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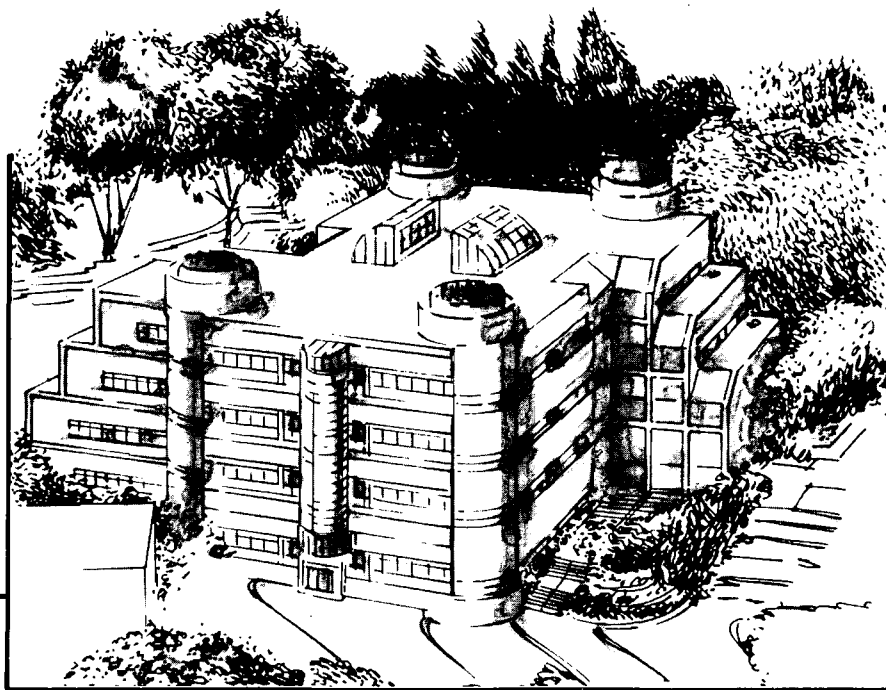
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INTERFACE STUDIES WITH NONLINEAR OPTICS

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Abstract

Optical techniques based on second-order nonlinear optical effects provide new and versatile probes for surface and interface studies.

The importance of interfaces for material science and electronic devices has stimulated great interest in the development of surface analytical tools.¹ Among them, modern optical techniques using lasers have attracted the most attention in recent years.² They have the advantage of being applicable to all interfaces accessible by light, whereas the high temporal, spatial, and spectral resolutions offer unique opportunities for studying ultrafast molecular dynamics and other transient phenomena at interfaces. Optical second harmonic generation (SHG) and sum-frequency generation (SFG) are particularly being noticed because of the many recent successful demonstrations of their versatility.³ This article is meant to give a brief introduction to these newly developed surface probes. We shall first outline the basic principles behind surface SHG and SFG, and then illustrate the power of the techniques with a number of selected examples. A more complete treatment of the theory can be found in Refs. 4-6. An overview of the earlier applications can be found in Ref. 3.

SHG arises from the nonlinear polarization $\vec{P}^{(2)}(2\omega)$ induced in a medium by an incident laser field $\vec{E}(\omega)$. In the electric dipole approximation \vec{P} is given by:

$$\vec{P}^{(2)}(2\omega) = \overleftrightarrow{\chi}^{(2)} \vec{E}(\omega) \vec{E}(\omega) , \quad (1)$$

where $\overleftrightarrow{\chi}^{(2)}$ is a second order nonlinear susceptibility. For a medium with inversion symmetry, it follows directly from Eq. (1) that $\overleftrightarrow{\chi}^{(2)} = 0$. However, at an interface, the surface nonlinear susceptibility $\overleftrightarrow{\chi}_S^{(2)}$ is nonvanishing because there, the inversion symmetry is necessarily broken. This leads to the highly surface-specific nature of the SHG

technique. The same description applies to SFG if $E(\omega)E(\omega)$ is replaced by $E(\omega_1)E(\omega_2)$ and 2ω by $\omega_1 + \omega_2$.

Consider a monolayer of molecules at an interface. The surface nonlinear susceptibility can be written in terms of the nonlinear polarizability $\alpha^{(2)}$ of the molecules:

$$(\chi_S^{(2)})_{ijk} = N_S \langle T_{ijk}^{\lambda\mu\nu} \rangle \alpha_{\lambda\mu\nu}^{(2)}, \quad (2)$$

where N_S is the number of molecules per unit area, $T_{ijk}^{\lambda\mu\nu}$ describes the coordinate transformation between the molecular (ζ, η, ξ) system and the lab (x, y, z) system, and the angular brackets $\langle \rangle$ denote an average over the molecular orientations. The SHG signal from such a monolayer is approximately given by³

$$S(2\omega) \approx \frac{32\pi^3\omega}{\hbar c^3 \epsilon(\omega)\epsilon(2\omega)^{1/2}} |\chi_S^{(2)}|^2 I^2(\omega) A T \text{ photons}, \quad (3)$$

for an input laser pulse with intensity $I(\omega)$, cross-section A , and pulsewidth T . For a monolayer of molecules, $\chi_S^{(2)}$ (more correctly, $\chi_S^{(2)}$ here should include the Fresnel factors for the transmission and reflection of the fields at the interface) is of the order of 10^{-17} - 10^{-14} esu. A pulsed Nd:YAG laser at $1.06 \mu\text{m}$ with $I = 10 \text{ MW/cm}^2$, $A = 0.2 \text{ cm}^2$ and $T = 10 \text{ nsec}$ would yield $S = 1$ - 10^6 photons/pulse. Such a signal is easily detectable and indicates the submonolayer sensitivity of the technique.

The surface specificity and sensitivity of SHG can be exploited to study the adsorption and desorption of molecular monolayers on clean metal surfaces.^{7,8} An example is shown in Fig. 1, where SHG is used to

monitor the adsorption of CO on Cu(100). Similar experiments on semiconductors^{9,10} and insulators¹¹ at various interfaces have been carried out. A study of the origin of the surface susceptibility of bare surfaces shows that SHG is sensitive to the crystalline order of a surface.¹⁰ This has been exploited to observe the dynamics of surface melting,¹² reconstruction¹⁰ and disordering.¹³

For simple molecules where the nonlinearity is dominated by a single component, SHG with different polarization combinations can be used to determine the orientation of molecules at an interface. An interesting example is shown in Fig. 2, where the orientation of the surfactant pentadecanoic acid (PDA) at an air-water interface is plotted as a function of its surface density.¹⁴ The kink in Fig. 2 actually signifies a two-dimensional phase transition of this system. One can also study the effect of environment on the surfactant orientation. For example, for sodium-dodecyl-naphthalene sulfonate we found that its orientations at water-air, water-decane and water-carbon tetrachloride interfaces are at 13° to 21° to 38° from the surface normal, respectively.¹⁵

Because of the monolayer sensitivity, SHG can also be used for monolayer surface microscopy to probe the arrangement of molecular adsorbates at an interface.¹⁶ Figure 3 provides an example. It is shown that SHG scanned over a surface can be used to find an 8- μ m hole in a monolayer of rhodamine 6G on glass. Such a surface microscope could find important applications in many disciplines.

The recent progress in opto-electronics has stimulated considerable interest in finding novel nonlinear optical materials. Organic materials are particularly attractive because they could be inexpensive

and easy to synthesize. In searching for suitable organic materials, it is necessary to determine the nonlinear polarizabilities of the organic molecules. Recently we have shown how one can conveniently measure $\alpha^{(2)}$ of such molecules by spreading them as Langmuir films at a water-air interface and measuring their SHG.¹⁷ By systematically varying the structure one can obtain insight in the relation between molecular structure and nonlinearity. For real opto-electronic devices, thin organic films would be needed, and SHG can be used to measure the molecular ordering in such films.¹⁸

Polymerization of monolayers is of fundamental interest since its reactivity and kinetics may then be studied under controllable and variable conditions of molecular separation and orientation. The breaking of carbon-carbon double bonds upon polymerization will cause a reduction of $\alpha^{(2)}$ and thus of $S(2\omega)$. SHG can therefore be used to follow the kinetics of the polymerization of a monolayer of monomers. This has recently been demonstrated using vinyl stearate and octadecyl methacrylate.¹⁹

SHG can also find applications in studying biological materials. As an example, we have used it to deduce the change of the dipole moment $\Delta\mu$ of a series of retinal molecules (responsible for the visual process) upon optical excitation.²⁰ This is possible because of the existing relation between $\Delta\mu$ and $\alpha^{(2)}$. Obviously, specific molecules imbedded in or adsorbed on a membrane can also be investigated using SHG.

Electrochemistry governs many important surface reaction processes such as electrolysis and corrosion. SHG can be exploited to study these processes in-situ at various interfaces. It has already been

demonstrated that SHG can follow the adsorption and desorption of a monolayer of molecules at an electrode in an electrolytical cycle,²¹ the adsorption of ions at an electrode to form a double charge layer,²² and the surface reconstruction of a single crystalline electrode after electrolytical cycling.²³

Though surface SHG is a versatile and sensitive interface probe, it is usually not operable in the infrared because of limitations in the detector sensitivity. It therefore lacks the power to identify molecular species through their vibrational spectra. This can be remedied, however, by extending the technique to infrared-visible sum-frequency generation (SFG) using a tunable infrared laser.²⁴ The infrared beam excites the vibrational resonance, which shows up as resonant enhancement in the SFG output in the visible. The surface sensitivity of SFG can then be as good as that of SHG.

We mentioned earlier how SHG could be used to obtain the orientation of molecules at an interface. Now, with SFG, we can be even more specific, in the sense that we can determine the orientation of a particular group of atoms in a molecule, for example, the terminal CH₃ group of a long alkyl chain.²⁵ Figure 4 shows the spectra of the CH stretch vibrations of PDA at different surface densities with different input laser polarizations. The change of the spectra can be explained by the fact that PDA molecules tilt and bend at low surface densities. With SFG, one can also do surface vibrational spectroscopy at liquid/solid interfaces, and selectively study in-situ the adsorption of particular molecular species at such interfaces.²⁶ An example is shown in Fig. 5 for the adsorption of octadecyltrichlorosilane (OTS).

In this paper we have tried to give an overview of the novel possibilities that the nonlinear optical techniques can offer for the study of interfaces. The high sensitivity and the fact that the techniques are applicable to almost all interfaces led to many unique research opportunities. Many others are yet to be explored. The most attractive aspects of SHG and SFG are probably the possibilities of probing surfaces in an hostile environment and surface dynamics and reactions with an ultrafast time resolution.

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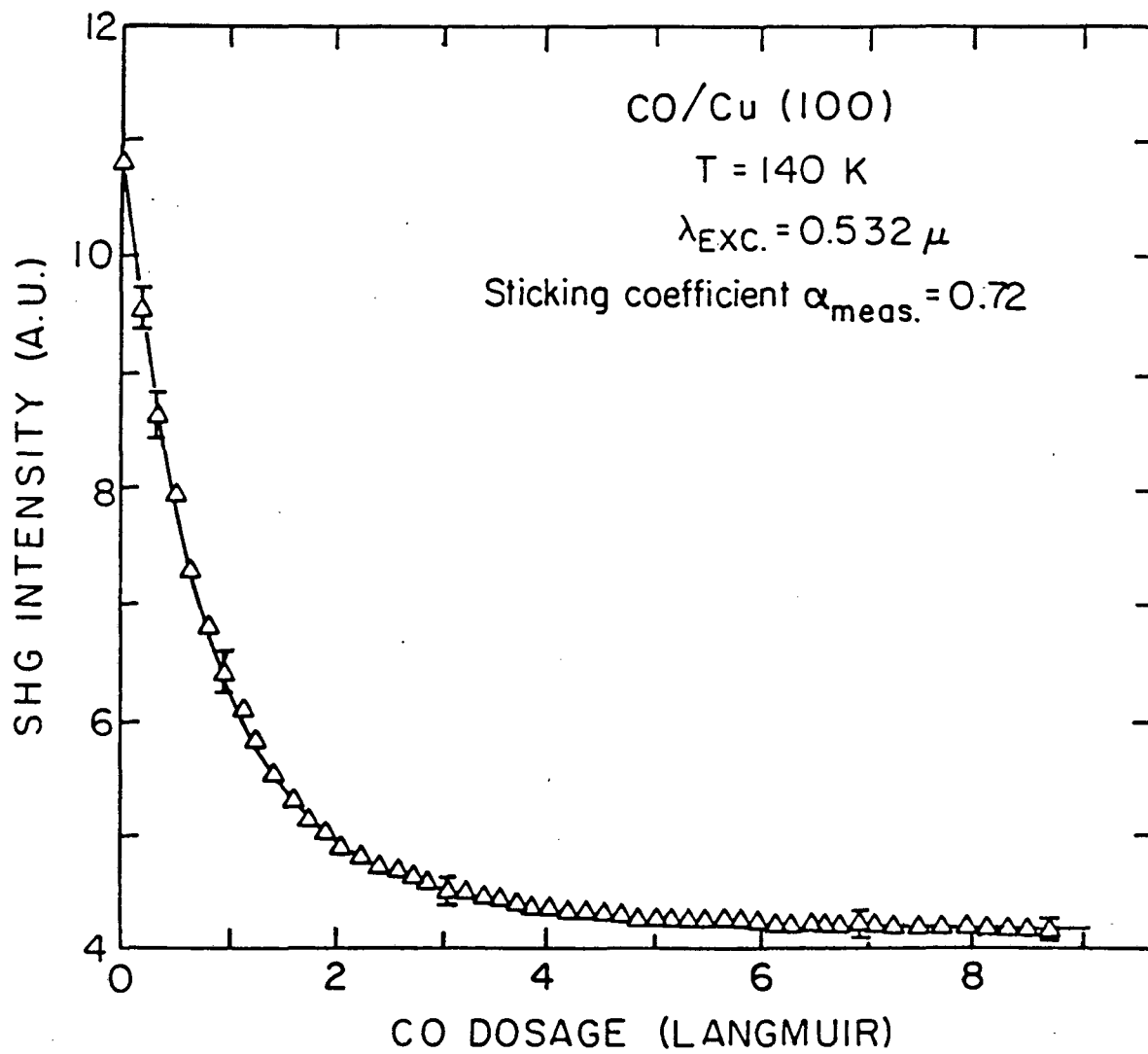
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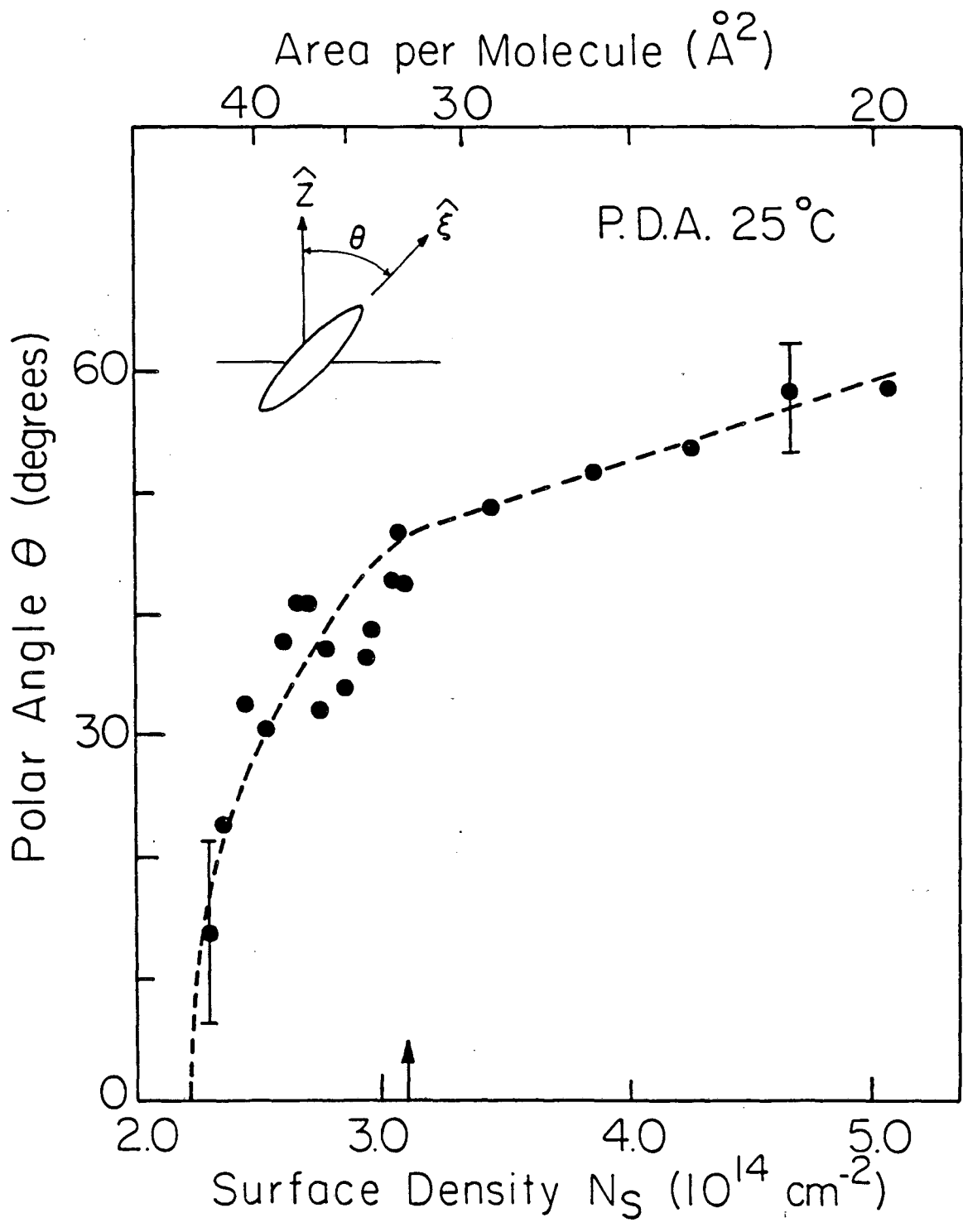
Figure Captions

- Fig. 1 Second harmonic generation as a function of surface coverage of CO on Cu(100) at 140 K. The solid theoretical curve derived from the Langmuir kinetic model is used to fit the experimental data points (Δ), from which the sticking coefficient for CO on Cu(100) is deduced.
- Fig. 2 Tilt angle θ between the molecular axis and the surface normal as a function of the surface density of PDA on water.
- Fig. 3 Second harmonic image of a laser-ablated hole in a Rhodamine 6G dye monolayer on a fused quartz substrate.
- Fig. 4 SFG spectra of a monolayer of PDA on water at various densities.
- Fig. 5 Adsorption of OTS at a solid-liquid interface as a function of time monitored by SFG.



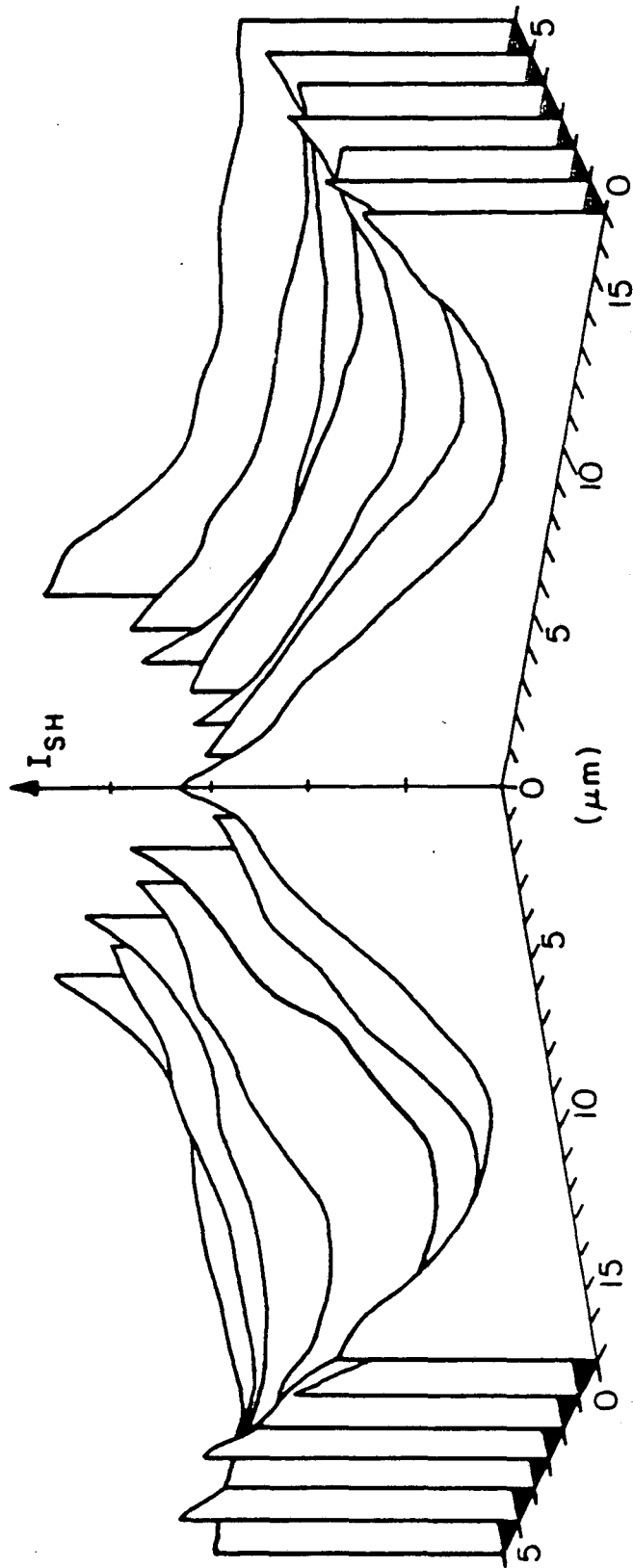
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Fig. 1



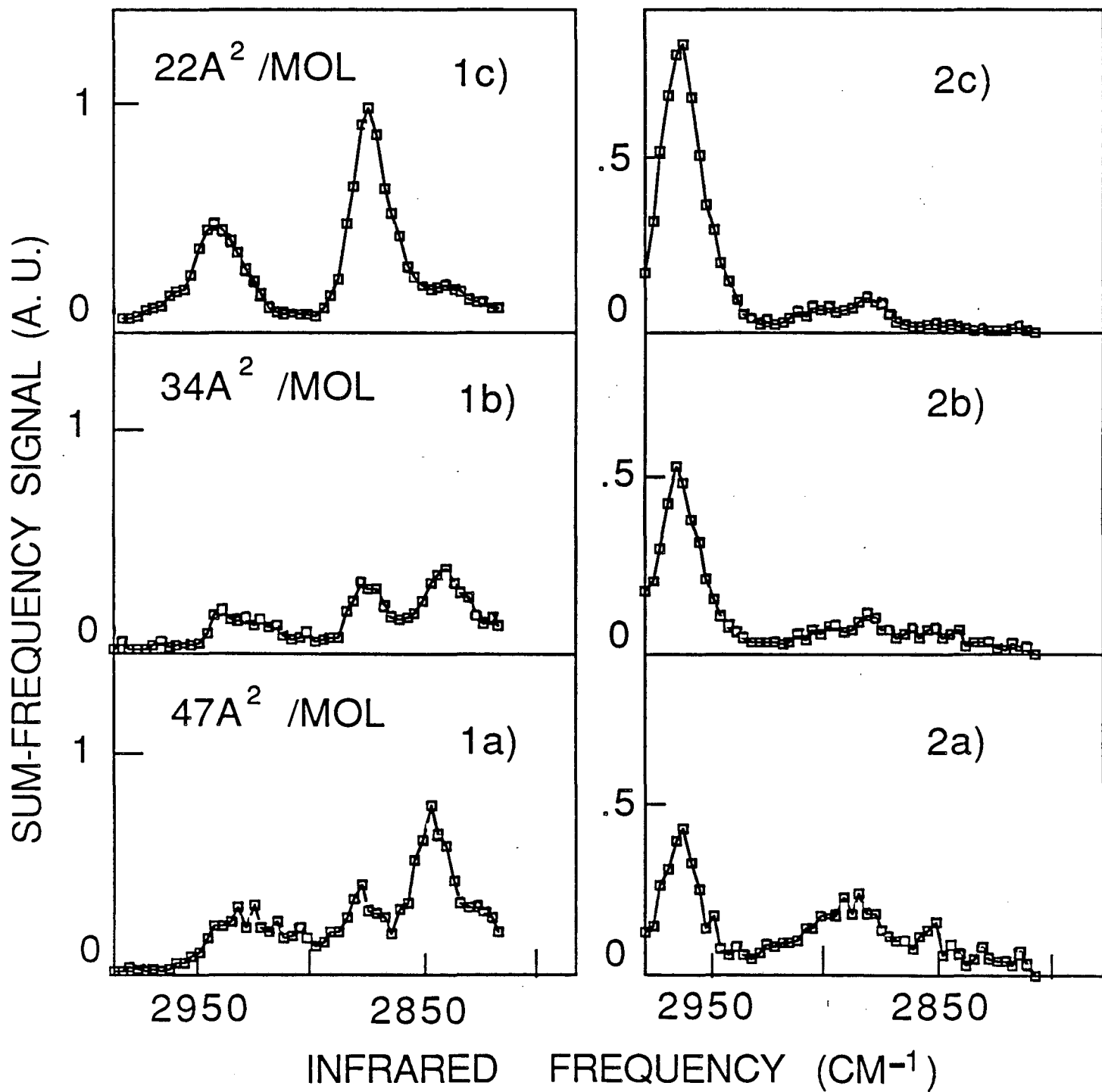
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Fig. 2



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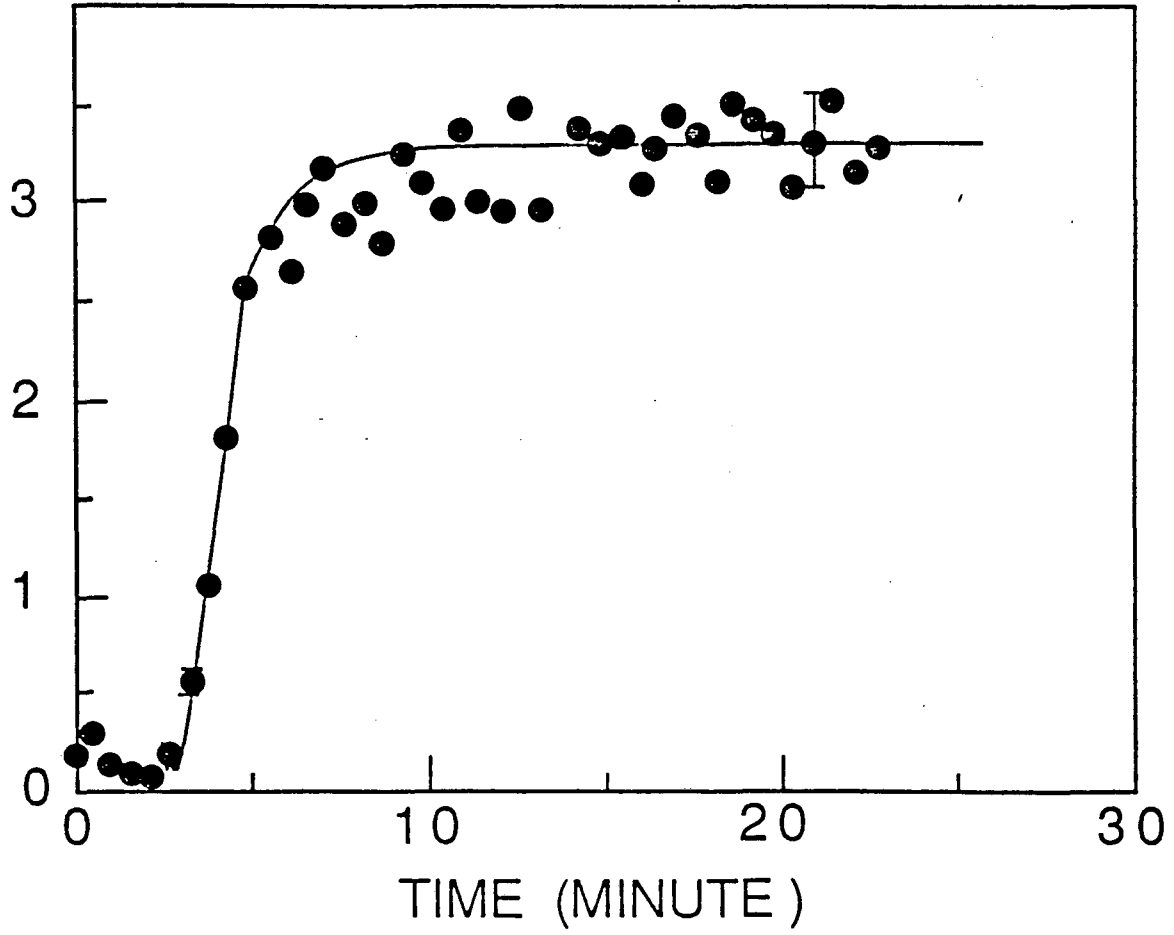
FIG. 3



- XBL 877-3072 -

Fig. 4

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-- XBL 8711-4603 --

Fig. 5

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