the thermal yield of R^{38}Cl from SnR$_4$ might be anticipated in analogy with similar experiments on the formation of R^{18}F from thermal ^{18}F reactions with SnR$_4$,[9] the direct yield of CH$_2$=CH^{38}Cl from V$_3$SnCH=CH$_2$ is unlikely to be more than 1%. The magnitude of any such direct reaction has no significant effect on the conclusions drawn from the half-stabilization pressure for the excited radical formed in (4).

Non-RRKM behavior was hypothesized earlier for the addition of thermal ^{18}F atoms to tetraallyltin, Sn(CH$_2$CHCH$_2$)$_4$,[10] and tetraallylgermanium, Ge(CH$_2$CHCH$_2$)$_4$,[11] with the release of CH$_2$=CH^{18}F from the excited A$_3$MCH$_2$CH^{18}FCH$_2$* radicals (A = CH$_2$CHCH$_2$; M = Sn or Ge), and was also attributed to failure of energy distribution through the central C–M–C bonding. Slow energy transmission through such bonding has been supported by simplified theoretical calculations.[12] However, experiments involving the addition of thermal hydrogen atoms to similar tetrasubstituted organometallic molecules have failed to provide support for the concept of very slow energy transmission through the heavy central atom, i.e., appropriately pressure-dependent yields of CH$_2$=CH$_2$ from H atom addition to A$_3$SnCH$_2$CHCH$_2$, or of CH$_3$CH=CH$_2$ from (CH$_3$)$_3$SnCH$_2$CH$_2$CH=CH$_2$.[13,14] The causes for the apparent disagreement between experiments involving the addition reactions of atomic hydrogen and of atomic ^{18}F have not yet been resolved. Experiments with tritium atom addition to tetrasubstituted metallic substrates are currently being carried out in our laboratory using atoms thermalized after nuclear recoil from the ^{3}He(n,p) nuclear reaction.[15]

Radioactive ^{38}Cl atoms are formed by irradiation in the UCI TRIGA nuclear reactor of 20-mL ampules containing 1 Torr of Sn(CH=CH$_2$)$_4$, 20 Torr of argon, and the remaining pressure furnished by CClF$_3$. Irradiation times of 1 min with the nuclear reactor at only 10 kW power held radiation damage in the system to negligible levels.[3] The yield of radioactive ^{41}Ar serves as a monitor for the thermal neutron exposure of the sample, allowing the calculation of the total amount of ^{38}Cl formed in the system. The volatile organic radioactivities are assayed by gas proportional counting in the standard manner, and include very small yields (<1% each) of CCl^{38}ClF$_2$ and C^{38}ClF$_3$ formed by energetic reactions of ^{38}Cl with the major CClF$_3$ component of the gaseous mixtures. The data of Figures 1 and 2 are graphed with the assumption that the maximum thermal yield of products labeled with ^{38}Cl is 95%, after allowance for the energetic reactions of ^{38}Cl with CClF$_3$.

In analogy to the reactions of thermal chlorine atoms with CH$_2$=CH$_2$ for which the abstraction of H is strongly endothermic,[1] the formation of H^{38}Cl from Sn(CH=CH$_2$)$_4$ is assumed not to occur. Formation of V$_3$Sn^{38}Cl from a direct substitution by thermal ^{38}Cl is also a reaction with negligible yield. The recovery of nearly all thermal ^{38}Cl atoms in the form of CH$_2$=CH^{38}Cl is consistent with these arguments.

Acknowledgment. This research has been supported by Department of Energy Contract No. DE-FG03-86ER 13469.

---

(9) Kikuchi, M.; Cramer, J. A.; Iyer, R. S.; Frank, J. P.; Rowland, F. S. *J. Phys. Chem.* **1982**, *86*, 2677.

(10) Rogers, P. J.; Montague, D. C.; Frank, J. P.; Tyler, S. C.; Rowland, F. S. *Chem. Phys. Lett.* **1982**, *89*, 9.

(11) Rogers, P. J.; Selco, J. I.; Rowland, F. S. *Chem. Phys. Lett.* **1983**, *97*, 313.

(12) Lopez, V.; Marcus, R. A. *Chem. Phys. Lett.* **1982**, *93*, 232.

(13) Wrigley, S. P.; Rabinovitch, B. S. *Chem. Phys. Lett.* **1983**, *98*, 386.

(14) Wrigley, S. P.; Oswald, D. A.; Rabinovitch, B. S. *Chem. Phys. Lett.* **1984**, *104*, 521.

(15) Wang, N.-Y.; Iyer, R. S.; Rowland, F. S. *J. Phys. Chem.* **1986**, *90*, 931.

Studies of Surface Diffusion by Second Harmonic Fluctuation Spectroscopy

Xiaolin Zhao, M. Cynthia Goh,[†] Suchitra Subrahmanyan, and Kenneth B. Eisenthal[*]

Department of Chemistry, Columbia University, New York, New York 10027 *(Received: November 29, 1989; In Final Form: February 8, 1990)*

We have shown how the fluctuations in the signal from surface second harmonic generation can be utilized for the study of a heterogeneous surface such as palmitic acid (C$_{15}$H$_{31}$COOH) spread on the air/water interface, under conditions of gas–liquid coexistence. We report observations of time-correlated fluctuations in the SH signal, with decay constant of approximately 6 s. This is attributed to motions of the liquidlike clusters of palmitic acid. If the motion is diffusive, a diffusion constant of about 10^{-8} cm^2/s is estimated for these clusters.

Introduction

Second harmonic generation (SHG) is a technique that has received much recent attention due to its surface specifity.[1-6] The SH signal is generated through a nonlinear susceptibility, $\chi^{(2)}$, which is related to the molecular hyperpolarizability, $\alpha^{(2)}$. Neglecting local field effects, one can write

$$\chi^{(2)} = N_s\langle\alpha^{(2)}\rangle$$

where N_s is the surface population and $\langle\ \rangle$ denotes orientational averaging.

Let us consider a heterogeneous surface that consists of two different types of molecular arrangements, as exemplified by a fatty acid spread on the water surface under coexistence conditions.[7] In one configuration, the molecules are clustered together at a density corresponding to a liquidlike surface phase. In the other arrangement, the molecules are sufficiently far apart so that there are no interactions between individual molecules; this corresponds to a gaslike phase of the molecules at the surface. In the coexistence region, the surface is heterogeneous in having regions of liquid clusters and regions of gas, interspersed among each other. This type of coexistence has been studied by using a variety of techniques.[7-11] The presence of liquidlike and gaslike

---

[*] To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

(1) Bloembergen, N.; Pershan, P. S. *Phys. Rev.* **1962**, *128*, 606.

(2) Chen, C. K.; Heinz, T. F.; Ricard, D.; Shen, Y. R. *Phys. Rev. Lett.* **1981**, *46*, 146; *Chem. Phys. Lett.* **1981**, *83*, 455; *Phys. Rev.* **1983**, *B27*, 1965.

(3) Hicks, J. M.; Kemnitz, K.; Eisenthal, K. B.; Heinz, T. F. *J. Phys. Chem.* **1986**, *90*, 560.

(4) Kemnitz, K.; Bhattacharyya, K.; Pinto, G. R.; Eisenthal, K. B.; Heinz, T. F. *Chem. Phys. Lett.* **1986**, *131*, 285.

(5) Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacone, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350.

(6) Richmond, G.; Robinson, J. M.; Shannon, V. L. *Prog. Surf. Sci.* **1980**, *28* (1), 1–70.

(7) Gaines, G. L. *Insoluble Monolayers at Liquid-Gas Interfaces*; Wiley: New York, 1966.

regions have been studied by surface potential,[9] ellipticity,[8] fluorescence microscopy,[10] and light-scattering measurement.[11] In this paper, we are interested in illustrating how SHG can be used to investigate surface heterogeneity. Among the special features of the nonlinear optical method are (a) it is a spectroscopic method and can therefore differentiate among various species present at the interface by varying the input wavelength(s), (b) it also has enormous dynamic range in time by using ultrashort pulsed laser and thus makes possible the examination of ultrafast phenomena, (c) the technique is surface specific and consequently the presence of solute molecules in the bulk do not contribute to the signal, and last (d) the spot size can be varied to examine the size of the large clusters at the surface. With these advantages, we measure the time-dependent fluctuations in the SH signal to investigate the motion of the liquid clusters into and out of the area illuminated by the incident beam. The system we have studied is palmitic acid spread on water at coverages corresponding to the gas–liquid coexistence region.

Let $I(t)$ be the measured SH signal at time t, I_l, and I_g be the signal if the surface is covered by a homogeneous layer of liquid (l) or gas (g), and A_l and A_g be the fraction of the area under observation covered by l and g, respectively. We can then write

$$I(t) = I_l A_l + I_g A_g \tag{1}$$

$$= (I_l - I_g)A_l + I_g \tag{2}$$

We then define $\Delta I(t) = I(t) - \langle I \rangle$, where $\langle I \rangle$ is the average signal, and obtain a correlation function

$$\langle \Delta I(0)\ \Delta I(t) \rangle = (I_l - I_g)^2 \langle \Delta A_l(0)\ \Delta A_l(t) \rangle \tag{3}$$

such that it signifies deviation from the average value. Note that I_l and I_g are time-independent, and the only time dependence is due to changes in the fraction of the area covered by l, i.e., the clusters. If the clusters are of the same size these changes are simply the fluctuations in the number of clusters in the irradiated area. The characteristic time of decay of the correlation function is thus related to the time that a liquid cluster remains within the beam. If the cluster motion is diffusive, a diffusion constant may be estimated by using the results for random walk in two dimensions, $\langle r^2 \rangle = 4Dt$, where r is a characteristic length, in this case the beam radius, and t is the decay time of the observed intensity fluctuations.

If the size of the beam is sufficiently small such that the area occupied by the clusters is fluctuating on a time scale that is larger than our experimental resolution, then we can directly observe these fluctuations. By focusing the incident beam to a radius of 13 μm, and resolving our signal to 0.5 s, we illustrate how the above idea can be utilized to examine the coexistence region of palmitic acid at the air/water interface.

Results

The basic experimental apparatus for SHG has been previously described.[3] The incident light from a tunable dye laser synchronously pumped by an Ar^+ laser is focused on the liquid surface at 70° angle. The generated 2ω radiation is measured by using a single-photon-counting detection system, which is hooked up to a computer. This computer interface allows the signal to be integrated every fraction of a second.

In previous experiments,[12] we have shown that a small amount of *p*-nitrophenol (PNP) dissolved in the water subphase can be used as a good probe of the spread palmitic acid because it is adsorbed in the loose structure of the interface, generating a large SH signal. Furthermore, PNP can be used as a probe of specific regions of the phase diagram for palmitic and pentadecanoic acid

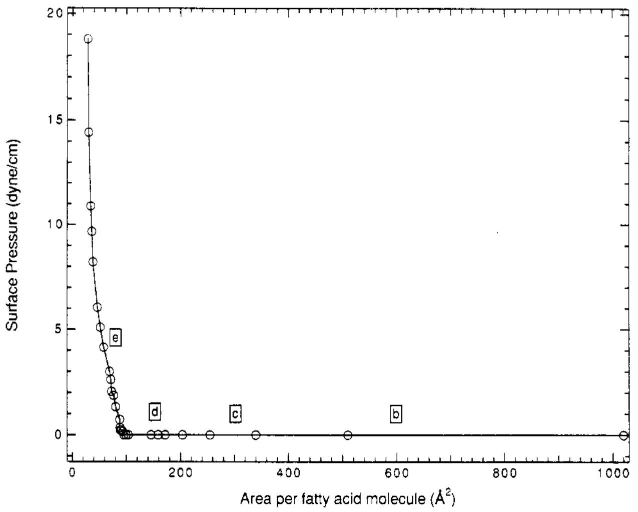

Figure 1. Surface pressure (dyn/cm) vs A (Å²/molecule) isotherm. b, c, d, and e indicate the surface density at which the fluctuation experiments were performed.

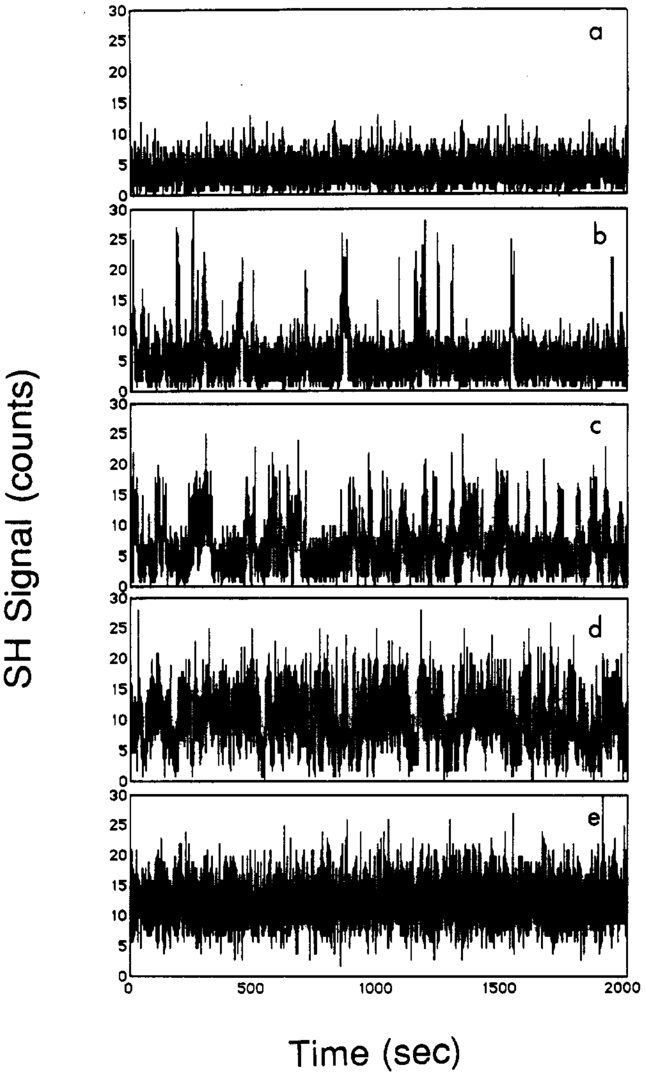

Figure 2. The second harmonic signal as a function of time, taken as 0.5-s averages: (a) pure PNP/water, (b)–(e), palmitic acid spread on PNP/water subphase at the following coverages (b) 600, (c) 300, (d) 150, and (e) 75 Å²/molecule.

---

(8) Rasing, Th.; Hsiung, H.; Shen, Y. R.; Kim, M. W. *Phys. Rev. A* **1988**, *37*, 2732.

(9) (a) Pallas, N. R.; Pethica, B. A.; *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 585. (b) Kim, M. W.; Cannell, D. S.; *Phys. Rev. A* **1976**, *13*, 411. (c) Kim, M. W.; Cannel, D. S. *Phys. Rev. A* **1976**, *14*, 1299.

(10) (a) Moore, B.; Knobler, C. M.; Braseta, D.; Rondelez, F.; *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 1753. (b) Losche, M.; Mohwald, H.; *Rev. Sci. Instrum.* **1984**, *55* (12), 1968. (c) McConnell, H. M.; Tamm, L. K.; Weis, R. M. *Proc. Natl. Acad. Sci. USA* **1984**, *31*, 3249. (d) Mohwald, H. *Thin Solid Films* **1988**, *159*, 1.

(11) Winch, P. J.; Earnshaw, J. C. *J. Phys.: Condens. Matter* **1989**, *1*, 7187.

(12) Zhao, X.; Goh, M. C.; Eisenthal K. B. Submitted for publication in *J. Phys. Chem.*

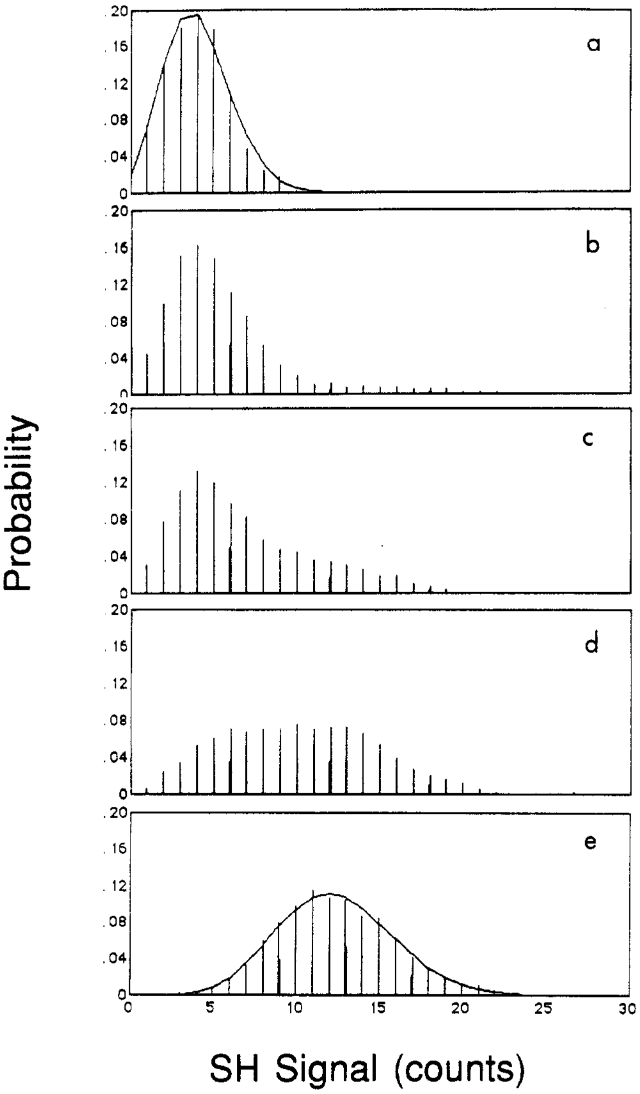

Figure 3. Histogram of the data in Figure 2, showing the fraction of times a particular signal is observed vs the signal. The solid lines shown in (a) and (e) correspond to Poisson distribution which centers at the averaged signal. (a) Pure PNP/water, (b)–(e), palmitic acid spread on PNP/water subphase at the following coverages (b) 600, (c) 300, (d) 150, (e) 75 Å^2/molecule.

spread on water, since its population at the surface, and hence the signal strength, is dependent on the fatty acid surface coverage.

A measurement of the area/molecule A vs surface pressure π phase diagram of palmitic acid on a 10 mM PNP subphase at pH 2 was performed using a film balance. The results are shown in Figure 1. The presence of PNP in the subphase did not alter the qualitative features of the phase diagram of palmitic acid; however, the location of the phase boundaries are shifted to larger area/molecule. In particular, the liquid–gas phase transition occurs at approximately 100 Å^2/molecule instead of about 30 Å^2/molecule in the absence of PNP.[7] The precision of our measuring apparatus did not allow for the determination of the transition to pure gas phase.

For the fluctuation experiments, palmitic acid was dissolved in hexane and spread by using a 5-μL syringe on a subphase of 10 mM PNP in water at pH 2. At least 20 min elapsed after spreading, in order to allow the solvent to evaporate. Data acquisition was then started; the number of counts generated every 0.5 s was recorded for at least 1/2 h.

We performed measurements at concentrations corresponding to 75, 150, 300, and 600 Å^2/molecule which correspond to point e, d, c, b in the π–A phase diagram. The signal from a pure PNP/water solution, without the palmitic acid, was also measured. The results are shown in Figure 2. It is readily evident, even from this raw data, that the fluctuations in the SH signal from the pure PNP solution (Figure 2a) is very different from that generated by the palmitic acid at coverages of 600, 300, and 150 Å^2 (Figure 2b–d). On the other hand, the data for 75 Å^2/molecule (Figure 2e) looks very similar to Figure 2a, except that the average magnitude of the signal is higher.

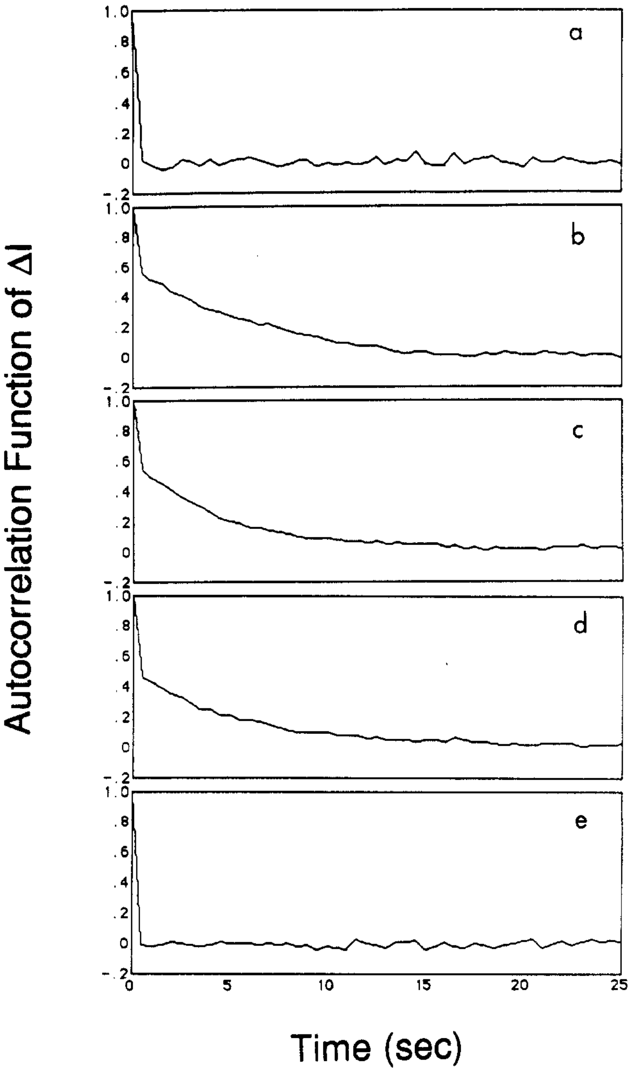

Figure 4. Autocorrelation ⟨ΔI(0) ΔI(t)⟩ vs time for the different surface coverages: (a) pure PNP/water, (b)–(e), palmitic acid spread on PNP/water subphase at the following coverages (b) 600, (c) 300, (d) 150, and (e) 75 Å^2/molecule.

Discussion

We can interpret the above results in terms of the phase diagram of palmitic acid, as shown in Figure 1. At 75 Å^2/molecule the palmitic acid on the surface is in a homogeneous liquidlike phase, while the other three measurements correspond to its being inside the gas–liquid coexistence region. Our previous work[12] has shown that, at very low coverages ("gas"), the SH signal is the same as for a bare PNP/water surface. However, as the palmitic acid packing is increased, a substantially larger SH signal is generated. It is notable that the "low" signal in Figure 2b is the same signal as in Figure 2a. This signal corresponds to patches of the surface with the low-density gaslike coverage in the irradiated region. The "high" signals, on the other hand, correspond to the high-density liquidlike coverage in the irradiated region. At 600 Å^2/molecule the coverage is low, and there are few liquidlike islands dispersed in gaslike coverage. As the packing is increased, at 300 and 150 Å^2/molecule, more high signals are obtained, corresponding to a higher fraction of the palmitic acid in a liquidlike state. Finally, at 75 Å^2/molecule, the surface is now covered by a homogeneous layer of palmitic acid in its liquidlike phase. The signal fluctuations for both the bare PNP/water surface (Figure 2a) and the ho-

J. Phys. Chem. 1990, 94, 3373-3376 3373

mogeneous liquid (Figure 2e) are ascribed to random noise as discussed below.

As a further test of the significance of the observed fluctuations, we plotted the histogram for our data, i.e., the fraction of time that a particular signal is recorded vs the signal (Figure 3). While there is always a statistical spread in any measurement, the distributions shown in Figure 3b–d do not look like any simple one. In the case of a purely random source of noise, as, for example, noise from the laser and detection systems, one expects a Poisson distribution of the data.[13] In Figure 3a,e, the line corresponds to a Poisson distribution centered at the average measured signal. The fits to the data are excellent and thus support our contention that the noise in the data at these coverages is random noise. Furthermore, it is obvious that such a distribution will not fit Figure 3b–d. However, it looks like these data can be fitted by a linear combination of the fits to Figure 3, a and e. This is consistent with the interpretation noted previously, that at 150, 300, and 600 Å^2/molecule we are looking at a heterogeneous surface that consists of liquidlike and gaslike regions.

We can also calculate the autocorrelation for each set of data. In Figure 4 is shown $\langle \Delta I(0)\, \Delta I(t) \rangle$ vs time for the different surface coverages. The data for 150, 300, and 600 Å^2/molecule show a monotonic decay in the correlation function, which can be fitted to an exponential. All three sets of data give approximately the same correlation time of 6 ± 1 s.

Since the high signals obtained for measurements at 150, 300, and 600 Å^2/molecule, i.e., in the coexistence region, are of the same magnitude as the signal obtained for the pure liquid state, e.g., at 75 Å^2/molecule, we conclude that the clusters are comparable in size with our incident beam. With this we make the plausible assumption that there is at most one cluster in the region of observation. We then determine the diffusion constant of the cluster from the measured correlation time and find a value of about 10^{-8} cm^2/s.

The above estimate on the size of the clusters is smaller than what is estimated by ellipsometry[8] and light scattering,[11] which also differ from each other in the gas–liquid region. The differences observed can be due to differences in the method of preparation as well as the presence of PNP in the subphase.

We believe that the fluctuations in the SH signal in Figure 2b–d are similar in origin to those observed by other techniques.[8,9,11] However, in our measurements, we are able to adjust the time resolution; this enables us to analyze the fluctuations and extract a decay constant for their time correlation. This time constant of approximately 6 s is much faster than any time dependence indicated from measurements of ellipsometry[8] and surface potential,[9] but slower than that obtained from light-scattering experiments.[11] This discrepancy could possibly be due to differences in size of the clusters as previously mentioned.

Conclusions

We have shown that fluctuations in the second harmonic signal can be utilized in the study of a heterogeneous surface, such as phase coexistence in two dimensions, as exemplified by the gas–liquid coexistence in the spread monolayer of palmitic acid. Furthermore, we have illustrated a means of examining time-dependent phenomena related to diffusion at the surface, which could be applied to other heterogeneous surface coverages. The observed fluctuations in the SH signal has a correlation time of 6 ± 1 s for the three coverages (150, 300, and 600 Å^2/molecule) that are inside the gas–liquid coexistence region. We attribute this to the motion of the liquidlike clusters. If their motion is diffusive, we estimate a diffusion constant for the clusters of about 10^{-8} cm^2/s.

Acknowledgment. We thank Prof. B. Whaley for the helpful discussions. We gratefully acknowledge support from the National Science Foundation, the Air Force Office for Scientific Research, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

[13] Cova, S.; Longoni, A. In *Analytical Laser Spectroscopy*; Omenetto, N., Ed.; Wiley: New York, 1979; Vol. 50.

A Theoretical Study of the Proton Affinities of Some Phosphorus Compounds

Robert G. A. R. Maclagan

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

(Received: December 18, 1989)

The proton affinities of PN, PO, PS, and HCP have been calculated in good agreement with values obtained from photon-transfer experiments. The effect on the calculated proton affinity of the basis set, level of theory, basis set superposition energy correction, and zero-point vibrational energy correction were studied. Protonation at the P atom is not preferred.

Introduction

The observation by Turner and Bally[1] and Ziurys[2] of PN in interstellar space has stimulated interest in the chemistry of other phosphorus-containing molecules that may exist in interstellar space. PH_3 has been observed in the Jovian atmosphere. The reactions of the ions PH_n^+ (n = 0–4) with various neutral molecules have been studied by Thorne, Anicich, and Huntress[3] and Smith, McIntosh, and Adams.[4] Maclagan[5] has carried out ab initio calculations on the ion $C_2H_2P^+$ formed in some of these reactions. Recently the proton affinity of PN, PO, PS, and HCP have been measured by Adams, McIntosh, and Smith.[6] In this paper ab initio calculations of these proton affinities are reported in very good agreement with the measured values of Adams, McIntosh, and Smith.

Except for HNP^+ and POH^+, ab initio calculations at different levels of theory and with different basis sets have been previously reported for these molecules and their protonated forms. The aim of this study is to obtain as reliable an estimate of the proton affinity using the same large basis set and high level of theory. Recent calculations include the study of Ahlrichs et al.[7] on PN, the studies of PO by Lohr and Boehm[8] and Bruna and Grein,[9] the study of HPO^+ by Nguyen, Hegarty, Ha and Brint,[10] the study

---

[1] Turner, B. E.; Bally, J. *Astrophys. J.* **1987**, *321*, L75.

[2] Ziurys, L. M. *Astrophys. J.* **1987**, *321*, L81.

[3] Thorne, L. R.; Anicich, V. G.; Huntress, W. T. *Chem. Phys. Lett.* **1983**, *98*, 162.

[4] Smith, D.; McIntosh, B. J.; Adams, N. G. *J. Chem. Phys.* **1989**, *90*, 6213.

[5] Maclagan, R. G. A. R *Chem. Phys. Lett.*, in press.

[6] Adams, N. G.; McIntosh, B. J.; Smith, D. *Astron. Astrophys.*, in press.

[7] Ahlrichs, R.; Bar, M.; Plitt, H. S.; Schnockel, H. *Chem. Phys. Lett.* **1989**, *161*, 179.

[8] Lohr, L. L.; Boehm, R. C. *J. Phys. Chem.* **1987**, *91*, 3207.

[9] Bruna, P. J.; Grein, F. *J. Phys. B: At. Mol. Phys.* **1987**, *20*, 5967.

0022-3654/90/2094-3373$02.50/0