (perhaps most) labs, we delineate below the specific construction efforts in our lab because they represent a significant (and essential) fraction of our research effort over the past three years. These efforts can be summarized as follows: (a) A visible region scanning Raman double monochromator was successfully converted to extended NIR use. This instrument was used (as described above) for the first resonance Raman studies in the extended NIR.¹⁴ (b) A new ultra-high sensitivity Raman system was assembled for general UV and visible region use. Particular effort was placed (in part, in collaboration with K.G. Spears at Northwestern) on the assembly of a very widely (and continuously) tunable laser source that is essential for excitation profile studies and for successful interrogation of polychromophoric systems. (c) An electronic Stark effect (electric field effect) spectrometer was constructed. (See appendix to proposal for representative preliminary results.) (d) A higher performance probe source (new design from the Schanze lab) and improved signal detection were incorporated into our existing transient absorbance instrument. Importantly, each of these new or upgraded instrumentation capabilities will be utilized in proposed new research.

Other. Additional studies relating to: (a) synthesis and characterization of several directly linked Ru(bpy)₃-pyridinium^{a+} and Ru(phen)₃-pyridinium^{a+} species, (b) accelerated excited-state quenching in supercritical fluoroform, and (c)

miscellaneous other effects, have been described in other DOE reports and conference records. In view of the current report length, elaboration on these studies will be omitted.

References.

(1 through 15 refer to the appended DOE publication list)

16. Heller, E.J.; Sundberg, R.L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822.
17. Doorn, S.K.; Hupp, J.T. *J. Am. Chem. Soc.* **1989**, *111*, 4704.
18. Doorn, S.K.; Hupp, J.T. *J. Am. Chem. Soc.* **1989**, *111*, 1142.
19. Nemeth, M.T.; Fogelman, K.D.; Ridley, T.Y.; Margerum, D.W. *Anal. Chem.* **1987**, *59*, 283.
20. Oh, D.; Sano, M.; Boxer, S.G. *J. Am. Chem. Soc.* **1991**, *113*, 6880.
21. Brunschwig, B.S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.
22. Marcus, R.A.; Sutin, N. *Comm. Inorg. Chem.* **1986**, *5*, 119.
23. de la Rosa, R.; Chang, P.J.; Salaymeh, F.; Curtis, J.C. *Inorg. Chem.* **1985**, *24*, 4229.
24. Blackburn, R.L.; Hupp, J.T. *Chem. Phys. Lett.* **1988**, *150*, 399.

Balance statement: No unobligated funds will remain at the end of the current budget period.

Papers acknowledging DOE support (1990-93):

1. "Resonance Enhanced Raman Scattering in the Near Infrared. Preliminary Studies of Charge Transfer in the Symmetric Dimers $(2,2'\text{bpy})_2\text{ClRu-4,4'bpy-RuCl}(2,2'\text{bpy})_2^{4+/3+/2+}$, $(\text{H}_3\text{N})_5\text{Ru-4,4'bpy-Ru}(\text{NH}_3)_5^{6+/5+/4+}$, and $(\text{NC})_5\text{Fe-4,4'bpy-Fe}(\text{CN})_5^{4-/5-/6-}$ ", S. K. Doorn, J. T. Hupp, D. R. Porterfield, A. Campion, and D. B. Chase, J. Am. Chem. Soc., **1990**, *112*, 4999-5002.
2. "Does Marcus-Hush Theory Really Work? Optical Studies of Intervalence Transfer In Acetylene-Bridged Biferrocene Monocation at Infinite Dilution and at Finite Ionic Strengths", R. L. Blackbourn and J. T. Hupp, J. Phys. Chem., **1990**, *94*, 1788-1793.
3. "Solvent Induced and Polyether-Ligand-Induced Redox Isomerization within an Asymmetrically Coordinated Mixed-Valence Ion: *trans*-(pyridine)(NH_3) $_4\text{Ru}(4\text{-cyanopyridine})\text{Ru}(2,2'\text{bpy})_2\text{Cl}^{4+}$ ", J.C. Curtis, Y. Dong, M. Massum, C.S. Johnson, J. A. Roberts, R. L. Blackbourn, J. C. Curtis, and J. T. Hupp, Inorg. Chem., **1991**, *30*, 3856-3860.
4. "Experimental Assessment of Dynamic Structural Parameters for Homogeneous and Interfacial Charge-Transfer Reactions: Case Studies Based on Time-Dependent Raman Scattering Methods", S. K. Doorn, R. L. Blackbourn, C. S. Johnson and J. T. Hupp, Electrochimica Acta, **1991**, *36*, 1775-1785 (invited paper, Asilomar Conference Proceedings issue).
5. "Electrochemical and Spectral Probes of Metal/Ligand Orbital Mixing in $\text{Ru}(\text{NH}_3)_4(2,2'\text{bpy})^{2+}$ and $\text{Ru}(\text{NH}_3)_4(\text{phenanthroline})^{2+}$ ", G. A. Mines, J. A. Roberts and J. T. Hupp, Inorg. Chem., **1992**, *31*, 125-128.
6. "Ultrafast Measurements on Direct Photoinduced Electron Transfer in a Mixed Valence Complex", G. C. Walker, P. F. Barbara, S. K. Doorn, Y.

Dong, and J. T. Hupp, J. Phys. Chem., **1991**, *95*, 5712-5715.

7. "A Complete Experimental Assessment of Franck-Condon Structural Effects for an Irreversible Outer-Sphere Electron Transfer Reaction: Applications of Time-Dependent Raman Scattering Theory to the One-electron Reduction of 4-Cyano-N-methylpyridinium", R.L. Blackburn, C.S. Johnson, J.T. Hupp, M.A. Bryant, R.L. Sobocinski, J.E. Pemberton, J. Phys. Chem., **1991**, *95*, 10535-10537.
8. "An Electrochemical Variational Study of Donor/Acceptor Orbital Mixing and Electronic Coupling in Cyanide-Bridged Mixed-Valence Complexes", Y. Dong and J. T. Hupp, Inorg. Chem., **1992**, *31*, 3170-3172.
9. "Selective-Solvation-Induced Intramolecular Electron Transfer: Time Resolution via Pulsed Accelerated Flow Spectroscopy", J. A. Roberts, J. C. Bebel, M. P. Absi and J. T. Hupp, J. Am. Chem. Soc., **1992**, *114*, 7957-7958..
10. "Thermochromic Effects in an Asymmetric Mixed-Valence System", Yuhua Dong and Joseph T. Hupp, Inorg. Chem., **1992**, *31*, 3322-3324.
11. "Ultrafast Studies on Intervalence Charge Transfer" K. Tominaga, D.A.V. Kliner, J.T. Hupp, and P.F. Barbara, Eighth International conference on Ultrafast Phenomena. J.L. Martin and A. Migus, Eds., Springer-Verlag, Berlin, in press.
12. "Perturbation of the Electronic Structure of the Creutz-Taube Ion via Asymmetric Encapsulation with Macrocyclic Ether Species" Yuhua Dong, Joseph T. Hupp, and Dong I. Yoon, J. Am. Chem. Soc., **1993**, *115*, 4379-4380.
13. "Does Marcus-Hush Theory Really Work? The Solvent Dependence of

Intervalence Charge Transfer Energetics in $(\text{NH}_3)_5\text{Ru}^{\text{II}}-4,4'$ bipyridine- $\text{Ru}^{\text{III}}(\text{NH}_3)_6^{5+}$ in the Limit of Infinite Dilution" Joseph T. Hupp, Yuhua Dong and Robert L. Blackburn, J.Phys.Chem., **1993**, 97, 3278-3282.

14. "Resonance Raman Studies in the Extended Near Infrared: Experimental Verification of a Three Site Mixing Mechanism for Valence Delocalization in the Creutz-Taube Ion", Vladimir Petrov, Joseph T. Hupp, Carolyn S. Mottley and Loren C. Mann, J.Am.Chem.Soc., submitted.
15. "Intervalence Energy Effects Accompanying Double Crown Encapsulation of the Creutz-Taube Ion: An Interpretation Based on Three Site Mixing", Joseph T. Hupp and Yuhua Dong, Inorg.Chem., to be submitted.

DATE

FILMED

5/23/94

END