carbon. The H atoms would then have to be eliminated as H_2 by reductive elimination.

This mechanism is consistent with the observed reduction in reactivity with increasing coordinative saturation. It requires that one metal atom have a four-electron deficiency or that neighboring metal atoms have a four-electron deficiency together. If the carbonyl ligands were very mobile, they would be able to move to provide whatever kind of site might be required for this process. The fact that CO yield increases relative to H_2 yield as coordinative saturation increases in the Re_4 clusters suggests, however, that the requirements for the active site are met by CO elimination rather than by CO migration. The fact that CO loss always accompanies H_2 loss suggests that the metal to CO bonds of metals involved in the dehydrogenation are weakened during the reaction. This is consistent with an oxidative addition.

The difference between the Re_3 and Re_4 clusters is more difficult to explain. The oxidizing power of the Re_4 clusters drops step by step until reactivity disappears. The reactivity of the Re_3 clusters, on the other hand, disappears with $Re_3(CO)_{10}^+$ even though $Re_3(CO)_9^+$ is a powerful oxidant (i.e., gives a high H_2 yield). It is interesting to note that the $M_3(CO)_{10}^+$ (M = Re or Mn) species are anomalously unreactive with $M_2(CO)_{10}$.[5b] It is also the case that on collision-induced decomposition (CID) $Mn_3(CO)_{10}^+$ loses $Mn(CO)_5$ in contrast to most $Mn_n(CO)_m^+$ ions

which lose predominantly CO on CID.[12] That suggests that the $M_3(CO)_{10}^+$ species consists of an $M(CO)_5$ moiety bound to $M_2(CO)_5^+$. One metal atom, then, would be completely saturated and unable to participate in the dehydrogenation. The other two metal atoms would be highly unsaturated, of course, but the $M(CO)_5$ may pose a steric problem for their reaction.

Internal energy could effect the relative reactivity of the metal clusters. The clusters probably have a distribution of internal energies limited by the lowest M–CO bond dissociation energy. The internal energy is distributed among a large number of internal modes. Highly excited species might be expected to react by nondissociative displacement of CO by cyclohexane. That process is not observed. All the observed reactions are at least 10% efficient. Taken together these factors suggest that the observed chemistry is characteristic of near-thermal reactant ions.

Finally we note that, consonant with notions about surface and cluster reactivity that drive research on metal clusters, the results show that reaction specificity can be obtained by controlling extent of aggregation and of ligation. $Re_3(CO)_{8,9}^+$, for example, convert cyclohexane exclusively to C_6H_8 while $Re_4(CO)_{10,11}^+$ convert cyclohexane almost exclusively to C_6H_{10}.

(12) Freas, R. B., III; Campana, J. E.; Ridge, D. P., unpublished results.

Electron-Transfer Times Are Not Equal to Longitudinal Relaxation Times in Polar Aprotic Solvents

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It has been found that the electron-transfer time τ_{et} of the intramolecular electron-transfer reaction of electronically excited bianthryl is not equal to the longitudinal relaxation time τ_l of the solvent in various polar aprotic solvents. This demonstrates that the recently observed agreement of τ_{et} and τ_l, in specific cases, is not general. In addition, microscopic solvation times τ_s have been measured for the solvents, and it has been observed that τ_s is very similar to τ_{et} for a broad range of polar aprotics.

Introduction

Dynamic solvent effects on the rates of electron transfer (et) and other charge-transfer reactions have recently been the subject of intense theoretical[1,2] and experimental[3-9] research activity. Dynamic solvent effects are particularly dramatic for small activation barrier (et) reactions ($\Delta G \ll k_bT$), in which case theory[1] shows that the et time τ_{et} (inverse et rate constant) should be equal to the solvation time τ_s of the medium in certain cases. Furthermore, simple theories predict that τ_{et} should be equal to the longitudinal relaxation time τ_l of the solvent.[1] This parameter is the solvation time for a specific solvent according to the dielectric continuum model for solvation.[1,10] The usual expression for τ_l is as follows

$$\tau_l = \frac{\epsilon_\infty}{\epsilon_s}\tau_D \qquad (1)$$

where ϵ_s and ϵ_∞ are the static and infinite frequency dielectric constants, respectively, and τ_D is the bulk dielectric relaxation time. Hence, (1) gives a prediction for τ_s (and τ_{et}) employing bulk properties of the solvent alone.

This amazingly simple relationship is not only predicted to be important for small barrier reactions, but theory suggests[2] that the preexponential factor of thermal ($\Delta G \gg k_bT$) et rate expressions should be a function of τ_l. Interestingly, experimental evidence supporting the validity of (1) has been published in the past few years,[3] but these papers have almost dealt exclusively with alcohol solvents. We became interested in testing the limitation of (1) in a broad range of solvents and, in particular, in the case of polar aprotic solvents, for which the solvent interaction should more closely parallel the assumed dipolar interactions of the dielectric continuum model for solvation. Specific hydrogen-bonding interactions between the solute and solvent can play an important role in electron transfer in alcohol solvents.[6]

(1) Warshel, A.; Hwang, J.-K. *J. Chem. Phys.* **1986**, *84*, 4938. Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894. Calef, D. F.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 470; *J. Phys. Chem.* **1983**, *87*, 3387. Friedman, H. L. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1465. Mozumder, A. *J. Chem. Phys.* **1969**, *50*, 3153.
(2) McManis, G. E.; Mishra, A. K.; Weaver, M. J. *J. Chem. Phys.* **1987**, *86*, 5550. Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3701.
(3) Kosower, E. M.; Huppert, D. *Annu. Rev. Phys. Chem.* **1986**, *37*, 127 and numerous references therein.
(4) Su, S.-D.; Simon, J. D. *J. Chem. Phys.*, in press.
(5) Nagarajan, V.; Brearley, A. M.; Kang, T.-J.; Barbara, P. F. *J. Chem. Phys.* **1987**, *86*, 3183.
(6) Anthon, D. W.; Clark, J. H. *J. Phys. Chem.* **1987**, *91*, 3530.
(7) Hicks, J. M.; Vandersall, M. T.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1987**, *135*, 413.
(8) Wang, Y.; McAuliffe, M.; Novak, F.; Eisenthal, K. B. *J. Phys. Chem.* **1981**, *85*, 3736.
(9) Wang, Y.; Eisenthal, K. B. *J. Chem. Phys.* **1982**, *77*, 6076.
(10) Hubbard, J.; Onsager, L. *J. Chem. Phys.* **1977**, *67*, 4850.

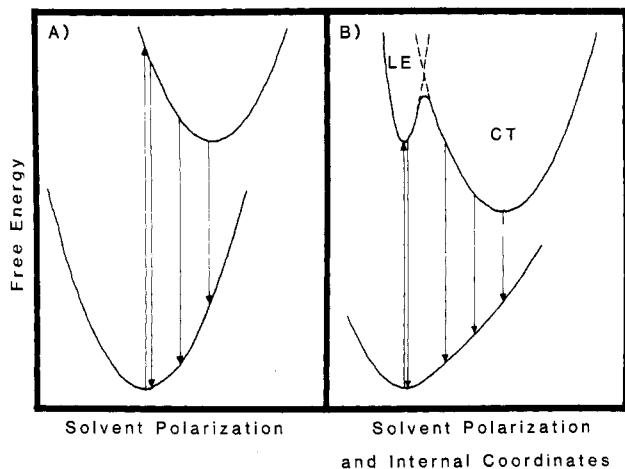† Alfred P. Sloan Fellow and Presidential Young Investigator.

Figure 1. (A) Nonequilibrium free energy as a function of instantaneous solvent polarization for the ground electronic state S_0 and the excited state S_1 of an ideal probe. In this example the equilibrium solvent polarization in S_1 (X_e^{eq}) is larger than that in S_0 (X_g^{eq}) because the dipole moment is larger in S_1 than S_0. (B) A schematic representation of the nonequilibrium free energy dependence on the reaction coordinate for bianthryl.

This paper describes ultrafast fluorescence measurements on the excited-state intramolecular et (charge separation) times τ_{et} of the molecule bianthryl. We also describe closely related experiments on the transient solvent τ_s of the polar dye molecules coumarin 311 and coumarin 102 in polar aprotics. The primary
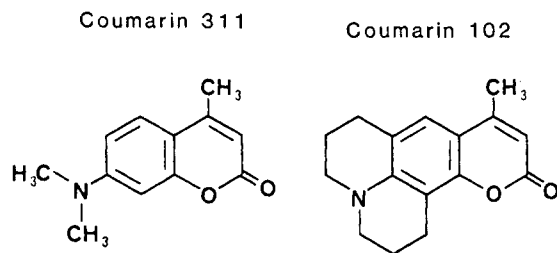
purpose of this research is to test the validity of (1) for et rates in polar solvents. But the related question of the validity of (1) for simple solvation processes[11-13] will also be discussed. Several papers on this latter question have recently been published.[5,14-16]

Experimental Section

The emission dynamics reported herein were recorded by a recently constructed ultraviolet, subpicosecond fluorescence apparatus that uses the upconversion technique[17] for time resolution.

(11) Bagchi, B.; Oxtoby, D. W.; Fleming, G. R. *Chem. Phys.* **1984**, *86*, 257. van der Zwan, G.; Hynes, J. T. *J. Phys. Chem.* **1985**, *89*, 4181. Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4272. Loring, R. F.; Yan, Y. J.; Mukamel, S. *J. Phys. Chem.* **1987**, *91*, 1302. Wolynes, P. G. *Annu. Rev. Phys. Chem.* **1980**, *31*, 345.

(12) Wolynes, P. G. *J. Phys. Chem.*, preprint. Calef, D. F.; Wolynes, P. G. *J. Chem. Phys.* **1983**, *78*, 4145.

(13) Rao, M.; Berne, B. J. *J. Phys. Chem.* **1981**, *85*, 1498. Karim, O. A.; Haymet, A. D. J.; Bonet, M. J.; Simon, J. D., in preparation.

(14) (a) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221. (b) Castner, Jr., E. W.; Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 1090. (c) Su, S.-G.; Simon, J. D. *J. Phys. Chem.* **1986**, *90*, 6475.

(15) Bakhshiev, N. G. *Opt. Spectrosc.* (*Engl. Transl.*) **1965**, *19*, 196 and earlier papers in this series. Mazurenko, Y. T.; Bakkhshiev, N. G. *Opt. Spectrosc.* (*Engl. Transl.*) **1970**, *28*, 490. Ware, W. R.; Lee, S. K.; Brant, G. J.; Chow, P. P. *J. Chem. Phys.* **1971**, *54*, 4729. Mazurenko, Y. T.; Udaltsov, V. S. *Opt. Spectrosc.* (*Engl. Transl.*) **1978**, *44*, 417; **1978**, *45*, 765. Hallidy, L. A.; Topp, M. R. *Chem. Phys. Lett.* **1977**, *48*, 40. Shapiro, S. L.; Winn, K. R. *Chem. Phys. Lett.* **1980**, *71*, 440. Okamura, T.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1983**, *94*, 339.

(16) Kahlow, M. A.; Kang, T.-J.; Barbara, P. F. *J. Chem. Phys.*, submitted for publication.

(17) Brearley, A. M.; Strandjord, A. J. G.; Flom, S. R.; Barbara, P. F. *Chem. Phys. Lett.* **1985**, *113*, 43 and references therein. Rudolph, W.; Diels, J. C. In *Ultrafast Phenomena V*; Fleming, G. R., Siegman, A. E., Eds.; Springer-Verlag: West Berlin, 1986; p 71.
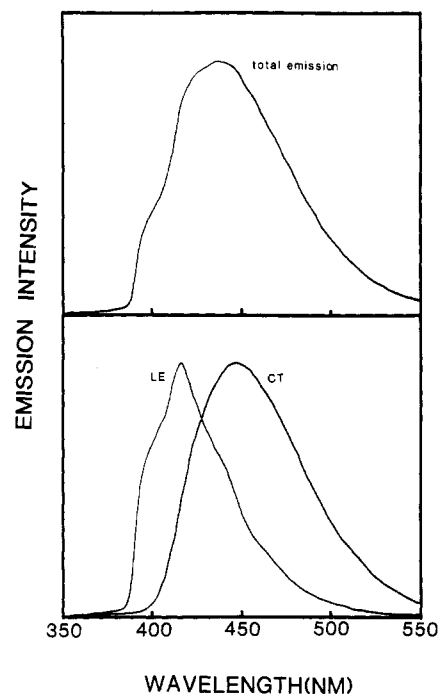

Figure 2. Top panel: Static emission spectrum of bianthryl in glycerol triacetate, containing contributions from both the LE and CT states. Bottom panel: Static emission spectrum of bianthryl in *n*-butyl ether, assumed to be pure LE emission. Static emission spectrum of pure CT, obtained by subtracting the LE emission from the total emission spectrum.
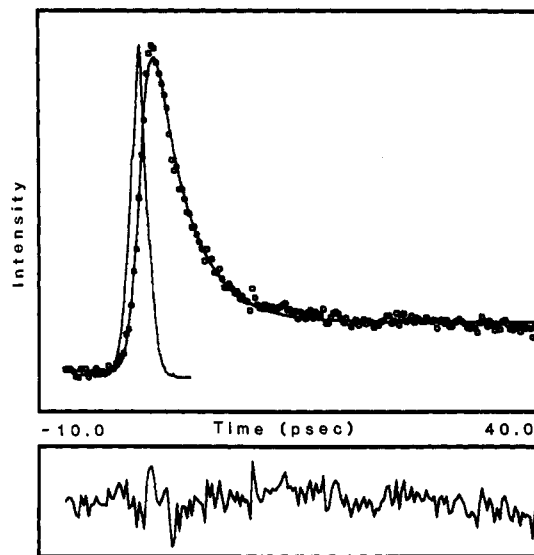

Figure 3. Fluorescence transient for BA in propylene carbonate, monitored at 420 nm. The points in the figure are experimental data, and the curve drawn through the points is a convolution fit of the data, (see Experimental Section for details). The other curve is the experimental instrument response function.

The apparatus will be described in detail elsewhere.[18] Briefly, the laser source is a Coherent Model 702 dye laser (pyridine 2 dye HITCI saturable absorber) that is synchronously pumped by the second harmonic of an actively mode-locked Nd:YAG laser (Quantronix Model 416). The laser wavelength is centered at 725 nm, and the pulse duration is 0.75–1.2-ps fwhm as measured by autocorrelation. The dye laser is amplified, at a 8.2-kHz repetition rate, by six passes through a thick dye jet that is optically pumped by a copper vapor laser (Plasma Kinetics Model 251). The doubled output of the amplified dye laser (362.5 nm, ~1-mW

(18) Kahlow, M. A.; Jarzeba, W.; Barbara, P. F. *Rev. Sci. Instrum.*, submitted for publication.
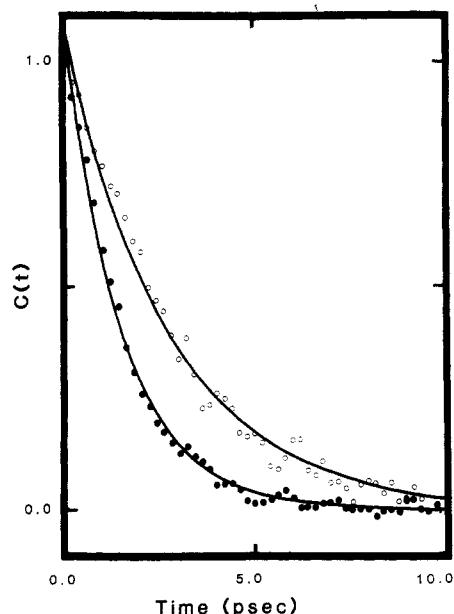
Figure 4. Experimentally determined $C(t)$ function for the polar probe molecule coumarin 102 in butyronitrile (solid circles) and ethyl acetate (open circles).

average power) is focused in the sample which is flowed to avoid sample degradation. Time resolution is achieved by mixing the fluorescence with the 725-nm light in a KDP type I nonlinear optical crystal to generate light at the sum frequency (upconversion). The apparatus is capable of resolving emission transients as short as 0.4 ps when the data are analyzed by convolution methods.[18]

Sample preparation and solvent purification methods used in this research are similar to those described previously.[5]

Results and Discussion

Optical excitation of bianthryl (BA) in the ultraviolet produces the nonpolar locally excited (LE) isomer of the lowest excited singlet state S_1 of this molecule, as portrayed in Figure 1. In polar solvents, LE is converted by intramolecular et to the highly polar charge-transfer (CT) isomer of S_1. In fact, the fluorescence

Intramolecular Charge Separation
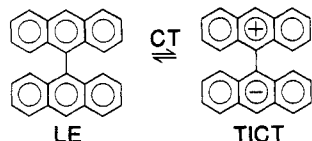
spectrum of BA (Figure 2) can be decomposed into two components.[5,6,19] The spectrum is the sum of an essentially solvent independent anthracene-like spectrum from LE and a strongly solvent dependent component due to CT. Depending on the chosen emission observation wavelength, transient fluorescence experiments on BA can measure the et kinetics of LE ($\lambda_f \simeq$ 400 nm) or a more complex kinetic behavior ($\lambda_f >$ 420 nm) that is a combination of the et process and solvation of the CT. The relaxation time of the ca. 400-nm emission dynamics (Figure 3) of BA should be identified[5,6,19] with τ_{et}. The long time scale tail in the emission intensity is due to the equilibrium concentration of LE in S_1.

The transient solvation dynamics of CT is similar to spectroscopic manifestations of solvation that have been observed for polar dye molecules that are not capable of excited-state et. The photodynamics[11–13] of the latter type of molecule are represented in Figure 1b. Optical excitation of a probe molecule of this type

(19) Kosower, E. M.; Tanizawa, K. *Chem. Phys. Lett.* **1972**, *16*, 419. Nakashima, N.; Murakawa, M.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 854. Retting, W.; Zander, M. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1143. Schneider, F.; Lippert, E. *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 1155; **1970**, *74*, 624.

TABLE I: A Comparison of τ_{et}, τ_s, and τ_l in Various Solvents

solvent	τ_{et}, ps	τ_l, ps	τ_s, ps	$E_T(30)$
acetonitrile	0.7	0.2	0.4–0.9[d]	46.0
propionitrile	1.2	0.3	1.1–1.5	43.7
butyronitrile	2.0	0.5	1.5–2.1	
pentanitrile	4.4	0.7	3.6	
PC[a]	3.4	1.7	4.9	
triglyme	11.7		25	38.9
GTA[b]	750		820	40.8

[a] Propylene carbonate. [b] Glycerol triacetate. [c] The GTA numbers are from Nagarajan et al.[5] T = 11.5 °C. The rest of the values in the table were recorded at ambient temperature. [d] These values represent the range of observed τ_s values with different probes; see Table II.

TABLE II: A Comparison of τ_s and τ_l for Various Solvents

solvent	τ_s, ps	τ_l, ps	probe[b]
acetonitrile	$\simeq$0.4[c]	$\simeq$0.2[a]	LDS-750
	$\simeq$0.7		C311
	$\simeq$0.9		C102
propionitrile	1.1	0.3	C311
	1.5		C102
butyronitrile	1.6	0.5	C311
	2.1		C102
	1.5[c]		C102
ethyl acetate	2.3	1.7	C311
	2.6		C102
	2.7[c]		C102
DMSO	3.1	2.1	LDS-750[b]
pentanitrile	3.6	0.7	C102
propylene carbonate	4.9	1.7	C102

[a] References for the dielectric relaxation data are given in Kahlow et al.[16] [b] The LDS-750 data are from Castner et al.[14] The rest of the measurements are described in detail in Kahlow et al.[16] C311 and C102 denote coumarin 311 and coumarin 102. [c] The τ_s values with the "c" superscript were determined by single-exponential fits to $C(t)$ functions that were determined by the traditional method. The remaining τ_s values were determined by single-exponential fits to $C(t)$ functions that were measured by the new alternative time-saving procedure.[16]

prepares the solute/solvent system in a nonequilibrium configuration which subsequently relaxes with a time constant τ_s (if the relaxation function is a single exponential). As the solvent relaxes from the initial configuration, the microscopic solvent relaxation is reflected in a time-dependent shift of the fluorescence spectrum.[11–13] The relaxation time of the empirical function $C(t)$ (2)

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \qquad (2)$$

should be identified with τ_s. Here $\nu(0)$, $\nu(\infty)$, and $\nu(t)$ are the optical frequencies that correspond to the wavelength maxima of the emission spectrum of the polar dye molecule at zero time (immediately after optical excitation), at infinite time (when the solvent system has reached equilibrium), and at intermediate time t (during the relaxation). Figure 4 shows an example of experimentally obtained $C(t)$ curves for coumarin 102 in the solvents butyronitrile and ethyl acetate.

Unfortunatley, the determination of a single $C(t)$ function can consume many hours of spectrometer time, since the required time-dependent spectra are usually determined by combining several intensity vs time transients for a large number of emission wavelength regions. In this paper we determine $C(t)$ primarily with a recently developed alternative time-saving procedure[5,16] for measuring $C(t)$ that requires a single emission transient and certain photophysical data on the probe. Once the probe is calibrated, it can be used in a broad range of solvents without further recalibration.

The electron-transfer times of BA in various polar aprotic solvents are compared to the τ_l dielectric relaxations times and the solvation time τ_s in Table I. In general, the agreement between the τ_{et} and τ_l values is poor, casting doubt on the experimental validity of (1) for electron-transfer reaction rates in polar aprotic solvent. Interestingly, the τ_{et} values are in much

better agreement with the empirically determined microscopic solvation times. This latter observation seems to support the notion the et rates of small barrier reactions are controlled by solvent relaxation. Apparently, the failure of (1) is a consequence of the failure of the dielectric continuum model for solvent dynamics of any type, including et and simple solvation, in these solvents. The validity of (1) has already been questioned for a limited number of polar aprotics by Maroncelli and Fleming[14a] and Castner et al.[14b]

Perhaps continuum models fail to correctly predict solvation and electron-transfer times because, while they include long-range correlations of the solvent motion, they ignore the molecular interactions and structure in the inner solvation shells. In fact, theoretical treatments[12,13] that go beyond the continuum approximation and actually consider molecular interactions correctly predict relaxation components that are considerably longer than τ_1. Indeed, two other predictions of contemporary theories for transient solvation are experimentally observed in our measurements and other data, namely nonexponential solvation functions[14,16] and a measurable probe dependence of the τ_s values;[20] see Table II.

One potential problem in interpreting the et times of BA is that torsional motion about the bond that connects the two aromatic

(20) Kang, T.-J.; Kahlow, M. A.; Gisser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.*, submitted for publication.

rings might play a role in the et mechanism.[19] This seems unlikely, however, since we have observed that a highly sterically hindered derivative of BA that has restricted torsional motion exhibits similar et times to unsubstituted BA.[20]

It is also interesting to note that the solvent dependence of et for BA is qualitatively different to that for the excited-state et process of the molecule (dimethylamino)benzonitrile (DMABN)[7] in polar aprotics. For this molecule τ_{et} is a function of the solvent polarity rather than the solvent dynamics. Perhaps the molecules differ simply because DMABN has a larger activation barrier as a result of vibrational reorganization energy associated with the reaction. Nevertheless, the striking difference between these molecules is worthy of further investigation.

Future work from our group on et reactions and solvation will deal with the extremely early time (less than 300 fs) behavior of the various molecules mentioned in this paper. This is a critical time scale for solvent motion effects on reactions in solution because the actual barrier-crossing process of thermal reactions occurs on this time scale.

Quantum Effects in Anisotropic Semiconductor Clusters: Colloidal Suspensions of Bi₂S₃ and Sb₂S₃

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Transmission electron microscopy (TEM), optical absorption, dynamic light scattering, and scanning tunneling microscopy (STM) have been used to characterize colloidal clusters of Bi₂S₃ and Sb₂S₃. These layered semiconductor clusters were found by TEM to grow to sizes ranging from 16 to 90 Å. Consistent with quantum confinement of charge carriers in small microcrystalline volumes, the optical absorption spectra were blue-shifted ≈0.7 eV from the bulk band gaps of the materials. These small clusters escaped detection by in situ dynamic light scattering, and only particles roughly 5 times larger could be readily detected. Preliminary results with a scanning tunneling microscope seem to support the anisotropic disklike geometry of the clusters, and for Bi₂S₃ we estimate cluster thicknesses of 20–30 Å. With the TEM and STM measurements of the cluster geometry and a simple particle-in-a-box model, we calculate band edge shifts which are in reasonable accord with the optical experiments.

There has been an intense focus on the properties of clusters in recent years. Though the major experimental emphasis has been placed on clusters generated in the gas phase,[1,2] increasing attention has been devoted to the properties of clusters synthesized as colloidal particles in solution.[3–13] While most of the gas-phase

work has concentrated on clusters composed of a single element, the colloidal clusters are generally binary compounds made by

(1) Heath, J. R.; Liu, Y.; O'Brien, S. C.; Zhang, Q.-L.; Curl, R. F.; Tittle, F. K.; Smalley, R. E. *J. Chem. Phys.* **1985**, *83*, 5520.

(2) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *J. Phys. Chem.* **1985**, *89*, 566.

(3) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1985**, *82*, 552.

(4) Brus, L. *IEEE J. Quantum Electron.* **1986**, *QE-22*, 1909.

(5) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555.

(6) Fojtik, A.; Weller, H.; Koch, U.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 969.

(7) Fojtik, A.; Weller, H.; Henglein, A. *Chem. Phys. Lett.* **1985**, *120*, 552.

(8) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. *J. Phys. Chem.* **1985**, *89*, 397.

(9) Nedeljkovic, J. M.; Nenadovic, M. T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1986**, *90*, 12.

(10) Sandroff, C. J.; Hwang, D. M.; Chung, W. M. *Phys. Rev. B: Condens. Matter* **1986**, *33*, 5953.

(11) Sandroff, C. J.; Kelty, S. P.; Hwang, D. M. *J. Chem. Phys.* **1986**, *85*, 5337.

(12) Sarid, D.; Rhee, B. K.; McGinnis, B. P. *Appl. Phys. Lett.* **1986**, *49*, 1196.

(13) Micic, O. J.; Nenadovic, M. T.; Peterson, M. W.; Nozik, A. J. *J. Phys. Chem.* **1987**, *91*, 1295.