

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231675204>

In Situ Characterization of Adsorbates in Solid–Liquid Interfaces by Reflection–Absorption Infrared Spectroscopy

ARTICLE *in* LANGMUIR · MARCH 2003

Impact Factor: 4.46 · DOI: 10.1021/la027031n

CITATIONS

45

READS

14

3 AUTHORS, INCLUDING:



Zhen Ma

Fudan University

98 PUBLICATIONS 2,145 CITATIONS

SEE PROFILE



Francisco Zaera

University of California, Riverside

372 PUBLICATIONS 11,993 CITATIONS

SEE PROFILE

In Situ Characterization of Adsorbates in Solid–Liquid Interfaces by Reflection–Absorption Infrared Spectroscopy

Jun Kubota,[†] Zhen Ma, and Francisco Zaera*

Department of Chemistry, University of California, Riverside, California 92521

Received December 18, 2002. In Final Form: February 1, 2003

A cell has been designed for the in situ characterization of catalytic intermediates adsorbed at liquid–solid interfaces by single-reflection infrared spectroscopy. The design of our cell is based on previous setups used for the study of electrochemical systems, and consists of a cylindrical Teflon body terminated by a calcium fluoride prism cut in a trapezoidal shape with two faces beveled to 60° to let the infrared beam in and out of the cell on one end and by a polished platinum disk (the solid sample) mounted on a retractable rod on the other. The solid sample is cleaned by repeated electrochemical oxidation–reduction cycles using KClO₄, HClO₄, or H₂SO₄ electrolytes, and a thin liquid film is then trapped between the two surfaces for the liquid–solid adsorption studies. The performance of this cell was first tested by studies on the adsorption of carbon monoxide from 1.0 M H₂SO₄ solutions. Significant signals were detected for the adsorbed CO, comparable to those seen under vacuum or under high pressures of CO gas, and also to data reported previously. A more detailed characterization of our experimental setup was carried out with cinchona alkaloids. Discrimination between adsorbed and dissolved species was accomplished by dividing spectra obtained with p- and s-polarized light, and was corroborated by a number of tests, including a variation in the liquid film thickness and the nature of the adsorbing surface. The importance of the in situ characterization was assessed by comparing spectra for quinoline deposited under vacuum versus adsorbed from a carbon tetrachloride solution.

Introduction

With the advent of new surface-sensitive techniques over the last few decades, considerable effort has been directed at the study of catalytic problems. Originally, as vacuum technology was developed, a number of electron, ion, and other particle-based techniques were designed to probe surfaces.¹ While the penetrating power of photons renders most optical techniques surface insensitive, the strong interaction of electrons and ions with condensed matter makes those particles incapable of traveling deeply into solids, and therefore ideal for providing information on the chemical and physical characteristics of the few outer layers of the solid under study. Thanks to the availability of those modern surface-sensitive techniques, a large body of work is now available in the literature about the details of the adsorption and reactivity of many chemical species of relevance to heterogeneous catalysis and other systems.^{2–4}

Modern surface science has indeed been quite instrumental in advancing our molecular-level understanding of heterogeneous catalysis. At the same time, however, it has allowed us to appreciate the high degree of complexity and the importance of subtle effects in catalytic activity and selectivity. Catalysis relies on kinetic factors, and operates by lowering the activation barriers of desirable reactions.⁵ When considering catalytic selectivity, what

matters is the relative barrier height of the reaction of interest compared to those of other undesirable side steps.⁶ Small changes in those relative values can easily lead to significant changes in the distribution of products obtained in catalytic processes.⁷ In particular, it has become apparent that catalytic selectivity can be affected by factors such as changes in the local environments of adsorbed intermediates. This has underscored the need for characterization studies in situ under catalytic conditions.

In view of this desire to study catalytic reactions in situ in nonvacuum environments, the initial idea of replacing optical spectroscopies by particle-based probes has been recently revisited.⁸ Indeed, several optical spectroscopies such as reflection–absorption infrared spectroscopy,^{9,10} surface-enhanced Raman spectroscopy,^{11,12} and second-harmonic and sum-frequency generation^{13,14} have been successfully used to characterize solid surfaces under vacuum conditions. However, much less work has been dedicated to the use of those techniques for the study of catalytically relevant systems under nonvacuum conditions,^{15–17} and virtually no effort has been placed on the

* Corresponding author. Phone: 1 (909) 787-5498. E-mail: francisco.zaera@ucr.edu.

[†] Present address: Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda Midoriku, Yokohama, 226-8503 Japan.

(1) Woodruff, D. P.; Delchar, T. A. *Modern Techniques of Surface Science*, 2nd ed.; Cambridge University Press: Cambridge, 1994.

(2) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.

(3) *Surface Science: The First Thirty Years*; Duke, C. B., Ed.; North-Holland: Amsterdam, 1994.

(4) Zaera, F. *Chem. Rev.* **1995**, *95*, 2651.

(5) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987.

(6) Zaera, F. *J. Phys. Chem. B* **2002**, *106*, 4043.

(7) Zaera, F. *Acc. Chem. Res.* **2002**, *35*, 129.

(8) Zaera, F. In *Encyclopedia of Chemical Physics and Physical Chemistry*; Moore, J. H., Spencer, N. D., Eds.; IOP Publishing: Philadelphia, 2001; Vol. 2, p 1563.

(9) Bradshaw, A. M. *Appl. Surf. Sci.* **1982**, *11/12*, 712.

(10) Hoffmann, F. M. *Surf. Sci. Rep.* **1983**, *3*, 107.

(11) Campion, A. *Annu. Rev. Phys. Chem.* **1985**, *36*, 549.

(12) Stencel, J. M. *Raman Spectroscopy for Catalysis*; Van Nostrand Reinhold: New York, 1990.

(13) Shen, Y. R. *Surf. Sci.* **1994**, *300*, 551.

(14) Somorjai, G. A.; Su, X. C.; McCrea, K. R.; Rider, K. B. *Top. Catal.* **1999**, *8*, 23.

(15) Xu, X. P.; Goodman, D. W. *J. Phys. Chem.* **1993**, *97*, 7711.

(16) Kubota, J.; Ichihara, S.; Kondo, J. N.; Domen, K.; Hirose, C. *Langmuir* **1996**, *12*, 1926.

(17) Cremer, P. S.; Su, X.; Somorjai, G. A.; Shen, Y. R. *J. Mol. Catal. A: Chem.* **1998**, *131*, 225.

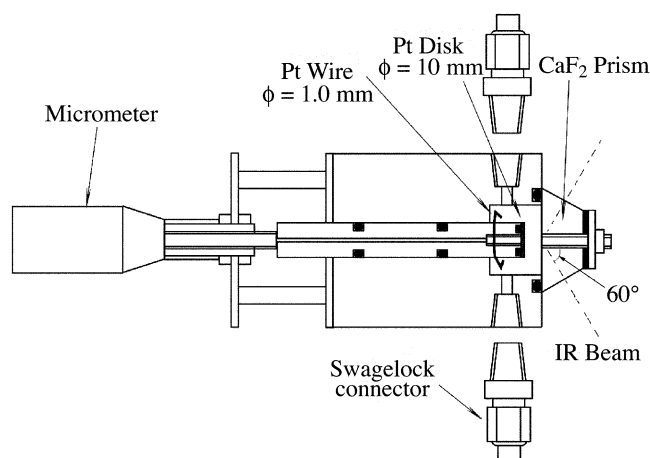


Figure 1. Schematic representation of the infrared liquid–solid IR cell built for the characterization of catalytic systems. This cell consists of a calcium fluoride prism and a manipulator for holding, moving, and applying voltages to the Pt surface. The liquid samples are pressed in the small volume between those two elements. The cell is part of an overall arrangement that includes gas and liquid sample introduction stages and an electrochemical oxidation–reduction circuitry used to clean the platinum disk.

investigation of catalytic reactions with liquid solutions. This report deals with the development of an IR cell for the in situ characterization of catalytic intermediates at the liquid–solid interface.^{18,19} The instrument developed in our lab has been tested for the characterization of the adsorption of cinchona chiral modifiers on platinum surfaces,^{20–22} a method that has proven useful for imparting enantioselectivity to certain hydrogenation catalytic processes.^{23,24} Below we expand on the details of our experimental setup and on its performance for the study of these systems.

Experimental Section

A special infrared cell was designed in our laboratory for the in situ characterization of adsorbates on liquid–solid interfaces along the lines of those previously used for electrochemical studies.^{18,19,25} A schematic representation of our cell is provided in Figure 1. The main body of the cell is made of Teflon. A Teflon supporting rod, placed at the center of the main body and sealed by two O-rings, is used to hold and translate the solid sample. A platinum disk (Goodfellow), 10 mm in diameter and 1 mm in thickness, was polished by sequentially using 10, 3, 1, 0.5, and 0.25 μm diamond pastes and mounted on the front of the supporting rod. A calcium fluoride prism was cut in a trapezoidal shape and placed in front of the Pt sample to let the infrared beam in and out of the cell. The distance between the Pt sample and the prism is controlled by a micrometer attached to the end of the sample rod. A thin liquid film of the solution of interest is placed between the surfaces of the prism and the metal by injection via a 1/16 in. Teflon tube connected to the bottom of the main volume with a Swage-Lock connector, and flushed out through a second tube attached to the opposite side of the cell. The inlet and outlet tubes are connected to a gas-handling system in order to add gas-phase elements to the solution as needed. The flow of the gases is monitored by using calibrated bubbling bottles.

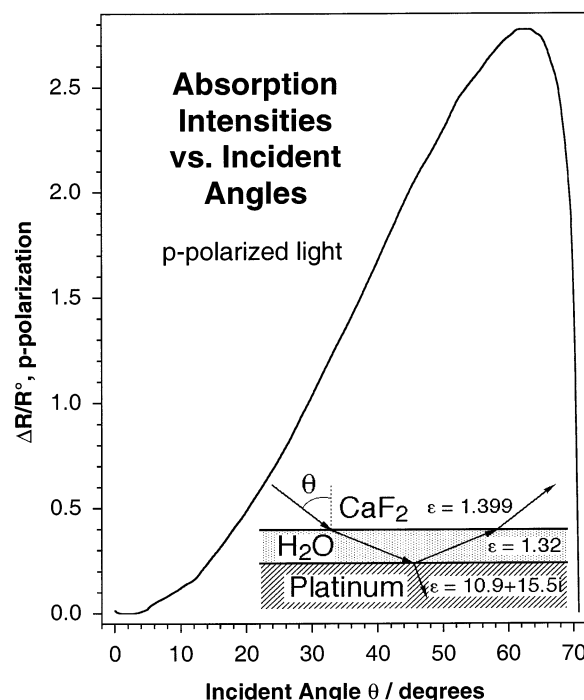


Figure 2. Calculated absorption factor, $\Delta R/R^2$, for p-polarized infrared light traveling through calcium fluoride and water media and reflecting off a platinum surface as a function of angle of incidence at the CaF_2 – H_2O interface. These calculations were carried out by using reported dielectric constants for the three materials and Snell's equations, and were used to determine the optimum angles for cutting the CaF_2 prism used in our liquid–solid IR cell (60°). The s-polarized component displays almost no absorption at any angle.

The reflection–absorption infrared spectroscopy (RAIRS) experiments are performed by focusing the infrared beam from a commercial Mattson Sirius 100 Fourier transform infrared spectrometer through a polarizer and the CaF_2 prism onto the platinum surface, after which the reflected beam is extracted through the same prism and refocused on a mercury–cadmium–telluride detector. A grazing incidence angle onto the sample was assured by setting the beam entrance angle into the CaF_2 prism at 60° . This angle was chosen based on a calculation using a simplified model with three isotropic phases, as depicted in the diagram of Figure 2. The optical properties of each phase—the CaF_2 prism, a water liquid phase, and the platinum surface—are described by their correspondent dielectric functions, $\epsilon = [n - ik]^2$, where n is the refractive index and k is the absorption coefficient.^{26,27} The incident IR beam impinges on the first (CaF_2 –water) interface at an angle θ from the normal, diffracts and impinges on the metal surface at a more acute angle, and is reflected and leaves the three-layer system through a path that is a mirror image to that followed by the incoming light. The absorption factor $\Delta R/R^2$ (where R stands for reflectivity and ΔR is the reflectivity difference between the system with the liquid film and a bare substrate) was calculated by using Snell's relationships; the results for the p-polarized component of the IR beam in our system are shown in Figure 2 as a function of incident angle. This treatment is analogous to that previously reported for the analysis of organic adsorbates on metal surfaces,^{28,29} except that in our case the index of refraction of the intermediate (water) layer is lower than that of the outside media (CaF_2), so the beam bends inward (toward higher values of θ) as it enters the liquid phase. The chosen angle of 60° for the prism outer surfaces leads to an incident angle on the platinum surface

(18) Seki, H.; Kunimatsu, K.; Golden, W. G. *Appl. Spectrosc.* **1985**, *39*, 437.

(19) Weaver, M. J.; Zou, S. *Adv. Spectrosc.* **1998**, *26*, 219.

(20) Kubota, J.; Zaera, F. *J. Am. Chem. Soc.* **2001**, *123*, 11115.

(21) Ma, Z.; Kubota, J.; Zaera, F. *J. Catal.*, submitted.

(22) Ma, Z.; Kubota, J.; Zaera, F. To be published.

(23) Baiker, A. *J. Mol. Catal. A: Chem.* **1997**, *115*, 473.

(24) LeBlond, C.; Wang, J.; Liu, J.; Andrews, A. T.; Sun, Y. K. *J. Am. Chem. Soc.* **1999**, *121*, 4920.

(25) Ashley, K. *Spectroscopy* **1990**, *5*, 22.

(26) *CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Cleveland, 1974.

(27) *American Institute of Physics Handbook*, 3rd ed.; Billings, B. H., Gray, D. E., Eds.; McGraw-Hill: New York, 1972.

(28) Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310.

(29) Hoffmann, H. In *Encyclopedia of Analytical Science*; Townshend, A., Ed.; Academic Press: London, 1995; Vol. 8, p 4930.

of close to 70°, and corresponds to the region of maximum total absorption of this system. Finally, p-polarized light is used because the s-polarized electric field is vanishingly small for all angles of incidence on metal surfaces. This polarization dependence does in fact provide an additional tool for determining adsorption geometries.^{30–32} The final results are reported as p/s spectral ratios.

The platinum solid surface is cleaned between experiments by cyclic voltammetry treatments in the electrolyte solution. Two electrodes are used for this procedure, the Pt disk used for the sample and an auxiliary Pt wire placed alongside the sample rod and inside the cell. Aqueous solutions of 0.1–1.0 M KClO₄, HClO₄, or H₂SO₄ are used as the supporting electrolyte. The solution is injected into the cell, the cell is purged with argon, nitrogen, or helium gas, and the electrodes are connected to a constant-current 1 Hz oscillator set to a sample current of approximately 15 mA in order to carry out repeating oxidation–reduction cycles (ORC). This treatment is carried out for approximately 30–60 min, a period of time sufficient to complete the sample cleaning, while bubbling hydrogen gas in order to remove any oxygen from the solution. Finally, the oscillator is disconnected, the electrolyte is flushed with pure solvent, and the solution to be studied is injected into the cell for the IR studies.

ORC cleaning and sample treatments are performed with the Pt sample retracted in order to maximize its contact with the liquid solutions. For IR spectra acquisition, on the other hand, the metal disk is pressed tightly against the calcium fluoride prism, a procedure that leaves a thin (~2–10 μm thick) solution film trapped between the two surfaces. Typically, averages of 512 IR scans with 4 cm⁻¹ resolution are acquired. Data for p and s polarizations are obtained and ratioed in order to eliminate most contributions from the isotropic liquid phase (the adsorbates absorb only the p component, as mentioned above). Additional ratioing against reference spectra from the clean surface is often carried out as well to eliminate other instrumental artifacts.

For the experiments reported here, quinoline, cinchonidine, cinchonine, and carbon tetrachloride were all obtained from Aldrich and used as supplied. Ar, He, N₂, H₂, and CO gases (>99.9% purity) were purchased from Matheson and also used without further treatment.

Results and Discussion

The performance of our liquid–solid IR cell for in situ infrared spectroscopy characterization of adsorbates was first tested for the chemisorption of carbon monoxide on platinum surfaces. Figure 3 compares the infrared spectra obtained for the C–O stretching mode of carbon monoxide bonded to on-top platinum sites when adsorbed in vacuum, from a CO-saturated solution, and under a CO gas pressure. For the liquid–solid interface study, a 1.0 M H₂SO₄ solution was saturated by bubbling CO at atmospheric pressure, while the vacuum and 35 Torr CO experiments were performed in a different cell explicitly designed for such experiments.^{33,34} The three top spectra, for the three systems, were obtained by ratioing data obtained with p-polarized light against traces recorded with s polarization in order to eliminate any IR absorption from gas or liquid species, as indicated above.

The first thing to notice from the data in Figure 3 is that CO adsorption can be detected in all three cases by the strong IR band seen near 2100 cm⁻¹. There are subtle shifts in peak position, from 2077 cm⁻¹ under vacuum to 2083 and 2062 cm⁻¹ for the gas and liquid systems, respectively, but those can be explained by slight changes in surface coverages and surroundings. The frequencies observed in our experiments are indeed consistent with

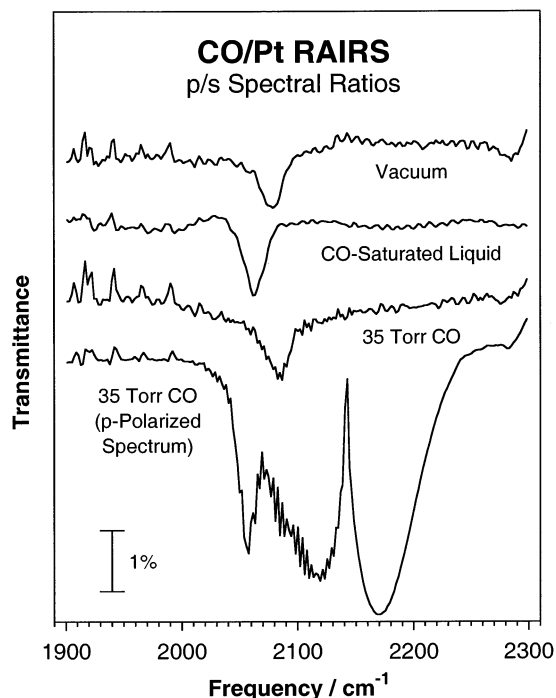


Figure 3. Reflection–absorption infrared spectra (RAIRS) for carbon monoxide adsorbed on a polished platinum polycrystalline disk under different environments. The top three traces correspond to CO surface saturation under vacuum, in a CO-saturated 1.0 M H₂SO₄ aqueous solution, and in a 35 Torr CO atmosphere. The liquid spectrum was recorded with the experimental setup described in this report while vacuum and gas-phase experiments were carried out by using a different gas-phase cell described elsewhere,³³ but all three were obtained by ratioing data acquired using p- and s-polarized light in order to separate the signals due to the adsorbates from those originating from the isotropic phases. A fourth (bottom) trace is provided for the p-polarized component of the spectra recorded under 35 Torr of CO in order to also detect the gas-phase species. The data in this figure point to the comparable performance of our liquid–solid infrared cell in detecting adsorbed species when contrasted to other RAIRS arrangements.

those previously reported under ultrahigh vacuum,^{35–37} gas,^{38,39} and liquid^{40,41} environments. In addition, the IR peak intensities are comparable in all three cases, suggesting similar saturation coverages. The lower (fourth) trace in Figure 3 corresponds to the p-polarized infrared spectrum obtained in the presence of 35 Torr of CO, without normalizing against the s-polarized data, and displays an overwhelming signal originating from the gas-phase species. Both P and R CO rotational branches, around 2115 and 2170 cm⁻¹, respectively, are clearly seen in this trace (with the individual rovibrational states of the P branch partially resolved),⁴² and an additional feature around 2060 cm⁻¹ is also detected, probably due to a gas-phase metal carbonyl impurity.⁴³ It is clear that the latter does not originate from a surface species, because

(30) Parikh, A. N.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927.

(31) Zaera, F.; Hoffmann, H.; Griffiths, P. R. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *54/55*, 705.

(32) Zaera, F. *Int. Rev. Phys. Chem.* **2002**, *21*, 433.

(33) Hoffmann, H.; Wright, N. A.; Zaera, F.; Griffiths, P. R. *Talanta* **1989**, *36*, 125.

(34) Kubota, J.; Ali, A. H.; Zaera, F. Unpublished results, 2002.

(35) Shigeishi, R. A.; King, D. A. *Surf. Sci.* **1976**, *58*, 379.

(36) Froitzheim, H.; Hopster, H.; Ibach, H.; Lehwald, S. *Appl. Phys.* **1977**, *13*, 147.

(37) Zaera, F.; Liu, J.; Xu, M. *J. Chem. Phys.* **1997**, *106*, 4204.

(38) Golden, W. G.; Dunn, D. S.; Overend, J. *J. Phys. Chem.* **1978**, *82*, 843.

(39) Cremer, P. S.; Su, X.; Somorjai, G. A.; Shen, Y. R. *J. Mol. Catal. A: Chem.* **1998**, *131*, 225.

(40) Kunimatsu, K.; Seki, H.; Golden, W. G.; Gordon, J. G., II.; Philpott, M. R. *Langmuir* **1986**, *2*, 464.

(41) Chang, S. C.; Weaver, M. J. *J. Phys. Chem.* **1991**, *95*, 5391.

(42) Levine, I. N. *Molecular Spectroscopy*; John Wiley and Sons: New York, 1975.

(43) Zaera, F. *Surf. Sci.* **1991**, *255*, 280.

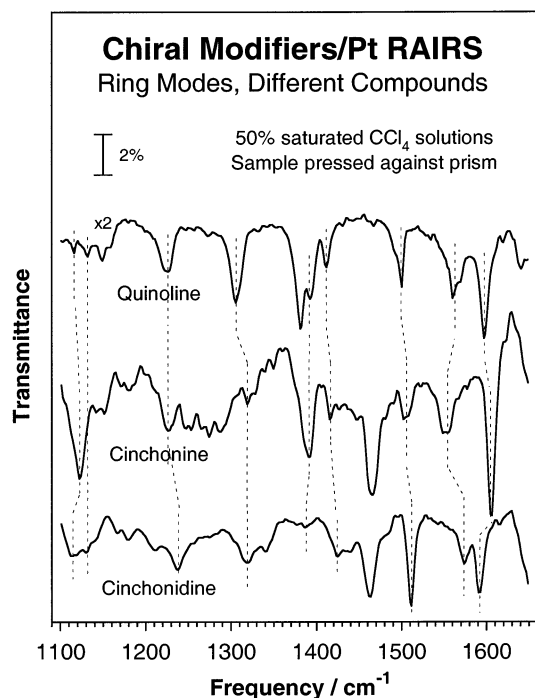


Figure 4. In situ RAIRS data for (from top to bottom) quinoline, cinchonine, and cinchonidine adsorbed on the platinum surface from carbon tetrachloride solutions. All three p/s traces display a large number of high-intensity IR absorption bands, mostly associated with the deformation vibrational modes of the quinoline aromatic ring. These results attest to the sensitivity of the liquid–solid IR cell for the in situ detection and characterization of submonolayer coverages of adsorbates relevant to heterogeneous catalysis. This setup is currently being used to study the mechanism for enantioselective hydrogenation catalysis induced by the use of chiral alkaloid modifiers (refs 20–22).

it also shows up in the s-polarized spectra, and cancels out when the p/s ratio is obtained. Independent experiments were also carried out with a static differential setup to obtain (p – s) polarization difference spectra in order to further corroborate the separation of the signal due to the adsorbates from those of the dissolved species (data not shown).^{32,33} Finally, the spikes seen in most traces below 2000 cm^{-1} are due to insufficient cancellation of the IR bands from water vapor in the path of the beam.

The next step in our study was to test the universality of the liquid cell for the study of systems of catalytic relevance. In particular, we have been interested in the adsorption of alkaloids from solution onto metal surfaces, as they relate to the ability of some chiral molecules to impart enantioselectivity to heterogeneous catalysts.²³ Specifically, the hydrogenation of α -keto esters on supported platinum can be performed with a high degree of enantioselectivity if the catalyst is modified with cinchona alkaloids.⁴⁴ It has been speculated that both the yields and the enantioselectivity excess ratios in those α -keto ester catalytic hydrogenations can be optimized by tuning the adsorption geometry of the aromatic ring of the cinchona modifier.²⁴ We have directed our research to investigating the validity of that and other related hypotheses directly by RAIRS.^{20,21} To that effect, the detectability of different adsorbed aromatic organic compounds related to the cinchona/platinum catalytic system was tested first. Figure 4 illustrates the type of data obtained from those studies, in this case for the adsorption of quinoline, cinchonine, and cinchonidine adsorbed on

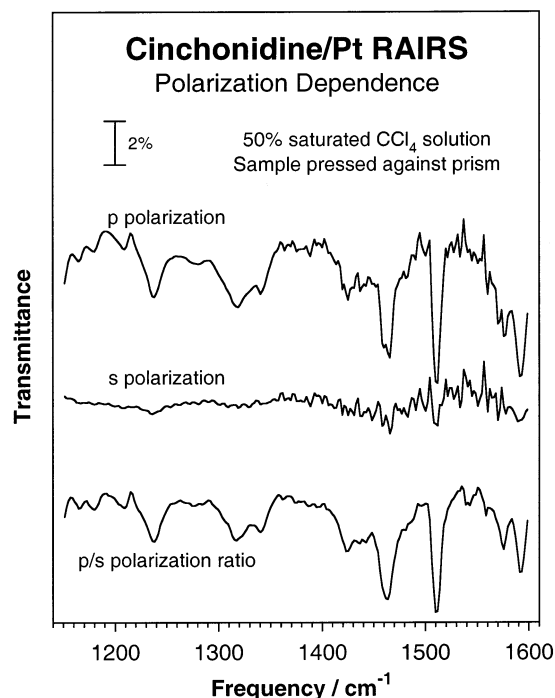


Figure 5. RAIRS data for cinchonidine adsorbed from a carbon tetrachloride solution onto a platinum disk, illustrating the effect of the polarization of the light on the IR absorption signal. The species in solution absorb light isotropically, so the same spectra are obtained with s- and p-polarized light. On the other hand, only the p component is absorbed by molecules adsorbed on the metal. Moreover, the surface helps enhance the infrared absorption signal of the adsorbates and therefore facilitates their detection: note the large bands seen in the upper spectrum of this figure. A ratio of the signals obtained with p- versus s-polarized light, the two top traces, yields a spectrum due to cinchonidine adsorbed on the platinum surface exclusively (bottom spectrum). This technique not only discriminates between solution and surface species, but also reduces the noise level of the final data.

the platinum surface directly from carbon tetrachloride solutions. A large number of vibrational modes are clearly visible for all three molecules, in particular in the 1100–1700 cm^{-1} range mostly associated with deformation modes of the quinoline ring.^{45,46} Of particular interest is the high intensity (0.01–0.05 absorbance units) of the in-plane ring deformation modes. The relative intensities of those modes can be used to estimate adsorption geometries.^{20,32}

A number of additional tests were performed to ensure that the recorded spectra do indeed correspond to chemisorbed, and not to dissolved, species. Figure 5 reports p- and s-polarized IR spectra obtained after exposing the platinum surface to a 50%-saturated cinchonidine solution in CCl_4 , together with the trace obtained by the ratio of those two. Clearly, the p-polarized trace displays much more intense IR absorption bands than those seen in the s-polarization data, indicating that they correspond to surface species. In fact, the peak positions of those bands are in most cases slightly displaced from the ones seen for pure cinchonidine, presumably because of slight changes in the chemical environment of the cinchonine upon adsorption (see below). There are some smaller features visible in the s-polarized spectra, but those could arise from imperfect polarization of the light or, alternatively, from species dissolved in the liquid film. In any case, the

(44) Orito, Y.; Imai, S.; Niwa, S. *Nippon Kagaku Kaishi* **1979**, 1118.

(45) Wait, S. C., Jr.; McNerney, J. C. *J. Mol. Spectrosc.* **1970**, 34, 56.

(46) Williams, C.; Zaera, F. To be published.

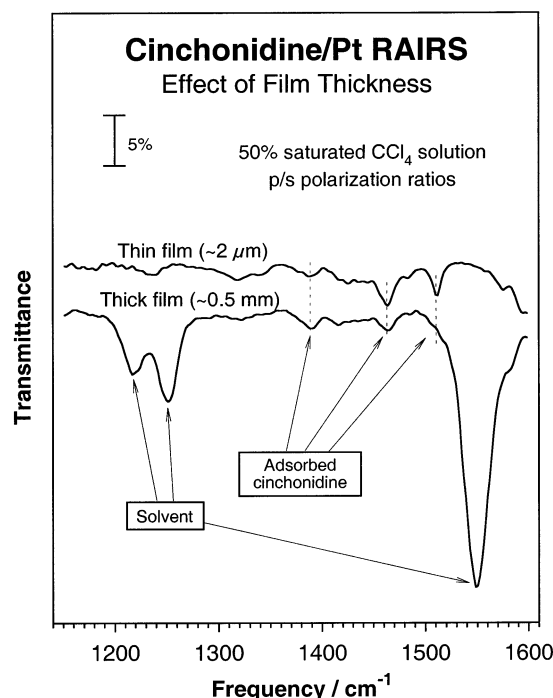


Figure 6. RAIRS data for cinchonidine adsorption from thin ($\sim 2 \mu\text{m}$, top spectrum) and thick ($\sim 500 \mu\text{m}$, bottom) cinchonidine/ CCl_4 solution films on top of a polished platinum disk. Notice that while the three peaks at 1215 , 1255 , and 1550 cm^{-1} corresponding to the solvent grow with increasing liquid film thickness, the remaining features, associated with adsorbed cinchonidine, do not. This provides further evidence that the data obtained with our liquid–solid IR cell under normal operating conditions reflect primarily the state of molecules adsorbed at the platinum–liquid interface.

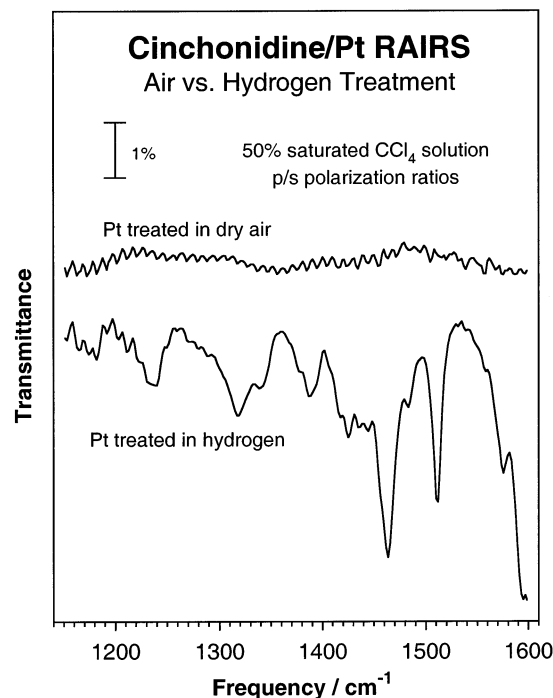


Figure 7. Reflection–absorption infrared spectra obtained after exposing clean (bottom) and oxidized (top) platinum surfaces to the same solution of cinchonidine in carbon tetrachloride. A meaningful infrared spectrum was obtained only in the former case, indicating that cinchonidine adsorbs exclusively on clean metallic surfaces. This rules out the possibility of condensation or precipitation of the alkaloid from the solution onto the surface, and argues for the formation of a chemisorbed adlayer instead.

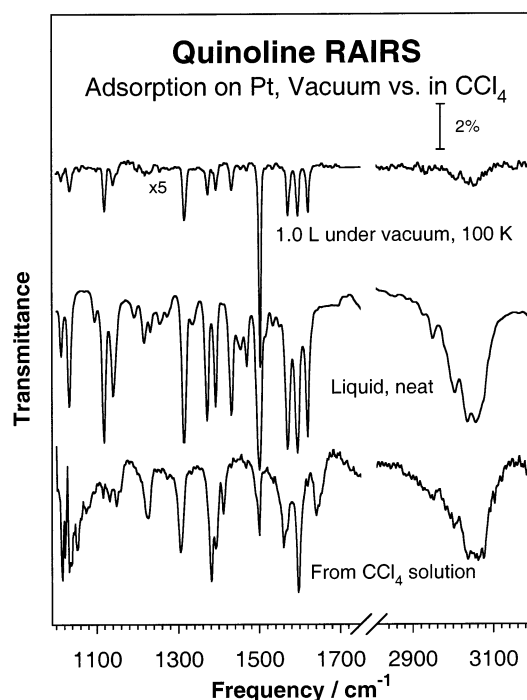


Figure 8. RAIRS data for quinoline, neat (middle trace) and adsorbed on platinum. This figure contrasts the dramatically different behavior seen in chemisorbed quinoline when dosed under vacuum versus when adsorbed from a carbon tetrachloride solution. The spectra of the cinchonidine adsorbed at low temperatures and under vacuum look quite similar to those from the pure compound, with peaks at virtually the same positions. Only the peak relative intensities are slightly different, indicating that quinoline adopts a specific adsorption geometry on the surface. The data for the quinoline adsorbed from solution, on the other hand, display clear differences from the other two, including peak shifts and wide variations in relative intensities. The combined information from the three spectra in this figure points to the key role that the solvent plays in the adsorption of cinchona modifiers onto the platinum surface.

p/s trace is used to eliminate any contributions from the liquid phase to the IR spectrum and, in addition, to improve the signal-to-noise ratio. The p/s spectra were used in most of the experiments reported here, and also in our studies of the cinchonidine/Pt system.

In another test aimed at identifying the origin of the vibrational absorption bands seen in the spectra from our liquid–solid cell, the IR peaks detected for the adsorbed cinchonidine in our experiments were shown to persist after flushing the system with the pure carbon tetrachloride solvent (data not shown).²² This not only proves that the species detected in the infrared spectra are associated with the surface, not the liquid, but also indicates that the adsorption is highly irreversible (at least under the conditions of this experiment). In addition, spectra were taken with different liquid film thicknesses. Figure 6 shows the data obtained for the cases where the platinum disk was pressed against the prism, leaving a liquid film between the two surfaces of only a few microns in thickness (top trace), and after pulling the solid sample approximately half a millimeter back (bottom trace). It was found that while the absorption bands around 1220 , 1250 , and 1550 cm^{-1} , due to the CCl_4 solvent, increase linearly in intensity with the thickness of the liquid film, those at 1390 , 1460 , and 1510 cm^{-1} , associated with the adsorbed cinchonidine, virtually do not change. Finally, no infrared peaks were detected when the adsorption experiments were carried out on an oxidized platinum surface; only on

a surface fully cleaned by hydrogen pretreatments is it possible to see adsorbed cinchonidine (Figure 7). This proves that the chemisorption of cinchonidine occurs only on clean and metallic platinum substrates and that there is no condensation or precipitation of cinchonidine from the solution onto the solid, only a chemical interaction between the cinchonidine and the Pt surface.²¹

The importance of carrying out infrared spectroscopy studies on the chemisorption of catalytic reactants (or chiral modifiers in the case of the cinchona/Pt system) in situ in the solid–liquid interface is exemplified by the data in Figure 8. Certainly, it is already known that the solvent plays a pivotal role in determining activity and enantioselectivity in chiral systems.^{47,48} Our ongoing studies suggest that this may be due to a combination of effects, including the role that different solvents may have on modifying the reversibility of the adsorption of the chiral modifier and the conformation that those adopt on the surface.²² The three traces in Figure 8 compare the vibrational spectra of quinoline neat (middle), adsorbed on Pt(111) single-crystal surfaces at liquid nitrogen temperatures and under vacuum (top), and adsorbed from a carbon tetrachloride solution (bottom). It can be seen that the peak positions in the spectrum for the species adsorbed under vacuum match those for the neat compound; only the relative intensities change somewhat. This indicates that the adsorbed species retain their molecular structure but adopt a specific adsorption geometry.^{31,49} The quinoline adsorbed from the CCl₄ solution, on the other hand, yields infrared spectra significantly different from the other two. Most infrared adsorption bands are broader, perhaps because of some disorder on the surface or because of rapid changes in configurations in the adsorbed species, and several peaks are displaced from

the original positions, most likely a consequence of interactions with the solvent. A more detailed analysis of these changes is beyond the scope of this report, and will be provided in a future publication.

Conclusions

An experimental setup has been developed for the in situ infrared spectroscopic characterization of adsorbates at solid–liquid interfaces. This setup, designed to address systems relevant to heterogeneous catalysis, was modeled along the lines of others used in electrochemistry, and is based on a single-reflection arrangement of the IR beam from the solid surface after going through a CaF₂ prism and a thin film of the liquid phase. The use of polarized light in these experiments helps with the discrimination between adsorbates and liquid-phase species. This arrangement was first tested for the adsorption of carbon monoxide dissolved in an aqueous solution onto a platinum surface. Significant adsorption was observed in that system, comparable to that obtained on the same substrate under vacuum or by using atmospheric pressures.

A more detailed evaluation of the performance of this liquid–solid IR cell was performed with aromatic compounds related to chiral heterogeneous catalytic systems, in particular with cinchona alkaloids and with quinoline, the aromatic ring fundamental for its adsorption. Several tests were performed to prove that the signal intensities in the infrared absorption spectra from these experiments are sufficient for the identification and characterization of the adsorbate and to ensure that the data correspond to adsorbed, not dissolved, species. Specific studies were carried out in terms of the direction of the polarization of the light, the thickness of the liquid film above the surface, and the state of the adsorbing surface, to test the latter point. Finally, the key role of the solvent in affecting the nature of the adsorbed species was documented.

Acknowledgment. Funds for this project were provided by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation.

LA027031N

(47) Blaser, H. U.; Imhof, D.; Studer, M. In *Heterogeneous Catalysis and Fine Chemicals IV: Proceedings of the 4th International Symposium on Heterogeneous Catalysis and Fine Chemicals*, Basel, Switzerland, September 8–12, 1996; Blaser, H. U., Baiker, A., Prins, R., Eds.; Vol. 108 of Studies in Surface Science and Catalysis Series; Elsevier: Amsterdam, 1997; p 175.

(48) Collier, P. J.; Iggo, J. A.; Whyman, R.; Hall, T. J.; Johnston, P.; Slipszenko, J. A.; Wells, P. B. *Chem. Commun.* **1998**, 1451.

(49) Zaera, F. *Prog. Surf. Sci.* **2001**, 69, 1.