Substantial Non-linear Optical Response of New Polyads Based on Ru and Os Complexes of Modified Terpyridines

Maria Konstantaki, Emmanuel Koudoumas, and Stelios Couris*,†,‡

Foundation for Research and Technology-Hellas (FORTH), IESL, P.O. Box 1527, 71110 Heraklion, Greece

Philippe Lainé, and Edmond Amouyal*,§

Laboratoire de Chimie Physique, CNRS UMR 8000, Université Paris-Sud, Bat. 350, 91405 Orsay, France

Sydney Leach

DAMAP, CNRS UMR 8588, Observatoire de Meudon, Meudon, France

The third-order non-linear optical behavior of two new series of multicomponent systems based on coordination compounds of transition metals is reported. These systems, soluble in acetonitrile, are made of a metal (Ru or Os) bis-terpyridyl (tpy) unit, as photosensitizer P, connected to one or two electron acceptor groups, or to both electron donor (D) and electron acceptor (A) groups to form polyads of D–P–A type. The non-linear absorption and non-linear refraction response was substantial and was examined using the *z*-scan technique. The results are presented for two different excitation conditions. For excitation under laser pulses of nanosecond duration the compounds with the Ru center exhibit reverse saturable absorption (RSA). The corresponding Os samples show saturable absorption (SA) for low incident intensities that turns to RSA above an intensity threshold that depends on the concentration of the solutions. In contrast, under sub-picosecond laser excitation the Ru and the Os samples each exhibit saturable absorption. The non-linear refraction monitored for nanosecond excitation is negative (self-defocusing) for both Ru and Os complexes.

Introduction

In recent years, non-linear optical processes have attracted great interest[1] due to the potential of utilizing optoelectronic devices for telecommunications and information storage. This has led to many studies of non-linear optical responses of a variety of materials and furthermore to the development of materials possessing tailored non-linear optical (NLO) properties.[2–5] Mainly, efforts have concentrated on purely organic materials such as fullerenes,[2] fullerene derivatives,[3] conjugated organic polymers,[4] and intermolecular charge-transfer complexes.[5]

Recently, organometallic structures[6,7] have been investigated as potential sources of a highly non-linear molecular optical blocker. Similar to organic molecules, organometallic complexes can possess strong responses, fast response time, ease of fabrication, and furthermore have the advantage over organic systems of much greater flexibility at the design stage. Due to the diversity of metals, the richness of excited states present in these systems, as well as to the possibility of various arrangements of the organic ligand around the metal a large variety of structures can be synthesized.

Studies on the non-linear optical response of organometallic compounds include both quadratic and cubic non-linear properties. A concise review of the techniques used and the materials studied can be found in refs 8 and 9, respectively. A wide variety of materials has been synthesized and tested to determine their non-linear behavior, including metallocenes, metal carbonyl complexes, silicon complexes, metal nitrido compounds, metallapolyyne polymers, metallo-porphyrines, and phthalocyaninato metal complexes. To our knowledge, few studies have been devoted to the NLO properties of multicomponent metallo-organic compounds, most of them being concerned with the quadratic optical non-linearities.[10–12]

Dupuis et al.[13] report on the optical limiting action of a porphyrin–viologen dyad while the hyperpolarizability of a photosensitizer–electron acceptor triad ($S–A_1–A_2$) was studied by Si et al.[14] In the present work, the third-order NLO behavior[15,16] of donor–chromophore–acceptor polyads is examined for the first time to our knowledge. The compounds are made of a transition metal (Ru or Os) bis-terpyridyl (tpy) unit (as photosensitizer P) connected to one or two electron acceptor groups, or to both an electron donor (D) and an electron acceptor (A) group to form a linear polyad of D–P–A type.[17] These ligand systems are also of great interest as components of molecular devices for photochemical and photoelectrochemical conversion of solar energy.[18–20] It should be noted that our species are in effect supermolecules in which the covalent interactions between P and A are weak in the ground state, so that in this state the intrinsic properties of the molecular subunits are preserved, being only weakly perturbed, and where the electron polarization is of the type usually considered as the classical inductive effect in chemistry. On the other hand, it was demonstrated[20] that electron donors D are strongly coupled to the photochrome P and can be considered as acting similar
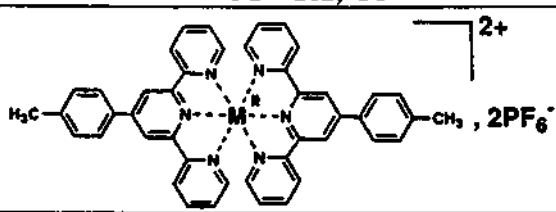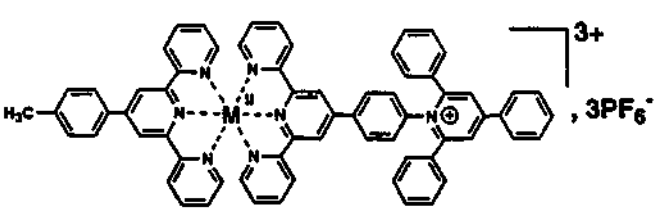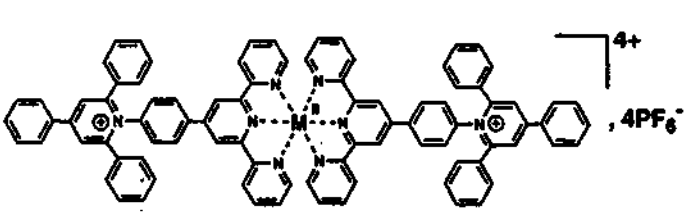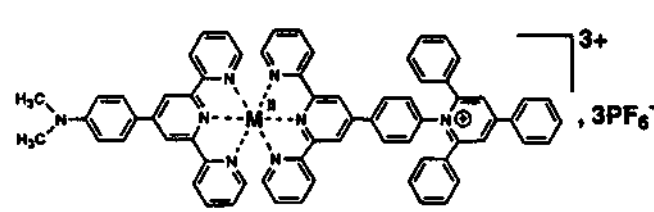
* Corresponding authors.
† Also, Institute of Chemical Engineering and High-Temperature Processes (ICEHT), P.O. Box 1414, 26500 Patras, Greece.
‡ Fax: +30 61 965223. E-mail: couris@iceht.forth.gr.
§ Fax: +33 1 69153053. E-mail: edmond.amouyal@lcpm.u-psud.fr.

TABLE 1: Structure and Code Names of the Molecules Studied

COMPOUND M = Ru, Os	CODE NAME
	Ru 1, Os 1·
	Ru 2, Os 2
	Ru 3, Os 3
	Ru 4, Os 4

Their three-dimensional stuctures are exemplified by the crystallographic data given in ref 20 for Ru 3.

to a perturbing substituent. In the D−P−A case the system is thus a virtual dyad in which the two elements are D−P on one hand and A on the other.

Experimental Section

The compounds were prepared by the methods described in ref 17 and their detailed synthesis, characterization, and physicochemical properties will be published elsewhere.[20] In Table 1 the compounds studied are depicted along with the code names used in this report. The Ru and Os complexes Ru/Os 1−4 correspond, respectively, to the following triad structures: Ru/Os1 = d−P−d, Ru/Os2 = d−P−A, Ru/Os3 = A−P−A, and Ru/Os4 = D−P−A, where P is the central photosensitizer unit, d and D are weak and strong donors, respectively (in the ground state), and A is an acceptor. The linear absorption spectrum of compounds Ru 4 and Os 4 are shown in Figure 1. The observed spectral features are discussed later. The other Os and Ru compounds studied (Table 1) have very similar absorption spectra to those of Os 4 and Ru 4, respectively.

The third-order non-linear optical response of the materials was probed using the z-scan technique, a well-established method that monitors the non-linear absorption and non-linear refraction. The technique, described in detail elsewhere,[21] is based on the variation of transmitted radiation intensity by alteration of the geometrical parameters of the interaction region. This is achieved by gradually moving a sample along the axis
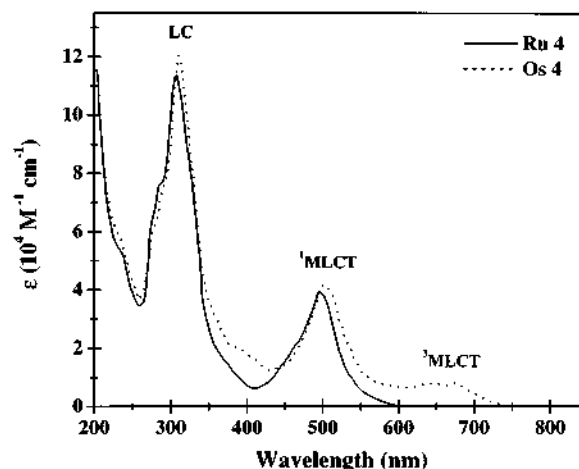

Figure 1. Electronic absorption spectra of Ru 4 (solid line) and Os 4 (dashed line) in acetonitrile.

of propagation (z) of a focused Gaussian beam through its focal plane and measuring the transmission of the sample for each z-position. As the sample experiences different electric field strengths at different positions the recording of the transmission as a function of the z-coordinate provides precise information about the non-linear effects present.

Two collection methods of the z-scan signal are performed (i) the open aperture z-scan where all the transmitted light is

NLO Response of Ru and Os Complexes of Terpyridines

J. Phys. Chem. B, Vol. 105, No. 44, 2001 **10799**

detected, which provides information about the non-linear absorption of the sample and (ii) the closed aperture *z*-scan where only the light transmitted through a pinhole placed in front of the detector is detected, which provides information about the non-linear phase variations and hence the resulting focusing or defocusing of the transmitted beam.

Non-linear Parameters and Optical Effects. Under intense irradiation the absorption and refractive index of a material can include non-linear terms and can be expressed as follows:[22]

$$\alpha = \alpha_0 + \beta I \tag{1}$$

$$n = n_0 + \gamma' I \tag{2}$$

where β (cm/W) is the two-photon absorption parameter, γ' (cm^2/W) the non-linear refractive index parameter, while α_0 (cm^{-1}) and n_0 are the linear terms, and I (W/cm^2) is the incident radiation intensity.

Using the *z*-scan technique the non-linear parameters β and γ' can be measured. A detailed description of the procedure adopted in deriving β and γ' from the transmission of the sample as a function of its position on the *z*-axis is given by M. Sheik-Bahae et al.[21] In brief, for an open aperture *z*-scan parameter β can be simply calculated from the normalized transmission signal through a simple fitting procedure. For a closed aperture *z*-scan and for negative non-linearity the normalized transmission shows a prefocal transmission maximum (called peak) followed by a post focal minimum (called valley). The opposite is true for materials exhibiting positive non-linearity. The non-linear refraction can be determined[21] by dividing the data of a closed aperture *z*-scan by that of an open aperture scan performed at the same incident intensity. The normalized difference ΔT_{p-v} between the peak and the valley of the resultant curve is related to the non-linear refractive index parameter γ'. For accurate measurement of this parameter the condition[26] $\beta/2k\gamma' < 1$ must be satisfied, where k is the wave vector. This imposes a limit in the determination of γ' in the case of materials with strong non-linear absorption. The parameters β and γ' are then related to the imaginary and real parts of the third-order susceptibility[22] $\chi^{(3)}$, respectively, so that $\chi^{(3)}$, and subsequently the second hyperpolarizability γ, can be determined from a set of open and closed aperture *z*-scans performed at the same incident intensity.

Equations 1 and 2 and the theory briefly described so far apply to instantaneous effects where the characteristic time of the non-linear response is much shorter than the width of the excitation pulse. In contrast, if the characteristic response time of the non-linearity is longer than the pulse width, excited-state absorption (sequential two-photon absorption) provides a major contribution to the overall third-order non-linearity.[22] Under this regime an absorption process creates population in an excited state. If the lifetime of this excited state is long enough, the ground state is depleted during the laser pulse and the absorption of the molecule is modified by the excited state. If σ_G and σ_E are the absorption cross sections of the ground and the excited state, respectively, we can distinguish between two different modifications of the absorption: if $\sigma_G > \sigma_E$ the absorption is reduced (saturable absorption-SA) while the absorption is increased if $\sigma_G < \sigma_E$ (reverse saturable absorption-RSA). Materials that exhibit RSA are transparent for low-energy inputs but show low transmittance for high-energy inputs, while the opposite is true for materials with SA.

Several organic materials exhibit RSA properties in the visible region and their energy level structure can be well approximated by a five level system[23] involving the ground-state S$_0$, the first

excited singlet S$_1$, and the lowest triplet T$_1$. If α_0 and α_1 are the linear absorption coefficients of the S$_0$ and T$_1$ states, respectively, the total absorption coefficient can be written as follows: [24]

$$\alpha = \alpha_0[S_0] + \alpha_1\alpha_0[S_0]I \tag{3}$$

where [S$_0$] is the ground-state population at instant *t*.

Comparing eqs 3 and 1 we can see that in the regime of RSA similarly to the instantaneous case, α can be considered as an intensity dependent absorption coefficient but where the effective non-linear absorption parameter is $\beta_{eff} = [S_0]\alpha_0\alpha_1$. Under this regime the measured non-linear parameters depend on the incident light intensity, they are excited-state population dependent and thus decay with a time dependence following pulsed excitation.

In the case of SA the simplest expression[22] for the absorption coefficient α is

$$\alpha = \frac{\alpha_0}{1 + I/I_S} \tag{4}$$

where I_s is the saturation intensity. In the weak saturation limit, i.e., $I/I_s \ll 1$, eq 4 is reduced to

$$\alpha \approx \alpha_0(1 - I/I_S) = \alpha_0 - \frac{\alpha_0}{I_S}I \tag{5}$$

Again expressions 5 and 1 are identical if, in the case of saturable absorption, we define

$$\beta_{eff} = -\frac{\alpha_0}{I_S} \tag{6}$$

Materials that exhibit excited-state absorption normally show excited-state refraction as well. This is a consequence of the redistribution of population that changes the absorption spectrum, which by causality (resulting from Kramers−Kronig relations[25]) modifies the refractive index. Similarly to the instantaneous case, the refractive index can be expressed as an intensity-dependent refractive index parameter, $n = n_0 + \gamma'_{eff}I$ as in eq 2.

Therefore expressions 1 and 2 that contain β and γ', respectively, can also be applied in the case of excited-state non-linearity. In our treatment of the non-linear parameters we will therefore conveniently use the formalism established for the instantaneous process but refer to the effective values of the parameters of non-linear refractivity and non-linear absorption and its related third-order susceptibility.

Results

First, results are presented for excitation with the second harmonic at 532 nm of a Nd:YAG laser with pulse duration of 10 ns. Solutions with concentration in the range of 0.05 to 0.5 mM were prepared, and the open and closed aperture *z*-scans were performed for incident intensities in the range of 10 to 100 MW/cm^2. A typical open and closed *z*-scan signal as well as their ratio is illustrated in Figure 2 for sample Ru 1 at 70 MW/cm^2 incident intensity. All the Ru samples examined gave similar *z*-scan curves evident of negative non-linear refraction (self-defocusing) and reverse saturable absorption−RSA. Open and closed aperture *z*-scan of pure solvent did not show any non-linear optical response for the intensities used in our nanosecond regime study.
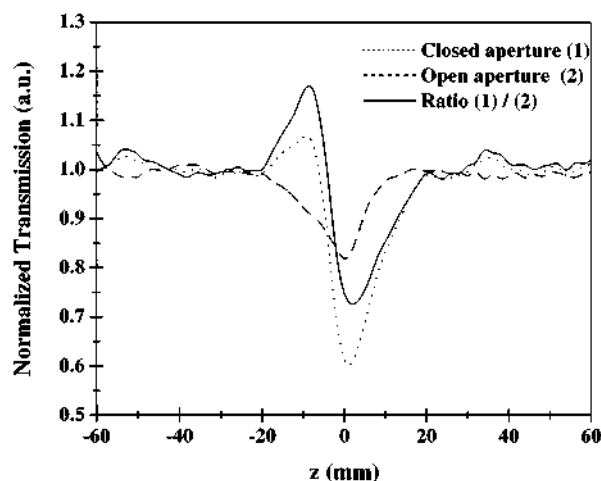
Figure 2. Typical *z*-scan signal for sample Ru 1 at incident intensity of 70 MW/cm^2 at 532 nm, 10 ns laser pulses.
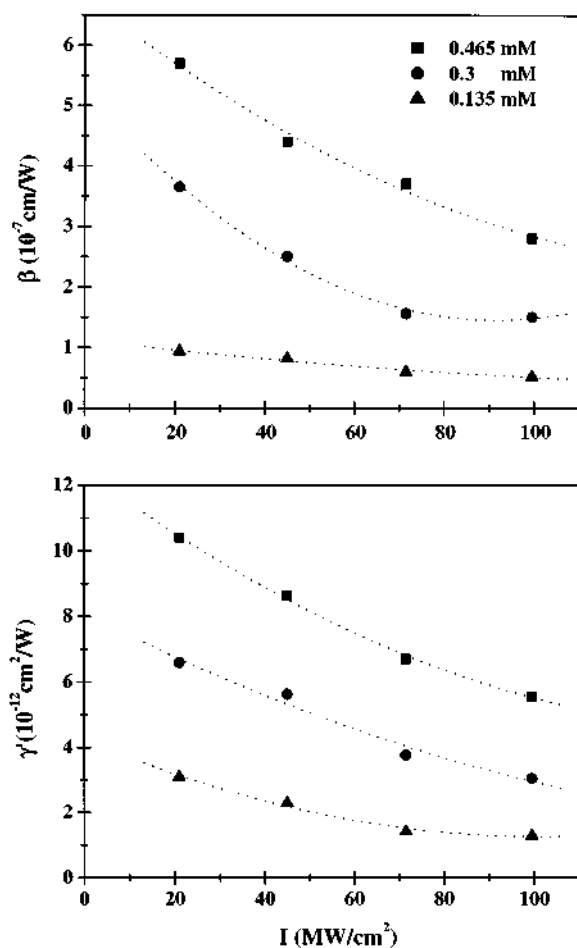

Figure 3. The two-photon absorption parameter β and the non-linear parameter γ' of the refractive index for three solutions of Ru 3 at different concentrations at 532 nm, 10 ns laser pulses. Lines are plotted as a guide to the eye.

Using these experimental results the two-photon absorption parameter β (cm/W) and the non-linear refractive index parameter γ' (cm^2/W) were calculated following the procedure described in the Experimental Section. For clarity, results are shown only for the Ru 3 sample in Figure 3 , parts a and b, respectively, for three different concentrations. As anticipated, both β and γ' decrease with increasing intensity, indicating that those values are excited-state population dependent consistent

TABLE 2: Linear and Non-linear Parameters of Ru Solutions of 0.35 mM Concentration under Incident Intensity of 20 mW/cm^2 at 532 nm, 10 ns Laser Pulses[a]

sample	α_0 (cm^{-1}) at 532 nm	β 10^{-7} (cm/W).	γ' 10^{-12} (cm^2/W)	γ 10^{-28} (esu)
Ru 1	5.38	1.4	3.1	0.77
Ru 2	6.67	2.8	6.3	1.3
Ru 3	7.93	3.65	6.6	1.4
Ru 4	10.72	3.3	10.8	2.28

[a] For all compounds the lifetime of the triplet state is less than 10 ns.

TABLE 3: Linear and Non-linear Parameters of Os Solutions of 0.35 mM Concentration under Incident Intensity of 15 MW/cm^2 at 532 nm, 10 ns Laser pulses[a]

sample	α_0 (cm^{-1}) at 532 nm	τ_T (ns)	β 10^{-7} (cm/W).	γ' 10^{-12} (cm^2/W)	γ 10^{-28} (esu)
Os 1	9.18	247	-1.85	4.88	1.03
Os 2	8.81	168	-2.57	5.99	1.31
Os 3	9.65	222	-3.78	8.06	1.77
Os 4	16.35	57	-3.9	8.4	2.03

[a] τ_T is the lifetime of the triplet state.

with the model described earlier. Using these results the second-order hyperpolarizabilty γ (esu) is calculated.

To allow comparison, the non-linear optical parameters of the examined Ru samples along with the linear absorption coefficient α_0 (cm^{-1}) are shown in Table 2 for solutions of 0.35 mM concentration and incident intensity of 20 MW/cm^2. As can be seen, progression from Ru 1 to Ru 4 results in an increase of the second hyperpolarizability by a factor of 2. It is interesting also to notice the general trend between the values of the non-linear parameters and the corresponding linear absorption coefficient at the excitation wavelength, indicating the increase of the non-linear response due to resonance effects. Furthermore, taking into account the nature of our complexes and considering the possibility that the weak donors acquire some acceptor character on photon excitation, we expect that the electronic polarization of the complex will increase in the order Ru/Os1 < Ru/Os2 < Ru/Os3 < Ru/Os4. This order is indeed found in the NLO parameters given in Tables2 and 3. We conclude that there are two factors that modulate the NLO properties of this series of Ru and Os complexes: (1) resonance effects, as seen by correlation with the linear absorption coefficient, and (2) structural effects, which determine electronic polarization properties.

The experiments were repeated for the corresponding Os samples listed in Table 1. In contrast to the Ru samples, for low incident intensities the response of the Os samples is that of SA. For higher incident intensities, the transmission still increases as the sample approaches the focal plane (SA), but closer to the focal plane the transmission starts to drop (RSA). In this case the recorded open aperture *z*-scan case is as shown in Figure 4 (dashed line): a dip is observed near the focal plane. Solutions of the same concentration of the other Os samples exhibit similar response. The intensity threshold for RSA behavior is the same for all four Os samples around 20 MW/cm^2 (0.25 J/cm^2). For higher concentrations (0.7 mM) the threshold is slightly lower around 14 MW/cm^2. Increase in concentration results in the enhancement of both the SA and the RSA response. Similarly to the Ru samples, all Os samples exhibit negative non-linear refraction.

Using the experimental results the non-linear optical parameters were calculated for incident intensities below the threshold
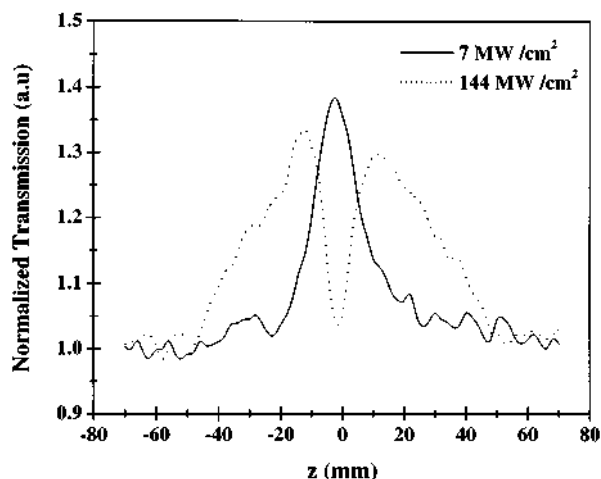
NLO Response of Ru and Os Complexes of Terpyridines

J. Phys. Chem. B, Vol. 105, No. 44, 2001 **10801**

Figure 4. Signal of an open aperture *z*-scan at 532 nm, 10 ns of sample Os 2 at two different intensities, respectively, below and above the intensity threshold for RSA behavior.

of RSA and the obtained values are illustrated in Table 3 for solutions of 0.35 mM at 15 MW/cm^2 incident intensity. Again we notice that progression from Os 1 to Os 4 results in an increase of the second hyperpolarizability by a factor of 2. The negative sign of the two-photon absorption parameter β indicates the occurrence of saturable absorption. In comparison to the corresponding Ru samples we observe the same relative magnitudes of β, γ', and γ, respectively, and slightly increased values.

Similar experiments were repeated with sub-picosecond laser pulse excitation using a hybrid excimer laser system based on the concept of the distributed feedback dye laser system that emits pulses of 500 fs duration at 497 nm. Under this excitation the solvent also exhibits a non-linear optical response, that of instantaneous two-photon absorption and positive non-linear refraction (self-focusing). Therefore the non-linear response of the examined solutions is a combination of the response of the sample plus that of the solvent. In this case, pure acetonitrile samples must also be examined at the same experimental conditions to determine the contribution of the solvent in the total non-linear response of the solutions.

For intensities too low for the solvent to exhibit non-linear absorption the open *z*-scan curves reveal a SA response as shown in Figure 5. As the incident intensities increase and the solvent exhibits non-linear absorption, the two opposite responses, SA and two-photon absorption, can be seen superimposed. To verify that the dip observed is due to the non-linear response of the solvent the measurements were repeated under identical conditions for solutions with concentrations in the range 0.05 to 0.5 mM. As can be seen from Figure 6, the relative decrease of the transmission at focus is the same for all concentrations studied indicating that the observed dip is due to the non-linear absorption of acetonitrile. Similar observations were made for all the samples. Therefore we can conclude that for the range of the intensities used, the response of all the samples is that of SA. The maximum intensity used in the experiments (747 GW/cm^2) corresponds to a fluence of 0.375 J/cm^2, which is slightly higher than the fluence threshold of 0.25 J/cm^2 in the nanosecond excitation where the response of the Os samples changes from SA to RSA. However, it must be noticed that the SA response is significantly stronger in the femtosecond regime as compared to that in the nanosecond, therefore a small signal of RSA response (superimposed to the non-linear absorption of the solvent) may not be observable.
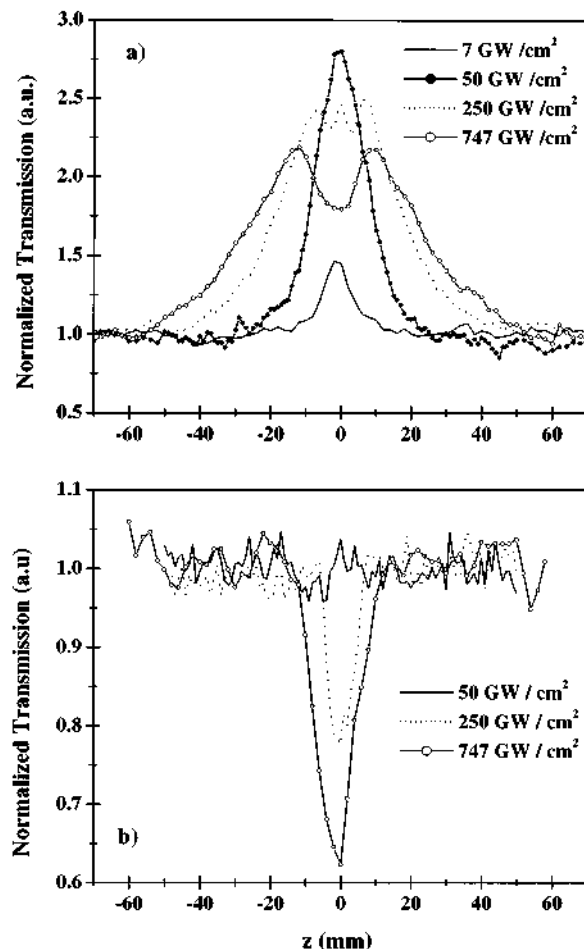

Figure 5. Open aperture *z*-scan signal (sample Ru 3) for (a) solution and (b) pure solvent at various incident intensities at 497 nm, 0.5 ps.
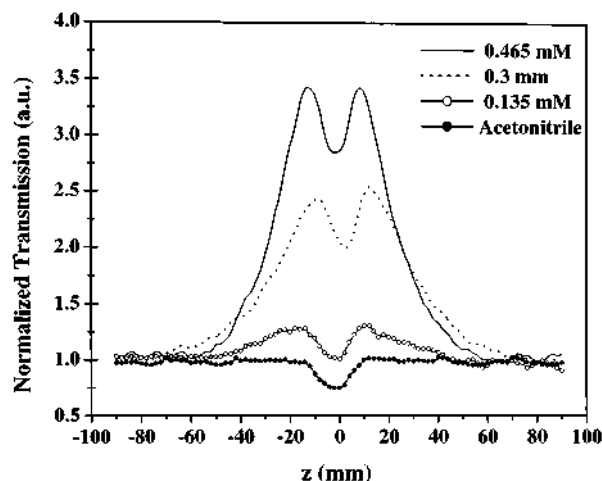

Figure 6. Open aperture *z*-scan signal (sample Ru 3) for three solution concentrations at 497 nm, 0.5 ps for incident intensity of 747 GW/cm^2. The signal of the pure solvent is also shown.

Using these results and the procedure described in the Experimental Section we calculated the two-photon absorption parameter β for all the samples as shown in Table 4. As in the nanosecond case, both resonance and structural effects influence the NLO properties of the Ru and Os complexes. Attempts to determine the non-linear refraction parameter were unsuccessful in the 0.5 ps case due to the high non-linear absorption present. As an example, for the Ru 4 sample, the closed aperture *z*-scan is so strongly affected by the saturable absorption (as shown in
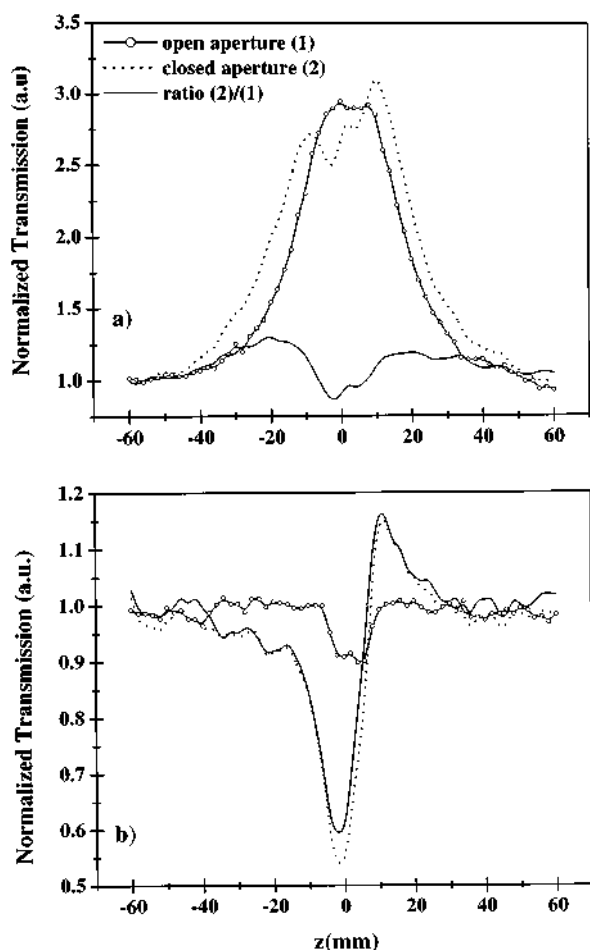
Figure 7. Open, closed aperture *z*-scan and their ratio for (a) Ru 4 and (b) pure acetonitrile at 497 nm, 0.5 ps, for incident intensity of 200 GW/cm^2.

TABLE 4: Linear and Non-linear Absorption Parameters of Ru and Os Complexes Studied with 497 nm, 0.5 ps Laser Pulses

sample	α_0 (cm^{-1}) at 497 nm	β 10^{-10} (cm/W)
Ru 1	19.62	−3.48
Ru 2	26.68	−5.18
Ru 3	32.71	−6.35
Ru 4	35.88	−7.04
Os 1	21.60	−3.53
Os 2	22.54	−3.89
Os 3	27.37	−5.23
Os 4	26.45	−4.57

Figure 7a) that the resulting curve cannot be used for the determination of γ'.[26] In contrast, as seen in Figure 7b, for pure solvent (acetonitrile), the open aperture *z*-scan signal is relatively small, allowing the determination of γ' for the solvent which is found equal to 8×10^{-16} cm^2/W.

Discussion

As mentioned earlier, the spectroscopic properties of the four Os compounds studied (Table 1) exhibit only small differences and the same applies to the Ru samples. In Figure 1 the absorption spectrum of samples Os 4 and Ru 4 are presented. As shown, the Os 4 absorption spectrum exhibits three main features: (a) a twin-peaked broad band whose two maxima are at 644 and 674 nm, respectively, and which corresponds to a transition between the ground state of the photosensitizer and a

triplet Metal-to-Ligand Charge Transfer state (^{3}MLCT ← S$_0$); (b) a band whose peak at 503 nm corresponds to the singlet−singlet transition (^{1}MLCT ← S$_0$); (c) a Ligand-Centered (LC) band at 313 nm resulting from a π^* ← π transition. The absorption spectrum of Ru 4 (Figure 1) has very similar ^{1}MLCT ← S$_0$ and LC bands but has no absorption in the ^{3}MLCT ← S$_0$ region. We note that in the MLCT bands an electron originally in a metal-based d-orbital is transferred to a π^* orbital of one of the two tpy ligands:[27]

$$[M^{II}(tpy)_2]^{2+} + h\nu \rightarrow [M^{III}(tpy^-)(tpy)]^{2+} \qquad (7)$$

Thus the acceptor in the primary step within the chromophore P is one of the terpyridine ligands. The absence of the ^{3}MLCT band in the Ru complexes is due to a much reduced spin−orbit coupling parameter in the Ru 4 species as compared with the Os 4 case. This is also reflected in the 1000-fold increase in the ^{3}MLCT → S$_0$ emission yield, in room-temperature ethanol solutions of the Os−tpy complex as compared with the analogous Ru complex.[28]

According to the absorption spectra shown in Figure 1, the excitation at 532 nm, with 10 ns pulses, corresponds to absorption at the red end of the ^{1}MLCT band and probably involves a relatively greater component of vibronic transitions from vibrationally excited states than does excitation with 497 nm, 500 ps, pulses which occurs at the maximum intensity region of the ^{1}MLCT band. At 532 nm, there could be partial direct excitation to the ^{3}MLCT state in the case of the Os complexes but not in the case of the Ru complexes.

Our results show that with the 500 fs laser pulse at 497 nm the Ru compounds, as well as the Os complexes, exhibit saturable absorption. This indicates that the ground state of the complex is replenished at a faster rate than concentration build-up of an excited state from which eventually intense absorption can occur (and which thus could give rise to RSA), or that the excited-state absorption cross-section is low relative to that of the ground state at that wavelength. It is noteworthy that while the rise time of the ^{3}MLCT state is probably of the order of 300 fs, as found in tris-(2,2′-bipyridine) ruthenium(II) complexes,[29] the 500 fs laser pulse is shorter than the lifetime of the ^{3}MLCT state for both Os and Ru complexes.[20] Thus, after absorption of an initial 497 nm photon, one can expect sequential excitation from the ^{1}MLCT state to reach a state at about 5 eV, (equivalent to around 250 nm in a direct absorption process; there are features in the absorption spectrum in this spectral region, Figure 1), while the ^{3}MLCT state is relatively little populated, so that absorption from this state should be not extensive.

The results with the 532 nm, 10 ns, pulses show that the Ru complexes exhibit RSA at both low and high intensities, whereas the Os complexes give rise to SA at low intensities, turning to RSA at high intensities. The 10 ns pulse is shorter than the lifetime of the ^{3}MLCT state in the case of the Os complexes (see below) but longer than the lifetime of this triplet state in the Ru complexes, which is of the order of 500−800 ps.[30] The excited-state absorption spectrum has been recently measured for the Ru complexes,[30] which has allowed us to estimate the absorption coefficient at 532 nm to be $\epsilon_{T-T} \leq 5000$ M^{-1} cm^{-1}. This is smaller than the ground-state absorption coefficient, $\epsilon_G = 7700-13360$ M^{-1} cm^{-1} at this wavelength.[20] However, to give rise to RSA behavior, the absorption cross-section from this excited state by 532 nm radiation should be greater than the ground-state absorption cross-section at this wavelength. The excited-state absorption coefficient of the Ru complexes is therefore not consistent with the conventional RSA model

NLO Response of Ru and Os Complexes of Terpyridines

J. Phys. Chem. B, Vol. 105, No. 44, 2001 **10803**

involving triplet excitation. We note that further investigation is therefore required as to the origin of the observed RSA in the Ru complexes in the nanosecond pulse regime. Since the [3]MLCT state population is undoubtedly relatively small for the Ru complexes in the nanosecond regime, the second photon absorption probably occurs from the [1]MLCT state to a state at about 4.66 eV. There is a marked shoulder at 240 nm (=4.66 eV) in the absorption spectrum (Figure 1).

The excited triplet state absorption spectrum of the Os 1 complex has been measured.[20,28] Its corresponding absorption coefficient at 532 nm has been estimated[20] to be of the order of or less than 5000 M^{-1} cm^{-1}. In this case, where the excited-state triplet rise time (probably about 300 fs)[29] is much shorter than the laser pulse duration, it follows that in order to give rise to RSA behavior, the absorption cross-section from this excited state by 532 nm radiation should be greater than the ground-state absorption cross-section at this wavelength. The excited-state absorption coefficient is therefore consistent with the absence of RSA for the Os complexes, at least at low laser intensities.

The RSA behavior of the Os complexes at high laser intensities is intriguing. It is interesting to contrast this behavior with that of metallo-porphyrin-like compounds studied by Si et al.[31] using 8 ns and 23 ps pulses. They observed RSA for nanosecond pulses but for picosecond pulses RSA occurred only at low fluences, and SA at high fluences, (i.e., the opposite behavior as compared with our Os complex nanosecond pulse results), indicating that absorption from the singlet excited state dominates at high fluences in their case.

A possible interpretation of our Os complex ns pulse results is as follows. The [3]MLCT state lifetimes are 247, 168, 222, and 57 ns for Os 1, 2, 3, and 4, respectively, and the corresponding luminescence quantum yields are of the order of 10^{-2}.[17] At low intensities the [1]MLCT excited state therefore undergoes intersystem crossing to the [3]MLCT state with a yield of the order of unity, by analogy with the behavior of [Ru(bpy)$_3$]$^{2+}$.[32] From this triplet state the principal decay mechanism is intersystem crossing to replenish the population of the S_0 state. There should be little absorption from the excited [1]MLCT state. At high intensities, two-photon absorption from S_0 also occurs, where the second photon is absorbed by the [1]MLCT and/or the [3]MLCT state, bringing the molecule to an electronic state whose energy could be as much as 4.66 eV. We propose that the complex in this D−P*−A (to take the example of Os 4) excited-state undergoes electron transfer from P* to the acceptor A resulting in the formation of the initial charge separated state (D−P$^+$−A$^-$)*. Photophysical results and thermodynamic considerations[20] indicate that this latter state does not undergo further complete electron transfer from D, but gives rise to a strongly polarized structure (inductive effect) of the following type: (D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$)*. In the case of the Os 1 complex, which has no formal acceptor (Table 1), it is important to note that, as for the other complexes, on excitation to the singlet and triplet P states, the excited electron is completely localized on one of the tpy ligands (eq 7), so that the Os 1 complex acquires some charge transfer character. We recall that the lifetime of this Os 1 complex triplet state, 247 ns, is considerably longer than the 10 ns pulse. The RSA inducing strong photon absorption is then considered to occur from the (D−P$^+$−A$^-$)* and/or (D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$)* structures. The dynamics leading to electron transfer must occur on a time scale faster than that of key intermolecular or intramolecular relaxation processes. Since we are in a nanosecond pulse regime, this suggests that it is solvent relaxation that is the key relaxation process in
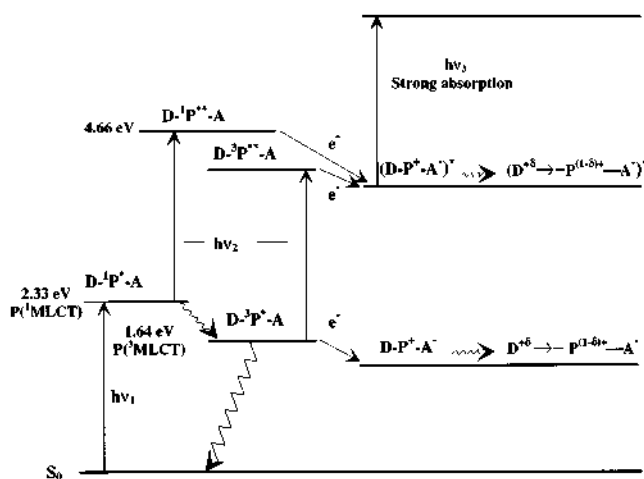

Figure 8. Energy level diagram showing optical excitation and relaxation in the model used for the theoretical analysis of reverse saturable absorption of high laser intensities in the case of D−P−A polyads where P is an Os complex. State energies are from data in ref 20.

competition with electron transfer. The evolution of the newly formed (D−P$^+$−A$^-$) and (D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$)* structures does not lead to replenishing the original complex ground state, at least at a rate faster than that of absorption of a 532 nm photon by the new structure, thus fulfilling the RSA conditions. Figure 8 illustrates this model which therefore involves absorption of three photons. This figure includes D−P$^+$−A$^-$ and D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$ levels that can occur by electron transfer from the P singlet and triplet states. Since only SA, and not RSA, is observed at low laser intensities in the ns case of the Os complexes, absorption from the D−P$^+$−A$^-$ and D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$ states at 532 nm must be negligible. In the case of the other polyads Os1, Os2, Os3, it is possible to construct similar diagrams, taking into account the degree of interaction between the components. For example, for Os2, there would be little or no electron redistribution in the stage analogous to D$^{+\delta}$→P$^{(1-\delta)+}$−A$^-$ in Os 4.

This model involving formation of charge transfer and electron redistribution stages in the case of the Os complexes, but not in the case of the Ru complexes, is supported by thermodynamic considerations. The relevant redox potentials obtained from differential pulse voltammetry[20] show that electron transfer is energetically more favorable for Os complexes as compared with the Ru complexes. This was confirmed by recent nanosecond and picosecond laser flash photolysis studies[20,30] which indicate that A$^-$ species are formed in Os complexes but not in Ru complexes.

Conclusion

The results of this study on D−P−A polyads indicate substantial NLO response (SA and/or RSA) of the Ru and Os complexes excited in the [1]MLCT band region. The optical nonlinear parameter values, measured by the *z*-scan technique, are quite high, reflecting resonance contributions. We find that in addition to resonance contributions, which correlate quite well with the linear absorption coefficient, there are structural effects, which determine electronic polarization properties, and which modulate the NLO properties of the complexes.

It was found that the occurrence of RSA or SA depends strongly on the duration of the excitation pulse as compared with the lifetime of the [3]MLCT state. The 500 fs pulse is shorter than the lifetime of the triplet in both Os and Ru complexes,

and the non-linearity exhibited corresponds to SA. On the other hand, the duration of the 10 ns pulse is greater than the triplet lifetime of the Ru complexes, which exhibit RSA, but shorter than the triplet lifetime of the Os complexes, which exhibits SA at low fluences and RSA at high fluences. Photophysical models involving conventional multilevel systems fail so far to provide an explanation for the RSA behavior of the Ru complexes. A new factor is introduced in the case of high fluence excitation of Os complexes with 10 ns pulses. This factor involves a non-linear process in which electron transfer processes occur in a highly excited state, leading to a photophysical scheme for RSA in which the initial photon absorption and the subsequent RSA inducing absorption occur in what amounts to different species.

A model of this type can be considered to correspond to the concept of supramolecular reverse saturable absorbers (SupraR-SAs) outlined by Sun and Riggs[33] as a new molecular engineering strategy for developing reverse saturable absorbers of much better optical limiting performance than have existing molecular species. In SupraRSA materials there are two sub-structures of the supermolecule which are respectively responsible for the weak ground-state absorption and the extremely strong excited-state absorption at the laser wavelength. Examples proposed by Sun and Riggs are donor−acceptor dyads. The donor−acceptor pairs can be either intramolecular or intermolecular. Our case is that of intramolecular donor−acceptor polyad complexes.

This possibility of placing the sequential absorption steps in separate molecular sub-structures leads us to envisage the development of other polyad complexes suitable for RSA. These could be based on other metals, having different oxidation states, and on other ligands, thus enabling the fine-tuning of electronic properties and the modulation of molecular NLO responses. Although the more novel part of our results concerns ns pulse excitation, fs excitation should be further explored, since intramolecular dynamic processes involving the formation of new substructures could then be fast with respect to the usual intramolecular radiationless relaxation processes.[29]

Work is in progress on refining the models discussed by carrying out further studies on the intermediate photophysical stages in the time-dependent evolution of the excited Os and Ru complexes and on the NLO properties of these complexes. Studies will also be carried out at other wavelengths, in particular by direct excitation in the ^{3}MLCT and in the LC bands. An alternative three-photon mechanism has been suggested[34] to explain the change of behavior from SA at low intensities to RSA at high intensities in the Os compounds. This mechanism involves a breakdown in the weak saturation limit. Detailed intensity-dependent studies will be carried out to help in determining the validity of applicable models.

References and Notes

(1) Zyss, J. *Molecular non linear optics*; Academic Press: New York, 1994.

(2) Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225.

(3) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097.

(4) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; Wiley: New York, 1991.

(5) Huggard, P. C.; Blau, W.; Schweitzer, D. *Appl. Phys. Lett.* **1987**, *51*, 2183.

(6) Long, N. J. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 21.

(7) Nalwa, H. S. *Appl. Organomet. Chem.* **1991**, *5*, 349.

(8) Whittal. I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.

(9) Whittal, I. R.; McDonagh, A. M.; Humphrey, M. G. *Adv. Organomet. Chem.* **1998**, *42*, 349.

(10) Coe, B. J. *Chem. Eur. J.* **1999**, *5*, 2464 and references therein.

(11) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.

(12) Le Bozec, H.; Renouard, T. *Eur. J. Inorg. Chem.* **2000**, 229.

(13) Dupuis, B.; Michaut, C.; Jouanin, I.; Delaire, J.; Robin, P.; Feneyrou, P.; Dentan, V. *Chem. Phys. Lett.* **1999**, *300*, 169.

(14) Si, J.; Wang, Y.; Yang, Q.; Ye, P.; Tian, H.; Zhou, Q.; Xu, H. *Appl. Phys. B* **1997**, *64*, 663.

(15) Bredas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243.

(16) Letard, J. F.; Montant, S.; Guionneau, P.; Martin, P.; Le Calvez, A.; Freysz, E.; Chasseau, D.; Lapouyade, A.; Kahn, O. *Chem. Commun.* **1997**, 745.

(17) Lainé, P.; Amouyal, E. *Chem. Commun.* **1999**, 935.

(18) Amouyal, E. *Homogeneous Photocatalysis*; Chanon, M., Ed.; John Wiley: Chichester, 1997; Chapter 8, p 263.

(19) Amouyal, E. *Sol. Energy Mater. Sol. Cells* **1995**, *38*, 249.

(20) Lainé, P.; Bedioui, F.; Albin, V.; Ochsenbein, P.; Marvaud, V.; Bonin, M.; Amouyal, E.; Berruyer-Penaud, F. To be published.

(21) Sheik-Bahae, M.; Said, A. A.; Wei, T. H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

(22) Shen, Y. R. *The principles of nonlinear optics*; Wiley: New York, 1984.

(23) Allan, G. R.; Labergerie, D. R.; Rychnovsky, S. J.; Bogess, T. F.; Smirl, A. L.; Tutt, L. *J. Phys. Chem.* **1992**, *96*, 6313.

(24) Couris, S.; Koudoumas, E.; Ruth, A.; Leach, S. *J. Phys. B: At. Mol. Opt. Phys.* **1995**, *28*, 4537.

(25) Hutchings, D. C.; Sheik-Bahae, M.; Hagan, D. J.; Van Stryland, E. W. *Opt. Quantum. Electron.* **1992**, *24*, 1.

(26) Debrus, S.; Lafait, J.; May, M.; Pincon, N.; Prot, D.; Sella, C.; Venturini, J. *J. Appl. Phys.* **2000**, *88*, 4469.

(27) Amouyal, E.; Mouallem-Bahout, M.; Calzaferri, G. *J. Phys. Chem.* **1991**, *95*, 7641.

(28) Amouyal, E.; Mouallem-Bahout, M. *J. Chem. Soc. Dalton Trans.* **1992**, 509.

(29) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. K. *Science* **1997**, *275*, 54.

(30) Harriman, A. Private communication.

(31) Si, J.; Yang, M.; Wang, Y.; Zhang, L.; Li, C.; Wang, D.; Dong, S.; Sun, W. *Opt. Commun.* **1994**, *109*, 487.

(32) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

(33) Sun, Y.-P.; Riggs, J. E. *Int. Rev. Phys. Chem.* **1999**, *18*, 43.

(34) We thank an anonymous referee for this suggestion.