

Lawrence Berkeley National Laboratory

Recent Work

Title

Surface Vibrational Spectroscopy of Pure Liquids

Permalink

<https://escholarship.org/uc/item/4712r3ns>

Authors

Superfine, R.

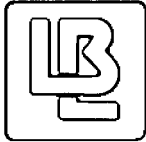
Huang, J.Y.

Du, Q.

et al.

Publication Date

1991-03-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

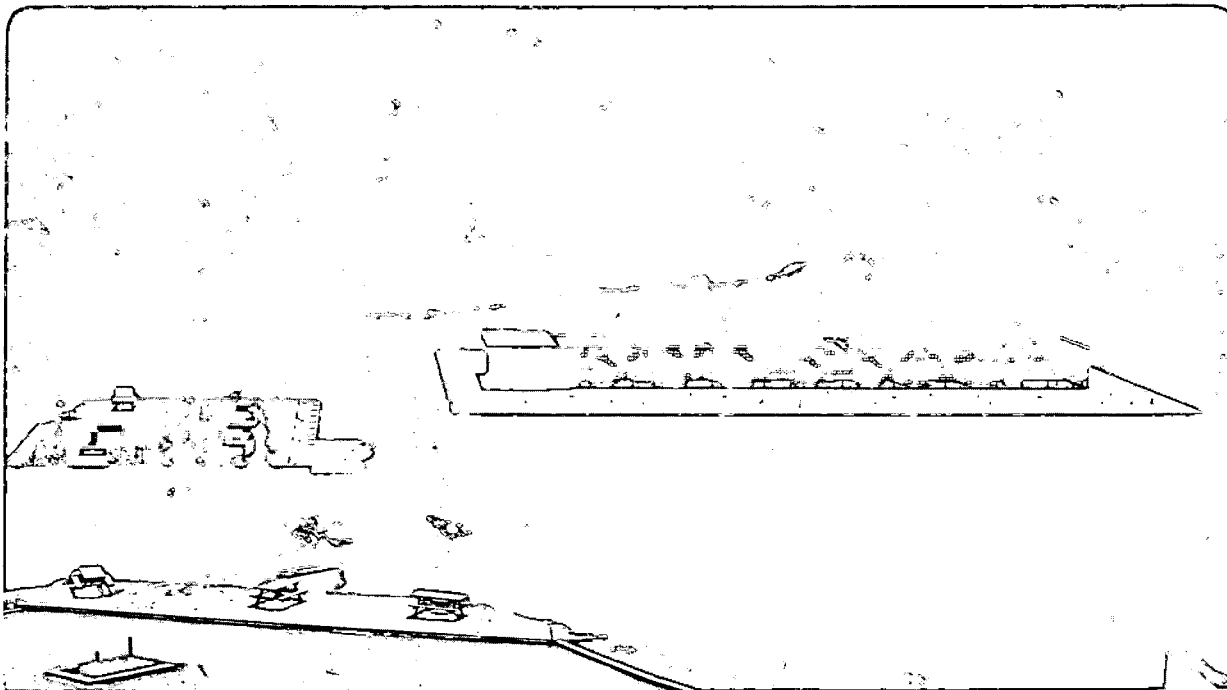
Materials & Chemical Sciences Division

Presented at the 10th International Conference on Laser Spectroscopy,
Strasbourg, France, June 17-21, 1991, and to be published in the Proceedings
of the International Union of Pure and Applied Chemistry, *Review Letters*

Two-Dimensional Carrier-Carrier Screening in a Quantum Well Surface Vibrational Spectroscopy of Pure Liquids

J.-Y. Bigot, M.T. Portella, R.W. Schoenlein, J.E. Cunningham, and C.V. Shank
R. Superfine, J.Y. Huang, Q. Du, and Y.R. Shen

July 1991
March 1991



LOAN COPY |
Circulates |
for 4 weeks |
Bldg. 50 Library.

LBL-30723

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Surface Vibrational Spectroscopy of Pure Liquids

R. Superfine, J. Y. Huang, Q. Du, and Y.R. Shen

Department of Physics
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

March 1991

SURFACE VIBRATIONAL SPECTROSCOPY OF PURE LIQUIDS

R. Superfine, J. Y. Huang, Q. Du and Y. R. Shen
*Department of Physics, University of California, and
Materials Sciences Division, Lawrence Berkeley Laboratory,
Berkeley, California, 94720*

ABSTRACT

We report the use of infrared visible sum frequency generation (SFG) to obtain the surface vibrational spectra of pure liquid methanol and water. These are the first surface vibrational spectra ever obtained for pure liquids. We have also deduced from the SFG results the absolute orientations of molecules at the pure liquid/vapor interface. The surface methanol molecules appear to have their CH₃ groups projecting out of the liquid in agreement with the theoretical prediction. For the orientation of surface water molecules, however, different calculations have yielded very different predictions. Our SFG measurement provides clear evidence that the molecules are oriented with an unbonded hydrogen projecting out of the liquid.

The structure and properties of liquid interfaces are of vital interest to many areas of science and technology.¹ Unfortunately, our understanding has been impeded by the lack of experimental probes due to two difficulties. First, the experimental technique must distinguish between the surface and bulk molecules. Second, it must be applicable at ambient pressures or to buried interfaces. These challenges are met by second order nonlinear optical techniques, which recently have been demonstrated to be versatile probes of liquid interfaces.² In particular, infrared-visible sum frequency generation (SFG) can measure the vibrational spectrum of surface monolayers to obtain information about their molecular orientation, conformation and interaction³.

We have applied SFG to study the pure liquid/vapor interfaces of two liquids in which intermolecular interaction is dominated by hydrogen bonding: water and methanol. While water is the most important liquid, methanol is the simplest molecule to possess both hydrophobic and hydrophilic moieties. Hydrogen bonding is a fundamental molecular interaction in nature and is thought to determine interfacial liquid structure in many important chemical and biological systems.⁴

The theoretical background and experimental details of SFG have been presented elsewhere.³ A modelocked Nd:YAG laser in conjunction with frequency doubling and a LiNbO₃ optical parametric amplifier provide 15ps pulses at .532 μ m (.5mj) and tunable infrared radiation between 2.6 to 4 μ m (~.2mj). The two beams are overlapped on the liquid surface at a focus about 500 μ m in diameter. The signal level from the symmetric stretch of the methanol CH₃ group at the liquid/vapor interface is about 50 photons/pulse, readily detectable with standard photon counting techniques. The liquid is contained in a teflon trough and absorption of the infrared beam in the vapor is kept below 5% by making the beam path less than 5mm.

The effective susceptibility that describes the nonlinear optical response of the interface of an isotropic medium can be written as the sum of three parts: a surface

dipole susceptibility due to the breaking of inversion symmetry, and two quadrupole susceptibilities, one from the surface, the other from the bulk.⁵ Our tasks are first, to deduce the surface contribution, and second, to determine the surface dipole susceptibility which can be related to the orientation of the molecules at the interface.

Fig.1 shows the SFG spectrum from the methanol pure liquid/vapor interface over the CH stretch region.⁶ The peak at 2832 cm⁻¹ comes from the symmetric (ν_s) stretch of the CH₃ group. The peaks at 2925 and 2951 cm⁻¹ have been assigned in Raman scattering studies to two Fermi resonances of the CH₃ ν_s mode with overtones of the CH₃ bending modes. How can we experimentally determine if the SFG spectrum is from the interface?

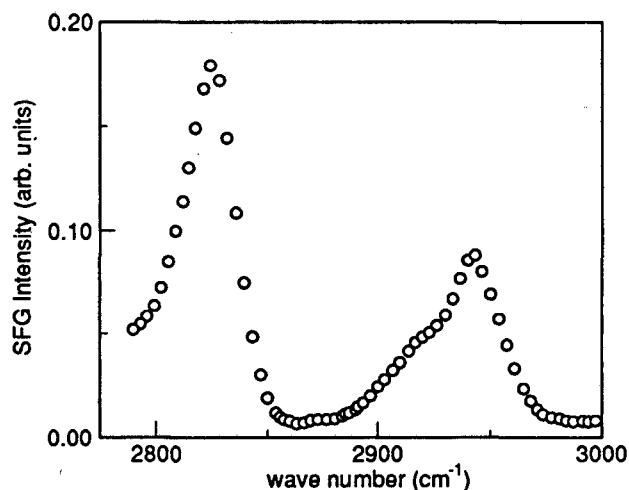


Fig. 1. SFG spectrum obtained from the liquid/vapor interface of pure methanol. The beam polarizations are *s*, *s*, and *p* for the sum frequency, visible (0.532 μm), and infrared beams, respectively.

To be sure that the spectrum is from the interface, we have performed the following experiments. First, we measure the bulk nonlinear susceptibility and find that its contribution to surface SFG is indeed negligible. Second, we measure the spectrum from the liquid/vapor interface of the water:methanol solution (1:1). As seen in Fig.2, we find that the 7 cm⁻¹ shift in the bulk infrared absorption spectrum of the mixture is not shared by the SFG spectrum. Therefore the observed spectra must be dominated by the interface contribution. We have further established in a separate experiment that the surface SFG signal is largely due to the surface dipole contribution.⁶ The results indicate that the observed SFG spectrum must come from a polar oriented layer of methanol molecules at the liquid/vapor interface.

What can we say about the absolute orientation of the surface methanol molecules, i.e., whether the CH₃ group is pointing inward or outward from the liquid? This information is contained in the sign of the surface nonlinear susceptibility, which

can be determined by a nonlinear phase measurement. By comparing the phase of the SFG signal from the methanol liquid/vapor interface with the phase of SFG from an adsorbed methoxy layer on quartz of known orientation, we have determined that the methanol molecules at the liquid/vapor interface are oriented with the CH_3 group pointing towards the vapor. This is consistent with the physical picture that the surface molecules should be orientationally ordered to maximize the number of hydrogen bonds at the surface, as substantiated by computer simulation.⁷ Furthermore, by comparing the spectrum from the methanol liquid/vapor interface with that from an ordered monolayer of CH_3 groups in a pentadecanoic acid monolayer film on water we have concluded that the orientational distribution is very broad, consistent with the dynamic nature of the interface.

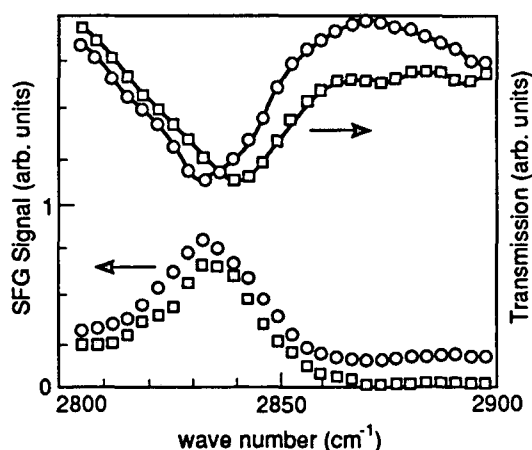


Fig. 2. Comparison of the bulk IR absorption spectra (top) with the reflected surface SFG spectra for pure methanol (circles) and for a 1:1 water/methanol solution (squares). All spectra are normalized and the two SFG spectra are shifted vertically from each other for clarity

While the ordering of the methanol surface can be simply understood in terms of the amphiphilic nature of the molecule, the water liquid/vapor interface is much more subtle. Any of the four tetrahedral sites of the water molecule, the two hydrogens or the two oxygen lone pairs, can participate in a hydrogen bond.⁴ Fig.3 shows the SFG spectrum of the OH stretch modes from the liquid/vapor interface of pure water. The broad region between 3200 and 3500 cm^{-1} is assigned to OH modes with H bonded to a neighboring molecule. The isolated peak at 3690 cm^{-1} has been observed in infrared absorption measurements of water clusters and is clearly identified as the H-unbonded OH mode of a water molecule whose other H is bonded to a neighboring molecule.⁸

The 3690 cm^{-1} peak is established as a surface feature by two observations. First, it lies well outside of the bulk absorption band. Second, as seen in Fig.3, the peak changes dramatically upon modification of the surface by the deposition of a long chain alcohol monolayer. The latter observation is due to the quenching of the

unbonded OH of the pure water surface by the adsorption of alcohol. Furthermore, the change in the bonded OH spectral region between 3200 and 3500 cm^{-1} indicates that the water layer underneath the alcohol monolayer has become more structured. The existence of free OH bonds at the water liquid/vapor interface is in qualitative agreement with the recent molecular dynamics simulations.⁹

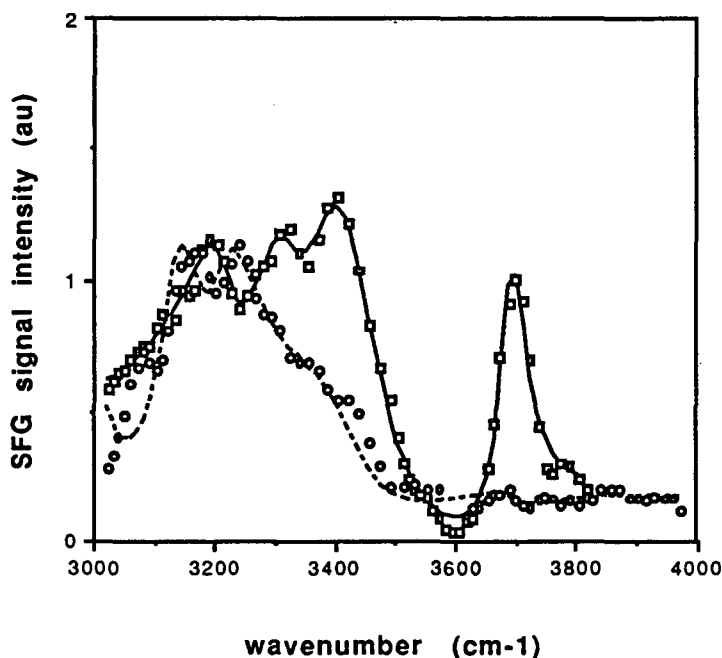


Fig 3. SFG spectrum from the liquid/vapor interface of water with beam polarizations s,s and p as in Fig. 1. Spectrum of clean surface (squares) is compared with surface after deposition of stearyl alcohol monolayer compressed to $22\text{\AA}^2/\text{molecule}$ (circles).

In conclusion, we have presented the first surface vibrational spectra obtained from pure liquids. The molecules at the methanol liquid/vapor interface appear to have the CH_3 group projecting into the vapor in order to maximize the number of hydrogen bonds at the interface. The SFG spectrum from the pure water surface provides direct evidence for the presence of water molecules oriented with a single unbonded OH group projecting out of the liquid. These studies demonstrate the enormous potential of SFG to study heretofore inaccessible liquid interfaces.

RS gratefully acknowledges generous support from the 3M Company. JYH acknowledges the support of an IBM postdoctoral fellowship. This work was supported by Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

1. *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986)
2. Y. R. Shen, *Annu. Rev. Phys. Chem.* **40**, 327 (1989); *Nature (London)* **337**, 519 (1989), and references therein.
3. P. Guyot-Sionnest, J. H. Hunt, and Y. R. Shen, *Phys. Rev. Lett.* **59**, 1597 (1988); J. Y. Huang, R. Superfine and Y. R. Shen, *Phys. Rev. B*, **42**, 3660 (1990).
4. K. D. Collins and M. W. Washabaugh, *Quarterly Rev. Biophys.* **18**, 323 (1985); *The Hydrogen Bond*, edited by P. Schuster, G. Zundel and G. Sandorfy (North Holland, Amsterdam, 1976).
5. P. Guyot-Sionnest and Y. R. Shen, *Phys. Rev. B* **38**, 7985 (1988); **35**, 4420 (1987).
6. R. Superfine, J. Y. Huang and Y. R. Shen, *Phys. Rev. Lett.* **66**, 1066 (1991).
7. M. Matsumoto and Y. Kataoka, *J. Chem. Phys.* **90**, 2398 (1988).
8. M. F. Vernon et al., *J. Chem. Phys.* **77**, 47 (1982); R. H. Page et al., *Chem. Phys. Lett.* **141**, 1 (1987); D. F. Coker, R. E. Miller and R. O. Watts, *J. Chem. Phys.* **82**, 3554 (1985).
9. M. A. Wilson, A. Pohorille, and L. Pratt, *J. Phys. Chem.* **91**, 4873 (1987); M. Matsumoto and Y. Kataoka, *J. Chem. Phys.* **88**, 3233 (1988)

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720