### **Announcements**

- To join clicker to class today (Clickers with LCD display join automatically):
- Turn on the Clicker (the red LED comes on).
- Push *d* oin button followed by *d* or followed by the *d* send button (switches to flashing green LED if successful).
  - No shorts, sandals or skirts allowed in Lab!!
  - Volunteer to help with Earth Day Science Fun



# Review

- Greenhouse effect from absorption of IR radiation by gases in the atmosphere
  - only gases with polar bonds can absorb IR
  - not all effective because of where they absorb.
  - Change in <sup>14</sup>C:<sup>12</sup>C ratios in atmosphere indicate that most of the growth in CO<sub>2</sub> is due to combustion of fossil fuels.
  - Predictions are 1-5 °C change in average temperature => significant sea level rise and changes in weather.
  - Science is not definite, what we do is a political decision.
- IR spectroscopy observes energy absorption which excites molecular vibrations.
  - can be used to identify molecules since particular bonds absorb at particular energies.
    - Trend: triple stronger than double stronger than single
    - shorter wavelength suggests stronger bond => single bond absorbs at longest wavelength.
  - Homonuclear diatomics have nonpolar bonds and do not absorb IR.

### IR spectra of some atmospheric gases





### Sur]-OH + $Zn(CH_3)_2 \rightarrow Sur$ ]-O-Zn-CH<sub>3</sub> + CH<sub>4</sub>



## Experimental Technique for Monitoring what's on a Surface Versus Time







Figure 8: Time resolved infrared spectra of near surface water replacing THF. The positive peaks are from water, negative from the THF that is leaving. The inset is to emphasize the peak shape difference between bulk and near surface water.

### Kinetics of solvent association with surfaces investigated using IR spectroscopy

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### Introduction

These studies gives out of atempts to understand the strem and out generics of purchase nearching with the constantiauts as of cognitives silicon. We have previously those in postantial and a giving 2004 thread theory of the silicon and the silicon and the theory of the silicon and the silicon and the silicon from the observation and silicon and the silicon from the solution and the silicon and the silicon from the solution and the silicon and the silicon from the solution and the silicon and the silicon from the solution and the silicon and the silicon from the solution and the silicon and the silicon from the solution and the silicon and the silicon from the solution and the solution and the solution from and the solution and the solution and the solution from and solution and the solution and the solution and the solution silicon and the solution and the solution and the solution of silicon and the solution and the solution

As an inclusion of our sensibly to species at the surface figure 1 shows a trace surface active conten insurf in berranes displacing berranes at the surface after the berrane displaced carbon tetraditoria.

Experimental

A officen attenziated total Hearnal Auflection (ATTI) rot was invised with water and offstred, then all diffect. The dry crystal frain was planns claused for one minute in an approximably 200 micro water was poor admosphere axing a frainfor Plasma clauser. The clauser crystal was placed into the local and invised with 50-100 mil. of the first achiever. The coll was allowed by off or all was it hear with the first achiever.

Data Collection

Data were collected using Ownic Series settware and a News 670 PT-IH from Nicolot. Date were transferred to igerPro (Wavemetrics) for

analysis. Specific were averaged logather in blocks of about 38 seconds at a resolution of 2.

before data collection.

Surface Preparation

# Figer 1. Take containing the two sets of two sets of the two sets of t

Figure 1: Tack contain fair to benchmer displacing benchmers at the surface. The negative going peaks (new 1000 on ") surface the disappearing benchmer signal. The positive peaks are the contain frant. Inset is upsection at about 4000 seconds (pick plane). The built signal from bencame has been retroved. (See section on Data Processing and Pigure 5).

### Data Processing

### Removing the Bulk Signal

Spectra are code districteremento ta a californsistering the his incluser. Read an contare in the last packs that are draring rights to the tilting of spectra that are draring rights to the tilting of spectra three uses and about 30 belowing the disappearance of pasks typical of the bulk and the packs and the pask of the bulk and the spectra three ups a very spicing courts or disappearance of pasks typical of the bulk and the pack of the spectra term and the spectra term the term of the spectra term and the spectra term the spectra of the spectra term and the spectra term the spectra of the spectra term and the spectra term contained the right spectra of the spectra term term and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the right single of the spectra term chains and the spectra term chains and the spectra term chains and the spectra term chains term t

### Data Processing Species Specific Kinetics

Each spectrum is treated as a fine at combine for of spectra (S ) from all the spectra involves:

$$\label{eq:spectrum(i)} \begin{split} &= a_1(iG_1+a_2(i)G_2+a_3(iG_3+\ldots,(1))) \\ &= b_1(iG_3+a_3(i)) \\ &= b_2(i) \\ &= b_2(iG_3+a_3) \\ &= b_3(iG_3+a_3) \\ &= b_3$$

gails well, but does not account for changes in peak shape that might be expected as interactions with nell phooing molecules change. The separate spectra S, can be projected out of the data matrix

uning the computational matrix algorithm singular value discomposition. This tesh space is conventione allogical reals composed and space and in other used to remove industrion ing treats contributions of the S<sub>2</sub>. We control the successfully matrix the space should be also be also be also be also be presented and the space should be also be the treat requests that the space should be also be treated to be also be also be treated to be also be also be also be treated by the scale to be also be the scale to be the space of the space of the space of the scale be also be treated to be the space of the space of the space of the scale be also be treated to be the space of the space of the scale be also be treated to be the space of the spa



Figure 5: Contributing spectra (5) estructed from data in figure 4, using singular value, decomposition principles composed availages (5) estrume (1) strucpercenter and water that are being restored, capactum 7 has control decomposition from airlying peak trappes from 7 has control approximation of the figure and may include combactions from airlying peak trappes from that the supercrime is over internetly and that the temporarib behavior augments it is mostly note (size (Spec 6).



Figure 6: Amplitude of contributions versus the (a) for the spectra estracted from data in Figure 4 using algular value electroposition (principle component analysis). Note that the third spectrum is mostly a noise contribution.



Figure 12: Contributions to the total signal from THF on the surface and in the near surface regional determined by the model for THF region ghoranew. Roles that the surface THF leads the near surface THF in contrast to the case where water replaca THF. See Figure 4 for the time do parador if ge data.

### Kinetic Model

The model consists of three layers (see ligure 7): I three lower built solution with a fixed concentrason; 2) the near autros solution which exchanges not ead as within the lower built at a rain that depends on 9 our rais; and 3) the autros to which neares out were on other molecular at solution. The model induces to a system of two nonlinear coupled differential all equations:

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 $[b]_{0}$  and incomunities density [Mi], once and rate construction  $[b]_{0}$  with concentration  $[b]_{0}$  with the context of the same of the second state is a concentration to the context is the same of the second state is a concentrate to the same of the second state is a concentrate to the same of the second state is a concentrate to the same of the second state is a concentrate to the same of the second state is a concentrate to the same of the second state is a concentrate to the same second state is a concentrate to the same second state is a concentration of the second state is a concentration to the same second state is a concentrate state.



Figure 7: Canton representation of the line do model used of the fister within of the signal. The Riswig bulk solution is assumed to have a constant condition (the para solution of constraints) in the data parameterial here). The near subcase adution of the solution of solid or solution of the solution. The solution of the solution of solid or solid or solid or solid paralle a weighted and of galant of solid for the near starbase adutors and subcase. The signal from the bulk and data of a solid or solid or solid or solid or solid paralle is neighted and of galant of solid for the host and data of the solid solid for the solid solid parallel. The solid solid for the solid parameters of parallel.

### Conclusion

The proposal linetic model file the obtained data well. The time behavior of the model contributions to the signal constitute that the second control come point model and the second second that many point models in the second second second and second second second second second second and second second second second second second term objects and second second second second term objects and second second second second period second period second second second second second period second second second second second period second second

### References

 W. H. Press, B. P. Parnery, S. A. Technoloky, W. T. Vetterining, *Namarcal Accipies: The Art of Scientific Computing, Cartibridge Univ. Press,* 1996.

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Results

Fits to Water Displacing THF Data

signal has been removed. Figure 9 shows the time dependence of the appearance of water signal (the deappearance of THF

has the same behavior only it is negative going). Also shown in this figure area clouble exponential fit and the fit using the pro-

posed kinelic model. Notice how much better the model flatthe data in the turnover region. Add tone by, the model correctly peed duthe initial induction peed of before the signal begins to

grow. This can be seen as a kink in the data rear time per oard as a kink in the surface water tace in Figure 10. Figure 10

shows the two contributions to the total signal. Notice that the surface contribution trails the near surface solution contribution.

This suggests that it is relatively hardfor water to displace the polar THP from the surface. This is to be contrasted with the rel

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Figure 10: Contributions to the total signal from water on the sur-

face and in the near surface region as determined by the reside It to water replacing THF at the surface. Notice that the surface

where the replaced be near surface, water in contrast to the case where THF replaced becomes.

alve scan with which polar THF displaces nonpolar benzene fore the surface (Swe Figures 4, 11 and 12)



Figure B: Time resolved infrared specta, of near surface water wplading THF. The positive peaks are from water, negative from the THF that is leaving. The inset is to emphasize the peak indeps offlements between bulk and near surface water.



Figure B. Fits to the time dependence of the signal as water replaces THF. The red curve uses the model described in this poster. The blue surve is a fit using a double exponential. The residuals are to the model fit.



Figure 3: First 350 seconds of raw data from benzene replacing CCIs. The benzene signal stabilizes by the third spectrum (76 seconds). CCIs has no IR absorbance in this spectra irregion.



replaces bergrene. The red carve uses there colei described in this poster. The blue carve is a ft using a double exponential. The residuals as for the red eitz.

### Results

### Fits to THF Displacing Benzene Data

Figure a science the spectra of THF replacing became wher the object special backwarm removed. Figure 11 shows their the dependence of the appearance of THF signal the data ppearance of becames the same backward replace the the science of the spectra of the signal the science of the science of the signal the science of the science science of the science of the science science of the science of the science science of the science of the science science science science science of the science science science science science of the science science

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