Zn^{2+}-rich ZnS colloids show no MV^+ signal. Thus, the CdS colloid MV^+ signal in Figure 3b appears to be entirely due to excitation of CdS crystallites.

A picosecond pump-probe experiment on the S^{2-}-rich CdS colloidal system shows a MV^+ spectrum (Figure 2b), but neither Cd^{2+}-rich nor equimolar CdS colloids show any MV^+ signal, at present detection sensitivity. In the case of the S^{2-}-rich ZnS control colloid, no MV^+ signal is detected. The MV^+ signal in Figure 2b is weak and sits on a large luminescence background. Nevertheless it is broadened and shifted slightly to lower frequencies than the nanosecond spectra.

In the case of the equimolar and Cd^{2+}-rich colloids, the higher (i.e., detectable) yield of MV^+ on the nanosecond time scale suggests a rise time between 5×10^{-9} and 2×10^{-11} s. Such a rise time is consistent with the very recent picosecond transient absorption studies of Serpone et al.[13] on similar colloidal systems. Such a long rise time would imply that e^- transfer occurs not from "hot electrons" or the relaxed exciton state, but from trapped electrons as discussed by Serpone et al.

In the case of the S^{2-}-rich colloid, MV^+ is detected at $\simeq$20 ps with a Raman spectrum that is broadened and shifted slightly to lower frequency (at modest signal-to-noise) with respect to the aqueous reference spectra, and to the nanosecond time-scale colloidal spectra. This signal results from photoexcitation of the CdS crystallite, as no MV^+ is observed following 396-nm excitation of ZnS colloids under identical conditions. The extent of the shift depends upon on the amount of excess S^{2-} as demonstrated in Figure 2c. It may be that we observe a complexed MV^+ (perhaps $MV^+ \cdot S^{2-}$), which subsequently dissociates and resolvates to give aqueous-like spectra.

These experiments demonstrate that picosecond transient Raman scattering is technically feasible in colloidal systems, and that the Raman data provide some discrimination among various local environments at interfaces. These initial data indicate that the chemistry is complex.

Conclusions

This is the first experimental report of picosecond transient Raman experiments applied to interfacial chemical kinetics. We observe that some MV^{2+} reduction on the surface of photoexcited, S^{2-}-rich colloidal CdS crystallites occurs within $\simeq$20 ps. Slight distortions of the observed MV^+ Raman spectrum suggest a presolvated or complexed reduced species, sensitive to surface and/or double layer chemical conditions. In order to better understand the kinetics of these processes, two-pulse time-delayed experiments on the picosecond time scale are required. Such work is presently in progress.

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Studies of Liquid Surfaces by Second Harmonic Generation

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Information on the orientation and relative composition of solute molecules at the surface of a liquid solution has been obtained by the technique of second harmonic generation. In an aqueous phenol solution, the phenol molecules at the vapor/solution interface are found to be oriented with their long axes tilted 50° from the surface normal. The orientation is found to be insensitive to the concentration of the phenol solution. A comparison with surface concentration information obtained from surface tension data is made.

A new application of second harmonic generation techniques, sensitive to the asymmetry of boundaries,[1] allows the direct study of surfaces. The nonlinear optical process of second harmonic generation is electric dipole forbidden within the bulk of centrosymmetric media but is allowed at an interface where the symmetry is broken. This property gives second harmonic generation a high degree of sensitivity to the detailed nature of interfaces.[2] The technique has been used to study molecules adsorbed on surfaces[3-10] and forming insoluble surfactant layers[11] but has not yet been applied to the case of liquid/vapor interfaces for neat liquids and solutions.[12] In this Letter we report on second harmonic measurements which yield quantitative information on the orientation and relative number density of solute molecules at the surfaces of aqueous solutions. The solute molecules were the simple benzene derivatives phenol (C_6H_5OH) and *p*-cresol ($CH_3C_6H_4OH$). The experiment consists of irradiating a liquid sample contained in a temperature-controlled sealed housing with the output of an amplified picosecond dye laser. The pump light was polarized to provide components of the electric field both parallel and perpendicular to the sample surface. The polarization and amplitude of the reflected second harmonic signal was measured with appropriate polarizers, filters, monochromator, and single-photon counting equipment. The sensitivity of the experimental setup allowed us to measure second harmonic signals from

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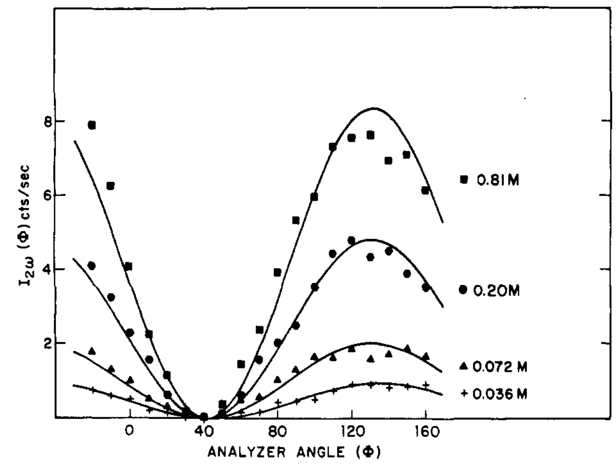

Figure 1. Polarization of the second harmonic signal from phenol/water mixtures with the molarities as indicated. The second harmonic intensity (corrected for the water background) is plotted against the analyzer angle, where $\Phi = 0°$ corresponds to the plane of incidence. The pump radiation at 616 nm is polarized along $\Phi = -45°$ and is incident on the sample at 70° from the surface normal. The solid lines are fits to $\cos^2$ functions.

molecules at surface coverages as small as 5%.

For the case of molecules with a strong nonlinear optical response primarily along one axis, such as the mono- and para-substituted benzene molecules studied here,[13] the polarization of the second harmonic radiation for a given pump excitation is directly related to the orientation of the emitting dipoles in the surface. Measurements of the intensity of the second harmonic signal at different analyzer angles yield a null angle and thus the polarization of the second harmonic light. The contribution of the water molecules to the second harmonic signal is found to be small from measurements of neat water. The results of the signal vs. analyzer angle at various bulk phenol concentrations shown in Figure 1 are not sensitive to subtraction of the water background.

Two interesting results are obtained from the polarization data. One is that the average orientation of phenol, i.e. the direction of its long axis, is 50 ± 5° from the normal to the solution surface.[14] We expect the hydrophilic OH end of the phenol to be pointed in toward the bulk solution. A second conclusion is inferred from the observation that the null angle is the same for all phenol concentrations. This suggests that the orientation of phenol does not change with the surface concentration of phenol. This constancy of orientation extends from low coverages at low bulk concentration up to a phenol monolayer, estimated to develop at 0.2 M bulk concentration,[15] and to even higher concentrations which exceed that required for the buildup of the monolayer. This result of the unchanging surface orientation with concentration is consistent with surface potential measurements on aqueous phenol solutions.[16] In these measurements it was determined that the surface potential is linear in the surface concentration. If the orientation of the phenol molecules at the surface were changing with concentration, then a linear dependence would not be expected.

Now that we have established that the orientation of the solute molecule's main axis does not change with concentration, we attribute the differences in the second harmonic signals obtained from solutions at different concentrations to changes in the surface solute concentration. Figure 2 shows the s-polarized component of the signal, i.e. the one perpendicular to the plane of incidence, for different phenol and cresol bulk activities. In this same figure, we plot (solid lines) the surface excesses Γ_2, which give the increase in the number of solute molecules per unit area in the interfacial region relative to a comparable bulk region. They are calculated from surface tension[15,17] and activity[18] data by using the Gibbs adsorption equation, $\Gamma_2 = -RT\,\partial\gamma/\partial \ln a$, where γ is the surface tension and a is the bulk solute activity.[19] Since phenol and cresol have much lower surface tensions than the water component, they preferentially go to the surface layer. The result of this marked enrichment is that Γ_2 has a value very close to the number of solute molecules per unit area of the surface.

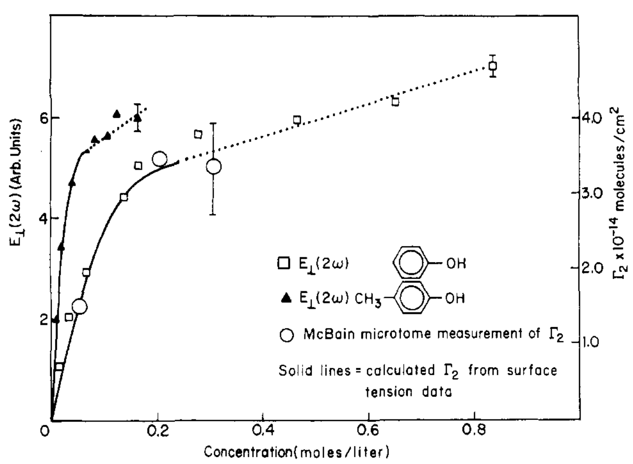

Figure 2. The amplitude of the s component of second harmonic field (corrected for water background) vs. concentrations of phenol and cresol in water. The solid lines are the Gibbs surface excesses, Γ_2, calculated from surface tension data.[15,17] The open circles give the results of a direct determination of the surface excess for the phenol/water system by a microtome measurement.[21]

We note from the results shown that the second harmonic field, $E(2\omega) \propto [I(2\omega)]^{1/2}$, is linear in the surface excess Γ_2 up to the concentration where phenol and cresol monolayers are estimated to form. This behavior is expected if the second-order surface susceptibility $\overleftrightarrow{\chi}_s^{(2)}$ is given by the product of the number of surface solute molecules per unit area, N_s, and the average of the second order molecular polarizability $\langle \overleftrightarrow{\alpha}^{(2)} \rangle$. The second harmonic field, which is proportional to the nonlinear polarization induced in the surface layer, $P_s^{NLS}(2\omega) = \overleftrightarrow{\chi}_s^{(2)}:\bar{E}(\omega)\bar{E}(\omega) = N_s\langle \overleftrightarrow{\alpha}^{(2)} \rangle:\bar{E}(\omega)\bar{E}(\omega)$, then varies linearly with N_s.

It is to be emphasized that the approximation that Γ_2 is equal to the total number of solute molecules per unit area in the interfacial region is valid only when there is a significant enrichment of the surface by the solute. For cases where there is not a large enrichment factor, the Γ_2 calculated from surface tension data would not yield definitive surface composition information. On the other hand, the second harmonic field, arising from all oriented molecules, would be proportional to the total number of molecules in the surface region. This latter statement would have to be considered more closely at high surface coverages where local field effects could arise.[20]

A further point of interest with regard to Figure 2 is the observation that the second harmonic signal continues to increase above the concentration of the Gibbs monolayer. This slower rate of increase with bulk concentration above the monolayer, relative to that at submonolayer coverages, could be due to a partial ordering of the solute in the region just below the monolayer. The average orientation of the phenol molecules in this region below the monolayer would be about the same as that in the surface as evidenced by the constancy of the second harmonic polarization in Figure 1. Another possibility is that a structural change in the monolayer occurs when the concentration required for the initial

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monolayer formation is exceeded, allowing for closer packing on the surface. To be consistent with an unchanging phenol orientation imposes the restriction that the structural change not alter the angle of the molecule's main axis, i.e., only rotations about the main axis of phenol would be allowed.

In conclusion, we have obtained detailed information about the composition and orientation of solute molecules at the surface of a liquid solution. The nonlinear spectroscopic technique of second harmonic generation has been applied to low surface concentrations even without the benefit of resonance enhancement. In an aqueous phenol solution, the phenol molecules at the solution/vapor interface are found to be oriented with their long axes tilted 50° from the surface normal. At concentrations above that required for monolayer formation, the second harmonic signal indicates further changes in surface structure or composition.

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FEATURE ARTICLE

Symmetry beyond Point Groups in Molecular Spectroscopy

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An attempt is made to distill from the published literature a summary of some new uses of group theory in high resolution gas-phase spectroscopic studies of molecules with large amplitude and/or tunneling motions, paying particular attention to questions like the following: (i) When is a point group sufficient, and when is it not? (ii) What kind of information is easy, and what kind is difficult to extract from a permutation–inversion group treatment? (iii) What seem to be the advantages and disadvantages of various extended groups of the permutation–inversion group? While most spectroscopists would agree that a general group theoretical approach, suitable for application without modification to the majority of floppy molecules, has not yet been synthesized from the particular cases studied in the literature, some feeling for one direction of progress in the field can be obtained from the several examples presented.

1. Introduction

In this article we shall attempt to present from a pedagogical point of view some opinions on the use of group theory in high resolution molecular spectroscopy. The scope of the discussion will deliberately be limited to the use of words, rather than mathematical equations, as the vehicle for transmitting information. The advantage of words lies in the fact that the reader can quickly grasp the general outline of a problem and its solution. The disadvantage lies in the fact that no matter which words are chosen, they cannot unambiguously reflect the mathematics upon which any proof of legitimacy or any procedure for obtaining results is actually based. The serious student is therefore referred to the original literature citations, for which this article can really only serve as an annotated table of contents.

There has been and still is ongoing controversy over how to extend symmetry treatments beyond point groups in molecular spectroscopy. This controversy, which is at times both heated and rancorous, flares up primarily at the interface where the physical problem (i.e., the measurable properties of the molecule) must be connected to pure mathematics (i.e., to group theory). An illustration of the importance of how this connection is made is contained in the statement that the point groups C_{2h} and C_{2v} are both isomorphic with the four-group, so that these two point groups are indistinguishable from a purely mathematical point of view. Nevertheless, because of the different way in which the mathematical operations of the four-group are connected to the molecular model, the group C_{2h} leads to selection rules in which infrared active vibrations *cannot be* Raman active, whereas C_{2v} leads to selection rules in which infrared active vibrations *must be* Raman active.

In trying to make the connection between molecular model and group theory in a mathematically consistent way, it is the author's strong opinion that strict attention must be paid to the precise transformation of variables in the molecular wave function which is to be associated with a given symmetry operation. Readers who are comfortable with a position proposed to the author in an argument long ago that "group theory is so powerful that one does not need to specify exactly what the symmetry operations mean", should read no further. In fact, as a second limitation of the scope of this article, no comprehensive review of opposing viewpoints in the literature will be attempted.

The material which follows will be divided into three sections, one dealing with point groups, one with permutation–inversion groups, and one with extended groups. We shall consider questions like: What information can or cannot be obtained easily from the group theoretical formalism in a given section? How does the way of looking at things differ in different sections? What molecules provide good illustrations of the various concepts?

2. Point Groups

Point groups, which we shall assume to be well-known to the reader,[1-3] make the connection between group theory and molecular model through the *shape* of the molecule, and it is therefore not surprising that point groups are most useful when the molecule exists in a single well-defined shape. To make the idea of shape

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