the generality of these cycloreversions. The photochemistry of **7** and **11** will be reported in a separate publication.

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Supplementary Material Available: Spectral data for **3**, **5**, **7**, **8**, **10**, and **11** (1 page). Ordering information is given on any current masthead page.

Conductivity Measurement of an X-ray Absorption Spectrum: Re $\mathrm{L_{III}}$ Near-Edge Structure of $\mathrm{Re_2(CO)_{10}}$ in 2,2,4-Trimethylpentane

T. K. Sham*

Department of Chemistry
Brookhaven National Laboratory
Upton, Long Island, New York 11973

S. M. Heald

Department of Energy and Environment
Brookhaven National Laboratory
Upton, Long Island, New York 11973

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We report in this communication the first measurements of an X-ray absorption spectrum by means of X-ray photoconductivity in a hydrocarbon solution. $\mathrm{Re_2(CO)_{10}}$ in 2,2,4-trimethylpentane has been used for these measurments. The main objective of this report is to demonstrate the feasibility of this technique and its potential applications.

Recent advances in synchroton radiation technology[1] have greatly facilitated the development of X-ray absorption spectrometry. Aside from direct absorption measurements in the transmission mode, various techniques such as electron yield,[2,3] ion yield,[4,5] and fluorescence yield[6-9] have been developed for special situations where high sensitivity is needed and the transmission measurement is not applicable. Of all these techniques, the basic assumption is that the yield is proportional to the absorption cross section. It has been demonstrated[2-9] that the assumption is generally valid particularly in the EXAFS portion of the spectrum, although precise agreement of the EXAFS amplitude is not always obtained.[10]

The technique we introduce here is the measurement of photoconductivity of a solution. The electrons and ions formed as a result of a photon absorption process are collected by an electric field applied across the solution. The signal in such an experiment can be written

$$I_1/I_0 = K(E)(1 - e^{-\mu t}) \qquad (1)$$

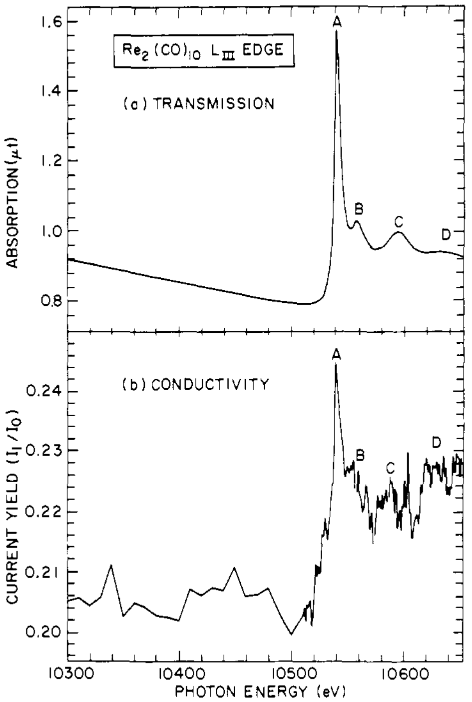

Figure 1. Re $\mathrm{L_{III}}$ near-edge structure of $\mathrm{Re_2(CO)_{10}}$ in 2,2,4-trimethylpentane obtained by (a) transmission measurement and (b) conductivity measurement. The transmission measurement has been calibrated to give the actual μt of the solution. The current measurement is simply a plot of I_1/I_0, which is not necessarily equal to μt (see text).

where I_1 and I_0 are the photocurrent and incident photon signals, respectively, μ is the total sample absorption, and t is the sample thickness. $K(E)$ is the proportionality constant (E being the photon energy) relating the absorption to the photoinduced current. The current comes about from photoionization and cascade processes involving the excited photoelectron and the decay of the core hole by Auger and fluorescent processes.[11,12] It is not our purpose here to make a detailed study of $K(E)$, but rather to point out some general features. Below the edge, as the photon energy is increased there is more energy available for current production, and thus, $K(E)$ should slowly increase with energy. At the $\mathrm{L_{III}}$ absorption threshold, however, the $2_{p_{3/2}}$ core hole is created. This core hole can decay either via an Auger process or by emission of a fluorescence photon. While the Auger electrons can generate a lot of secondary charges, the fluorescence photon has a finite probability of escaping the sample, resulting in no current. In the present case the probability of fluorescence is small, and therefore we expect $K(E)$ to be a function of energy with possibly a small decrease at the edge. It must be pointed out that $K(E)$ includes the collection efficiency of the cell. This is affected primarily by recombination of the electrons and ions before they reach the collection plates. This process is more likely as the absorption is increased and also would decrease $K(E)$ as the absorption increases through the edge.

The measurements were made at CHESS (Cornell High Energy Synchroton Source). A channel-cut Si(220) crystal monochrometer was used. The horizontal slit was closed down to ~0.2 mm to achieve high resolution. The experimental arrangement involves the use of solution cells made of quartz (5-mm i.d., 5 mm thick) and equipped with two Al-coated Mylar windows. The windows were used as electrodes. The cell was placed in a metal container that is positioned in place of the sample holder used in transmission measurements.[1] Ion chambers were used to measure

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the intensity of the incoming (I_0) and transmitted (I) photons. Photocurrent (I_1) in a solution ($\sim$0.005 M) of $Re_2(CO)_{10}$ in dry 2,2,4-trimethylpentane was recorded with a Keithley current amplifier. For the measurements, 100–300 V were applied to the electrodes. Further details of the set-up and related considerations will be published elsewhere. Re L_{III} absorption spectra have been obtained with both transmission and conductivity techniques. Typical single-scan spectra ($\sim$5 min) are shown in Figure 1.

Figure 1a shows the L_{III} edge transmission absorption spectrum of a $Re_2(CO)_{10}$ solution. The Re L_{III} edge exhibits a sharp resonance (peak A). This, a common feature for the $L_{II,III}$ edge of transition metal compounds with unoccupied d states,[13] can be attributed to a $2p_{3/2} \rightarrow 5d$ transition. Peak B, $\sim$20 eV above peak A, is tentatively assigned to higher energy unoccupied states of s and d character while peaks C and D can be regarded as EXAFS oscillations. It is interesting to note that although $Re_2(CO)_{10}$ is an 18-electron molecule, the fact that there exists such an intense resonance indicates the presence of partially unoccupied molecular orbitals containing Re 5d character. The primary concern of this paper, however, is the question of whether or not the conductivity measurement technique is feasible. The answer is given in Figure 1b, which plots the ratio conductivity (I_1)/photon monitor (I_0). It is very gratifying that not only the edge jump but also the accompanying structures are observed. The noise in the present measurements is attributed to the presence of considerable leakage currents. We expect that improved cells and counting techniques will alow a much better signal-to-noise ratio.

To interpret the results we return to eq 1 and note that for $\mu t \ll 1$

$$I_1/I_0 \simeq K(E)\mu t \tag{2}$$

while for a very thick sample all of the X-rays are absorbed and

$$I_1/I_0 \simeq K(E) \tag{3}$$

The present case is intermediate and I_1/I_0 is not directly proportional to μt. However, as expected the amplitude of peak A in the conductivity measurements is reduced relative to the edge since as the absorption increases the ratio I_1/I_0 is less sensitive to changes in μt.

Although the exact quantitative details of the I_1/I_0 spectrum cannot be revealed at present, the fact that all the absorption features are reproduced is a good indication that this technique may offer us an opportunity to study the decay of the core hole in ions (or molecule) upon deep core excitation and ionization in solution. As discussed above three processes are definitely important in conductivity measurement: first, the creation of the core hole (this is the only important process in transmission measurements) and then the decay of the core hole followed by secondary ionization of the solvent molecules by fluorescence X-ray (8561 eV for Re L_{III} edge) and L_3 MM Auger electrons. What follows are radiochemical processes in which the energetic electrons become equilibrated with the environment and when slowing down create a lot of secondary electrons, some of which finally escape the Coulombic potential of the ions to avoid ion-pair formation and recombination and are collected at the electrodes. In the case of dilute solutions the solvent molecule should play a main role because they provide most of the secondary electrons and ions that we can count as current. In essence, they serve as counting molecules analogous to gas molecules used in an ionization chamber. The fluorescence yield[12] of the Re L_{III} edge decay has been documented to be 0.2. This means that the Auger yield is 0.8 and is the dominant source for secondary ionization.

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Triplet Excitation Transfer to Carotenoids from Biradical Intermediates in Norrish Type II Photoreactions of *o*-Alkyl-Substituted Aromatic Carbonyl Compounds[1]

C. V. Kumar, S. K. Chattopadhyay, and P. K. Das*

Radiation Laboratory, University of Notre Dame
Notre Dame, Indiana 46556

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Biradicals (II) produced as a result of intramolecular hydrogen abstraction (Norrish type II photoreaction) in the triplet state of *o*-alkyl-substituted aromatic carbonyl compounds (I) are describable[2-6] as the triplets of the corresponding photoenols (III) (Scheme I). While, in some cases, the biradicals are observed[3] directly by their transient absorption, a more convenient method[7] of probing these intermediates has been based on electron transfer from the ketyl site to an acceptor, notably, paraquat (1,1′-dimethyl-4,4′-bipyridinium) dication. Except for the finding[3,6] that these biradicals are oxygen quenchable, to our best knowledge, their triplet nature has not been explicitly established. In this communication we demonstrate that the biradicals (II) derived from *o*-alkyl-substituted aromatic carbonyl compounds interact with long-chain carotenoids producing the triplets of the latter. This behavior not only permits estimation of the triplet energies (E_T) of the biradicals that apparently act as donors but also provides a convenient method of probing these transient species and their triplet precursors in situations not accessible to the paraquat technique.

When a photoenolizable substrate such as *o*-methylacetophenone (OMA), *o*-methylbenzaldehyde (OMB), or 2,4,6-trimethylbenzaldehyde (TMB), each at 0.04–0.06 M, is flash photolyzed in solutions containing β-carotene at (1–5) × 10^{-4} M with nitrogen laser pulses (337.1 nm, 2–3 mJ/pulse, $\sim$8 ns), intense transient absorptions at 500–550 nm growing on a nanosecond time scale are observed. Figure 1A shows an experimental trace obtained with OMA as the substrate in toluene. The transient absorption spectrum matches completely with that of β-carotene triplet observed with benzophenone or *p*-methoxyacetophenone as the triplet donor under similar conditions. The growth of transient absorption (Figure 1A) follows first-order kinetics, and the corresponding rate constants (k_{obsd}) show a linear dependence on β-carotene concentrations. Figure 1B shows the plots of k_{obsd} vs. [β-carotene] for OMA and TMB. The slopes of the plots, representing the bimolecular rate constants for triplet energy transfer to β-carotene, are practically the same (4.1×10^9 M^{-1} s^{-1}) for the two substrates (in toluene). On the other hand the intercepts are quite different for the two systems, giving lifetimes

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