

Second harmonic generation from the surface of centrosymmetric particles in bulk solution

H. Wang, E.C.Y. Yan, E. Borguet, K.B. Eisenthal

Department of Chemistry, Columbia University, New York, NY 10027, USA

Received 4 June 1996; in final form 18 June 1996

Abstract

Second harmonic generation (SHG) is reported for the first time from the surfaces of centrosymmetric particles in bulk isotropic solution. Although SHG is generally described as electric dipole forbidden in centrosymmetric systems, we show that this requires the system to be centrosymmetric on length scales much less than the coherence length of the process. This condition is not satisfied for micron-size particles, and accordingly we have observed a strong SH signal from various particles of this length scale. This promising discovery provides a powerful spectroscopic method for the investigation of physical and chemical processes on the surfaces of microscopic centrosymmetric particles.

1. Introduction

Surface and interfacial phenomena are of practical and fundamental interest. Nevertheless, the experimental investigation of the interface region, defined as the atomic or molecular layers that constitute the junction between two dissimilar media, has been a major challenge. As the interface contains far fewer species than the bulk, it is difficult to distinguish between the small surface contribution and the overwhelming bulk contribution to most probe signals. Recently, surface specific techniques based on second-order non-linear optical phenomena, such as second harmonic generation (SHG) and sum frequency generation (SFG), have proven extremely useful for studying the chemical and physical properties of surfaces and interfaces [1–4].

SHG is generally thought to be forbidden, in the electric dipole approximation, in centrosymmetric media such as bulk liquids [5,6]. The surface speci-

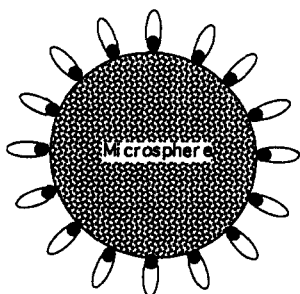
ficity of SHG arises from the fact that surfaces and interfaces are intrinsically non-centrosymmetric. In most cases SHG experiments are performed on planar surfaces. This has restricted the range of systems studied. In particular, it has not yet been possible to investigate in liquids and gases the surfaces of centrosymmetric particles, such as colloids, sols, vesicles, microspheres of polymeric and solid state materials, and aerosols using these powerful spectroscopic methods. Individual, isolated, non-centrosymmetric molecules can generate second harmonic radiation [7]. However, the net coherent radiated field from such a collection of molecules in a centrosymmetric bulk medium is zero for symmetry reasons. This can be understood through the following argument. For every molecule oriented in a given direction there is another, pointing in the opposite direction and located at a distance that is much less than the coherence length of the process. The non-linear polarization of these species, driven by the incident

optical field, are out of phase with each other. As a consequence, the net polarization is zero, and no coherent second harmonic light is generated.

In contrast, incoherent second-order light scattering, called hyper-Rayleigh scattering, has been observed from bulk centrosymmetric media [8,9]. It originates from the orientational and density fluctuations of the molecules in the bulk solution. These fluctuations disrupt the phase cancellation mentioned above. SHG has also been observed in an interesting study from solutions of randomly oriented suspensions of purple membrane where the individual suspensions are non-centrosymmetric, and are the source of the SHG [10]. In neither case does the second-order process have a surface origin. Nanometer diameter semiconductor quantum dots and metallic crystals also give rise to SHG. The second-order response of these particles is believed to originate from their non-centrosymmetric nature and is quite distinct from what is reported here for much larger polystyrene microspheres [11].

One can eliminate the phase cancellation if the source terms (e.g. molecules) are both oriented and separated as on the surface of a sphere (Scheme 1). As a simple example consider a centrosymmetric system consisting of two identical molecules separated by a distance L , with opposite orientations (Fig. 1). Using the fact that the oppositely oriented molecules have non-linear polarizabilities $\alpha^{(2)}$, of opposite sign, we find that the total second harmonic field $E_{2\omega}$ at the detector due to the two particles is of the form

$$E_{2\omega} \approx \alpha^{(2)} E_{\omega} E_{\omega} (1 - e^{i\Delta k \cdot L}), \quad (1)$$



Scheme 1. Though the particle is centrosymmetric, the contribution of the oppositely oriented adsorbates, located on opposite sides of the microsphere, do not cancel. Hence the observation of SHG.

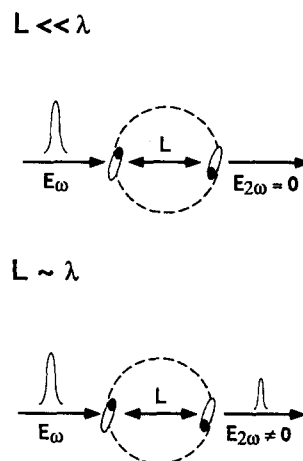


Fig. 1. Schematic description of SHG in a centrosymmetric system for an intermolecular length scale L in the two limits of L being small or comparable to the wavelength of the light. The constructive interference shown in the lower part of the figure is the basis for the observation reported here of SHG from centrosymmetric microparticles.

where

$$\Delta \mathbf{k} = \mathbf{k}_{2\omega} - 2\mathbf{k}_{\omega}$$

and $\mathbf{k}_{2\omega}$ and \mathbf{k}_{ω} are the light propagation vectors for the light at 2ω and ω , respectively.

If the separation L between the molecules is much less than the wavelength of light, then $\Delta \mathbf{k} \cdot L \ll 1$ and $E_{2\omega} = 0$. This is the case of centrosymmetry on the scale of tens to hundreds of Angstroms, characteristic of bulk centrosymmetric media. If, on the other hand, the separation is such that $\Delta \mathbf{k} \cdot L \sim \pi$, then there can be constructive interference. For example, if $\Delta \mathbf{k} \cdot L \sim \pi$, then there is constructive interference and $E_{2\omega}$ will be twice that of the individual molecule. It is on the length scale of microns that one must consider the interference described above.

Based on the above mentioned concept, we report in this Letter the first observation of a new phenomenon: surface SHG from the surfaces of centrosymmetric particles in bulk solution. In addition to its fundamental interest, this discovery provides a useful method for investigating surfaces of relatively small particles in centrosymmetric environments. We have verified that the SHG reported herein originates from the surfaces of the particles and not from the bulk solution nor the bulk (interior) region of the particle. The molecules adsorbed on the surface of

the microsphere are oriented because of the asymmetry at the water/sphere interface which aligns the adsorbed molecules. Malachite green, a water-soluble triphenylmethane dye, was chosen as a probe molecule because it has a strong second-order non-linearity at the wavelength of our Ti:sapphire laser [12].

2. Experimental

A Ti:sapphire oscillator provides 100 fs pulses at 854 nm, at a repetition rate of 82 MHz. The fundamental light is focused into the 0.2 cm long sample cell. Second harmonic photons are detected in the transmitted direction using single-photon counting. Filters and a monochromator separate the second harmonic photons from the fundamental and any background signals such as fluorescence and Raman scattering. Signals were normalized to solution turbidity at ω and 2ω , when either the solute or particle concentration was varied.

The particles used in these experiments were polystyrene (latex) microspheres (Polysciences). The particle surfaces are negatively charged due to the presence of sulfate ($-\text{SO}_4^-$) groups. The particles are uniformly spherical and are supplied as monodisperse aqueous solutions (diameter $1.05 \pm 0.03 \mu\text{m}$), with approximately 10^7 charges per particle. All samples were prepared using doubly distilled water. The solution pH in all the experiments was 6.5 ± 0.2 . Ionic strength was adjusted using KCl. Malachite green chloride (Aldrich) was checked for purity using high-pressure liquid chromatography (HPLC). All measurements were performed at 22°C. More complete details of the experiment will be provided elsewhere.

3. Results and discussion

Second harmonic generation was only observed from bulk solutions containing microspheres. Water alone showed no detectable signal. Bulk samples of aqueous malachite green ($< 10^{-3}$ M) showed a two-photon excited fluorescence signal with a small tail extending to the second harmonic wavelength, 427 nm. The fluorescence is an unrelaxed emission,

centered at 460 nm, from an excited (S_2) state to the ground state (S_0). On addition of polystyrene microspheres to the malachite green solution an intense second harmonic signal at 427 nm is observed. This signal is a factor of 1000 greater than that observed from solutions of microspheres without malachite green, and a factor of 300 greater than bulk solutions of malachite green alone. The origin of the SH signal when only the microspheres are present is discussed later.

A number of experiments was performed to establish that the signal we observe is indeed second harmonic, that it originates from the surface of the particles and that it is not due to a non-linear bulk process. We have examined the spectrum of the signal and verified that it is sharply peaked at 2ω (427 nm). A small two-photon fluorescence signal, centered at 460 nm is observed for malachite green samples. The monochromator effectively reduces the signal from two-photon fluorescence to less than 1/200 of the SHG signal. By varying the focus of the input laser and using cells that were 2 mm and 1 cm in path length we showed that the SHG did not originate from either the input or output surfaces of the cell. Furthermore, the signal from all samples displaying SHG showed the expected quadratic dependence on the incident fundamental intensity (Fig. 2).

To demonstrate that the SH signal originates from the surface of the particles, the adsorption isotherm, which gives the surface population of malachite green on the microparticle as a function of bulk malachite green concentration, was measured. The SH signal should vary quadratically with the adsorbate density on the microsphere as it does for planar surfaces [13]. Using the adsorption isotherm to obtain the interface population it was shown that the SH from the microparticle solutions obeyed the expected quadratic dependence on the density of malachite green adsorbed on the particle surfaces (Fig. 3). The data shown is for the linear region of the adsorption isotherm where the density of malachite green adsorbed is linearly related to bulk concentration. This is further evidence that the SH signal observed arises from the surfaces of the particles, and rules out hyper-Rayleigh scattering since the latter would scale linearly with the number density of the malachite green. The more than 300-fold enhancement of the

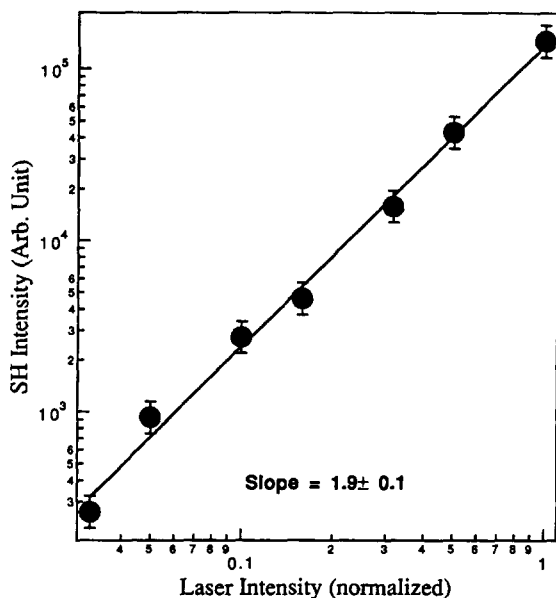


Fig. 2. Second harmonic signal as a function of incident laser intensity for a bulk aqueous solution of 1.05 μm diameter polystyrene sulfate microspheres with malachite green (5 μM). The solid line is the theoretically expected quadratic dependence, which shows excellent agreement with the data.

SH signal observed when the microspheres are added to the malachite green solution indicates that the species adsorbed at the particle surfaces are primarily responsible for the observed SHG.

In order to probe the coherent nature of the process we also investigated the dependence of the SHG on the density of microspheres in solution. Fig. 4 shows the results for solutions of malachite green at a fixed concentration of 5 μM that contain microspheres over a range of 0.2×10^8 – 8.3×10^8 microspheres/ cm^3 . At these particle densities the average interparticle distance ranges from 36 to 11 μm . The bulk solution concentration of malachite green was sufficient to saturate the particle surfaces. The observed linear dependence on the microsphere density indicates that the particles do not interact coherently. If the particles were interacting coherently a non-linear dependence of the SH signal on the particle density would be observed.

SHG from an interface can also result from the action of a static electric field on the bulk solution due to surface charges [14,15]. This field is responsible for a $\chi^{(3)}$ contribution to the SHG due to the

polarization of solvent species by the surface charges. The total second order polarization, $P_{2\omega}$, including $\chi^{(2)}$ and $\chi^{(3)}$ contributions, from a charged solid/liquid interface is given by Eq. (1), where e is the electronic charge, ϵ is the bulk dielectric constant, C is the bulk electrolyte concentration, and σ_0 is the interface charge density:

$$P_{2\omega} = \chi^{(2)} E_{\omega} E_{\omega} + \chi^{(3)} \frac{2kT}{e} \sinh^{-1} \left(\sigma_0 \sqrt{\frac{\pi}{2C\epsilon kT}} \right) E_{\omega} E_{\omega}. \quad (2)$$

We have previously observed this $\chi^{(3)}$ contribution at silica/water and charged monolayer/water interfaces, and furthermore have shown that its contribution to the total second harmonic polarization varies with the electrolyte concentration (ionic strength) as described by Eq. (2) [14,15]. Increasing the electrolyte concentration (C) at constant surface charge density (σ_0) should reduce the penetration of the static electric field into the bulk water, thereby re-

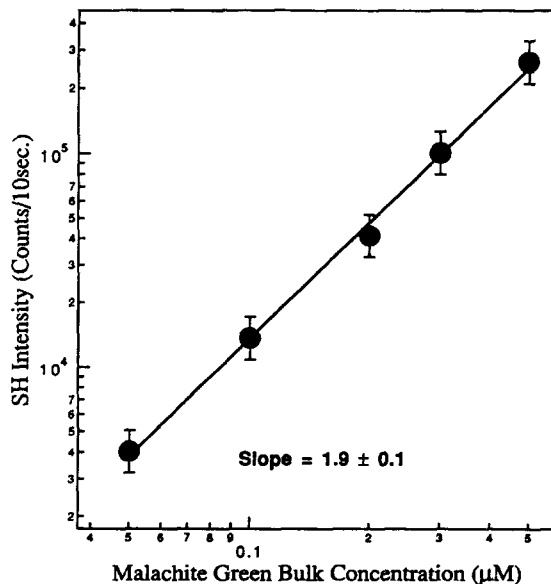


Fig. 3. Second harmonic signal as a function of bulk malachite green concentration at a constant density of 8.3×10^8 microspheres/ cm^3 for 1.05 μm diameter polystyrene sulfate microsphere. The data shown is for the linear region of the adsorption isotherm where the density of malachite green adsorbed is linearly related to bulk concentration. The solid line is the theoretically expected quadratic dependence, which shows excellent agreement with the data.

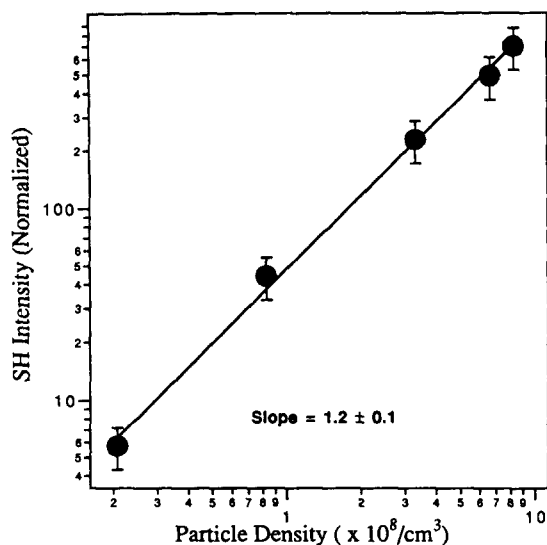


Fig. 4. Second harmonic signal, normalized to solution turbidity at ω and 2ω , as a function of density of $1.05 \mu\text{m}$ diameter polystyrene sulfate microspheres with malachite green ($5 \mu\text{M}$). The best fit solid line indicates a linear dependence.

ducing the polarization of the water molecules and hence the $\chi^{(3)}$ contribution to the signal. This is indeed what we have observed for solutions of mi-

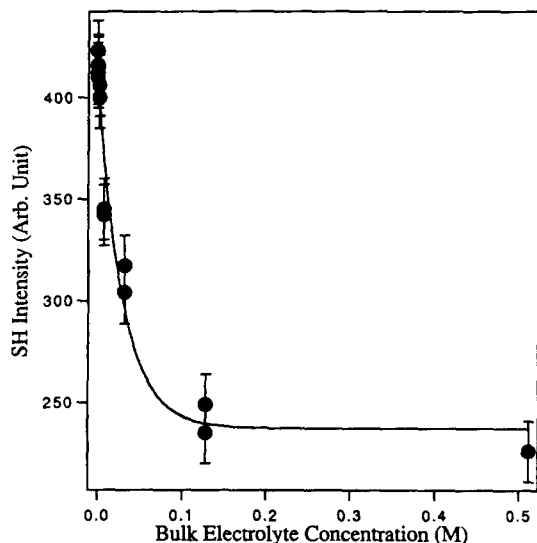


Fig. 5. Second harmonic signal as a function of ionic strength for a bulk solution of $1.05 \mu\text{m}$ diameter charged polystyrene sulfate microspheres. Solid line is the theoretical fit given by Eq. (2) of the SHG arising from polarization of bulk water by surface charges.

croparticles as indicated in Fig. 5. No such dependence of signal on electrolyte concentration for microparticle solutions containing malachite green was observed. This suggests that the $\chi^{(3)}$ contribution is not significant relative to the $\chi^{(2)}$ contribution of malachite green adsorbed on the particle surface.

4. Summary

SHG has been observed for the first time from the surfaces of centrosymmetric particles in bulk solution. Though SHG is typically forbidden in centrosymmetric media such as bulk solutions, a surface SHG signal is observed from the centrosymmetric microspheres. Evidence for the surface specific nature of this SHG is presented. The observed signal is a result of the opposite non-linear polarizations due to adsorbed molecules or surface charges, not cancelling because they are separated by dimensions comparable to the coherence length for SHG, as shown by the simple example described by Eq. (1) and shown in Fig. 1. This promising discovery provides a powerful spectroscopic method for the investigation of equilibrium and time-dependent phenomena at surfaces of small centrosymmetric particles such as colloids, vesicles, microspheres of polymeric or other solid state materials, sols and aerosols, in centrosymmetric environments.

Acknowledgements

The authors wish to thank the Division of Chemical Science of the Department of Energy for their support and the National Science Foundation for their equipment support. The authors thank Professor Tony Heinz and Dr. Jerry Dadap for useful discussions.

References

- [1] G. Richmond, J.M. Robinson and V.L. Shannon, *Prog. Surf. Sci.* 28 (1988) 1.
- [2] Y.R. Shen, *Ann. Rev. Phys. Chem.* 40 (1989) 327.
- [3] K.B. Eisenthal, *Ann. Rev. Phys. Chem.* 43 (1992) 627.

- [4] R.M. Corn and D.A. Higgins, *Chem. Rev.* 94 (1994) 107.
- [5] J.A. Giordmaine, *Phys. Rev. A* 138 (1963) 1599.
- [6] N. Bloembergen, *Nonlinear Optics*, (Wiley, New York, 1965).
- [7] A.D. Buckingham and B.J. Orr, *Q. Rev. Chem. Soc.* 21 (1967) 195.
- [8] R.W. Terhune, P.D. Maker and C.M. Savage, *Phys. Rev. Lett.* 14 (1963) 681.
- [9] K. Clays and A. Persoons, *Phys. Rev. Lett.* 66 (1991) 2980.
- [10] Q. Song, C. Wan and C.K. Johnson, *J. Chem. Phys.* 98 (1994) 1999.
- [11] O.A. Aktsipetrov, P.V. Elyutin, A.A. Nikultin, E.A. Ostrovka, *Phys. Rev. B* 51 (1995) 17591.
- [12] X. Shi, E. Borguet, A.N. Tarnovsky and K.B. Eisenthal, *Chem. Phys.* 205 (1996) 167.
- [13] J.M. Hicks, K. Kemnitz, K.B. Eisenthal and T.F. Heinz, *J. Phys. Chem.* 90 (1986) 560.
- [14] S.W. Ong, X.L. Zhao and K.B. Eisenthal, *Chem. Phys. Lett.* 191 (1992) 327.
- [15] X.L. Zhao, S.W. Ong and K.B. Eisenthal, *Chem. Phys. Lett.* 202 (1993) 513.