Probing Molecular Vibrations at Catalytically Significant Interfaces: A New Ubiquity of Surface-Enhanced Raman Scattering

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The development of "in-situ" methods for characterizing chemisorbed molecules at metal and related surfaces in higher-pressure gas or liquid-phase (i.e., ambient) environments constitutes a centrally important goal of contemporary interfacial science.[1] Vibrational spectroscopy, with its consummate sensitivity to molecular structure and bonding, forms a crucial element of such efforts. However, both of the in-situ vibrational methods commonly utilized, infrared reflection−absorption spectroscopy (IRAS) and infrared−visible sum frequency generation (SFG), suffer from major drawbacks. These include sensitivity restrictions, bulk-phase interferences, limited wavenumber ranges, and an inability to detect vibrational modes parallel to the interfacial plane as a result of surface-selection rules. Consequently, the breadth of chemisorbate-surface systems so far amenable to such in-situ vibrational characterization, especially for transition metals and related catalytic interfaces, remains meager in comparison with systems in ultrahigh vacuum (UHV), where electron energy-loss spectroscopy (EELS) has been extensively exploited in addition to IRAS. While EELS offers excellent sensitivity over wide frequency ranges and can detect most adsorbate vibrational modes,[2] it is inherently limited to UHV. We report herein an experimental strategy, based on surface-enhanced Raman scattering (SERS), which enables such rich vibrational information to be obtained for numerous adsorbates on transition-metal (and likely other catalytically significant) surfaces in liquid-phase or other ambient environments.

The SERS technique, developed originally for electrochemical systems,[3] shares several major attributes with EELS, including excellent sensitivity toward low wavenumbers and the ability to detect most adsorbate molecular vibrations. Most importantly, and unlike EELS, SERS can yield detailed vibrational information free from bulk-phase interferences even at metal−liquid interfaces over wide wavenumber ranges with excellent frequency and temporal resolution. A major drawback that has restricted the breadth of applications of SERS to interfacial chemistry, however, is that the Raman enhancement effect is limited for practical purposes to copper, silver, and gold substrates.

Earlier work from our laboratory showed that the SERS effect could nonetheless be extended to transition metals and related materials by electrodeposition as ultrathin films on gold.[4] This procedure can alter the surface chemical properties to those of the deposited film while maintaining large SER signal enhancements for species adsorbed on the overlayer by transmission from the underlying substrate. The approach has been utilized to explore adsorbate vibrational properties on transition metals in electrochemical[5] and elevated-temperature gaseous environments.[6] The key factor limiting the scope of these applications, however, has been the presence of interfering spectral components from adsorbates bound to exposed Au "pinhole" sites in the overlayer film. This "pinhole problem" has until now thwarted our hoped-for characterization of the myriad of larger (and hence vibrationally more complex) adsorbates, especially organic species, of broad-based importance in interfacial chemistry.

Recently, however, we discovered that modifying the film electrodeposition procedure, specifically by employing *constant-current* electrodeposition from suitable electrolytes (e.g., phosphate buffers), can yield transition-metal films (e.g., Pt, Pd, Ir, Rh) on gold substrates that are sufficiently thin (say, 3−10 monolayers, ML) to yield excellent SERS, yet are essentially *free of pinholes*.[7] This last property can be gleaned readily from the cyclic voltammetry for oxide formation and removal, specifically from the absence of the Au oxide reduction wave,[4] and, most pointedly, by examining the C−O stretching (ν_{CO}) bands for adsorbed carbon monoxide. Thus adsorbate bound to residual Au sites yields a characteristically higher-frequency (ca. 2110 cm^{-1}) ν_{CO} feature compared to bands (<2070 cm^{-1}) due to CO bound to the transition-metal overlayer.[4,5b] However, the present films consistently yield SER spectra featuring intense ν_{CO} bands for CO bound to the transition metal, yet *entirely devoid* of the 2110 cm^{-1} "pinhole" band.[7]

One benchmark class of adsorbates are aromatic molecules. While often chemisorbed strongly on transition metals, their propensity for π-bonding via the aromatic ring(s) largely precludes in-situ characterization by either IRAS or SFG. The vibrational properties of these (and numerous other) important systems have therefore been examined previously *only* in UHV environments by using EELS.[8] We describe here some salient SERS vibrational features of benzene on palladium in aqueous media in order to illustrate the power of the technique for exploring molecular structure and bonding on transition metals in non-UHV environments, specifically in comparison with EELS data.

Displayed in Figure 1 are typical SER spectra obtained on a palladium-coated Au electrode[9] held at −0.2 V vs saturated calomel electrode (SCE) in near-saturated (ca. 10 mM) solutions of benzene and benzene-d_6 in aqueous 0.5 M H_2SO_4. Similar spectra were observed at electrode potentials from −0.2 to 0.5 V vs SCE. The wavenumber region, from 800 to 1250 cm^{-1}, was selected to encompass the "symmetric ring-breathing" mode (ν_1 in the Wilson notation). This band, appearing at 992 cm^{-1} for liquid benzene,[10] is red-shifted (and broadened) substantially by adsorption on palladium, yielding a feature centered around 945−950 cm^{-1} along with a low-frequency shoulder (Figure 1). Identification of this SER band is facilitated by the frequency downshift to about 905 cm^{-1} observed upon ring deuteration (Figure 1). Benzene adsorbed on gold electrodes also displays a red-shifted ν_1 mode.[12] However, the band *envelope* for the ν_1

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[1] For example, see: (a) Su, X.; Jensen, J.; Yang, M. X.; Salmeron, M. B.; Shen, Y. R.; Somorjai, G. A. *Faraday Discuss.* **1996**, *105*, 263. (b) Weaver, M. J. *J. Phys. Chem.* **1996**, *100*, 13079.

[2] For a recent review, see: Ho, W. In *Physical Methods of Chemistry*, 2nd ed.; Rossiter, B. W., Baetzold, R. C., Eds.; Wiley: New York, 1993; Vol. 9A, *Investigations of Surfaces and Interfaces*, Chapter 4.

[3] Van Duyne, R. P. In *Chemical and Biochemical Applications of Lasers*; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. 4, Chapter 5.

[4] Leung, L.-W. H.; Weaver, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 5113; *Langmuir* **1988**, *4*, 1076.

[5] (a) Zhang, Y.; Gao, X.; Weaver, M. J. *J. Phys. Chem.* **1993**, *97*, 8656. (b) Zou, S. and Weaver, M. J. *J. Phys. Chem.* **1996**, *100*, 4237.

[6] For example, see: Williams, C. T.; Takoudis, C. G.; Weaver, M. J. *J. Phys. Chem. B* **1998**, *102*, 406.

[7] Zou, S.; Weaver, M. J. To be published. Also, see the Supporting Information.

[8] For an overview, see: Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589.

[9] The palladium films (about 3.5 monolayers) were formed by constant-current cathodic deposition at 75 $\mu A\ cm^{-2}$ from 5 mM $PdCl_2$ in 1 M $HClO_4$ for ca. 20 s onto SERS-active gold, electrochemically roughened as described in the following: Gao, P.; Gosztola, D.; Leung, L.-W. H.; Weaver, M. J. *J. Electroanal. Chem.* **1987**, *233*, 211.

[10] Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; Wiley: New York, 1974; Chapter 13.

[11] Varsanyi, G. *Vibrational Spectra for Benzene Derivatives*; Wiley: New York, 1974.

[12] Gao, X.; Davies, J. P.; Weaver, M. J. *J. Phys. Chem.* **1990**, *94*, 6858.

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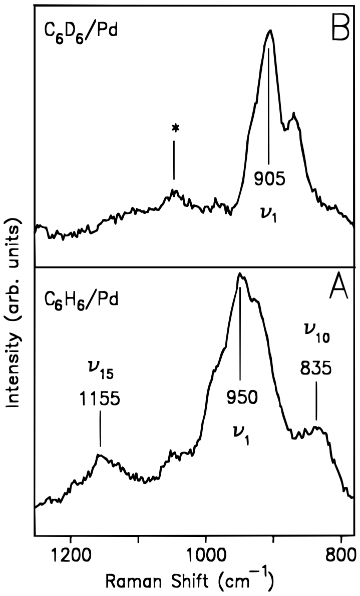

Figure 1. Surface-enhanced Raman (SER) spectra for (A) benzene and (B) benzene-d_6 adsorbed on a 3.5 ML palladium film on gold at −0.2 V vs SCE from 10 mM benzene in aqueous 0.5 M H_2SO_4. Raman excitation was at 647.1 nm, with a power of ca. 20−40 mW. The spectrum acquisition time was 20 s. The feature marked with an asterisk possibly arises from trace aluminum oxide used for electrode polishing.

SERS feature on palladium is down-shifted well beyond the feature (of comparable intensity) observed at ca. 975 cm^{-1} on unmodified gold, showing that the former must arise at least predominantly (and probably exclusively) from binding flat to the transition-metal surface. As expected, the ν_1 (and other) band intensities are attenuated progressively for thicker Pd films. However, the intensities decrease, for example, by only 4−5-fold from 3 to 30 ML films.[7] The band frequencies are affected little (<5 cm^{-1}) by film thickness, especially above ~10 ML.

Turning now to other adsorbate vibrational modes, Table 1 compares the spectral characteristics of eight representative vibrations for liquid benzene[10,11] with the corresponding SERS bands for benzene adsorbed on palladium, along with the reported EELS vibrational features on Pd(110) in UHV.[13] In addition to the band frequencies and approximate relative intensities, the H/D isotopic frequency ratios are also listed in parentheses. The SERS band assignments in Table 1 were deduced partly by matching the observed isotope shifts with those for the bulk-phase species, as well as considering the band frequencies and relative intensities. The detection of adsorbate ring modes having significant polarizability tensors normal to the ring plane (α_{zz} modes), along with the observed *absence* of the ν_2 mode (C−H stretch, for which $\alpha_{zz} \approx 0$), provides further evidence that the benzene ring is parallel to the metal surface. Thus, the e_{1g} symmetry modes (e.g., ν_{10}) yield larger SER enhancements than for e_{2g} modes (e.g., ν_6), as expected since only the former feature a moderate α_{zz} polarizability.[12] The band frequencies (and assignments) from the EELS data (Table 1) are largely in accordance with the present findings. The benzene ring is deduced to have an essentially flat orientation also on Pd surfaces in UHV, again partly on the basis of vibrational selection rules, although in the EELS case the most intense (usually dipole-allowed) bands chiefly involve out-of-plane C−H vibrations.[13]

The frequency and relative intensities of some benzene SERS bands are sensitive to both the solute concentration and the transition metal. For example, the ν_1 band envelope for C_6H_6 in Figure 1 contains at least two components, the more strongly red-shifted (950/920 cm^{-1}, “chemisorbed”) portion dominating increasingly over the unresolved higher-frequency shoulder toward lower solute concentrations. This SERS feature is seen to be even more red-shifted on rhodium films, to about 890 cm^{-1}, close to that observed by EELS for the same vibration on Rh(111).[14]

Table 1. Comparison of Major Raman Spectral Features for Benzene at Palladium-Aqueous Interface with Corresponding Bulk-Phase and UHV-Based EELS Data

benzene normal mode[a]	vibrational mode description	vibrational frequencies (cm^{-1})		
		bulk liquid[b,c]	EELS[d] Pd(110)	SERS[c,e] Pd
ν_{16}	C−C−C out-of-plane bend	404 (in) (1.20)		430 (w)
ν_6	C−C−C in-plane bend	607 (s) (1.05)		580 (w) (1.05)
ν_{11}	C−H out-of-plane bend	673 (in) (1.33)	705/745 (1.4/1.33)	735 (m) (1.43)
ν_{10}	C_6 libration	846 (m) (1.28)	890 (1.33)	835 (m) (1.33)
ν_1	ring breathing	992 (vs) (1.05)	890? (~1.0?)	950 (vs) (1.05)
ν_9	C−H in-plane trigonal bend	1178 (s) (1.36)	1150 (1.32)	1155 (?) (1.33)
ν_{14}	C−C stretch	1309 (in) (1.02)	1340 (1.09)	1325 (s)
ν_{19}	C−C stretch	1482 (in) (1.11)	1460 (1.03)	1435 (w) (1.10)

[a] Wilson number notation for normal mode vibration. [b] Vibrational frequency in liquid phase. Values given in parentheses are isotopic frequency ratios for C_6H_6 relative to C_6D_6 (ν_H/ν_D), from ref 11. [c] Key to symbols: in = Raman inactive, vs = very strong, s = strong, m = medium, w = weak, vw = very weak. [d] EELS vibrational frequencies for benzene adsorbed on Pd(110) at 300 K in UHV, from ref 13. The (ν_H/ν_D) ratios are given in parentheses. [e] Vibrational frequencies for benzene on Pd film electrode, observed in the present work. The (ν_H/ν_D) ratios are given in parentheses.

The key point exemplified by this abbreviated analysis is that the SER spectra can yield at least as detailed and reliable picture of surface coordination of polyatomic chemisorbates on transition metals in ambient environments as can be deduced by EELS, even though the latter technique is restricted to UHV. More detailed analyses for these and other aromatic systems will be described elsewhere.[15] The strategy clearly has considerable promise for the detailed vibrational characterization of polyatomic adsorbates on such strongly chemisorbing (and catalytically significant) surfaces in liquid-phase and other ambient environments. Moreover, the detection of inherently weak vibrational signals is becoming much more tractable with the advent of high-throughput Raman spectrometers and efficient detectors even for longer-wavelength radiation. Consequently, one can expect to obtain measurable SER spectra even on substantially thicker overlayers (i.e., for markedly smaller SER enhancements),[7] opening up the present technique to diverse other surface materials. With proper attention to film characteristics, then, there are persuasive reasons to anticipate that SERS-based vibrational strategies may quietly revolutionize our understanding of molecular chemisorption at such interfaces.

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Supporting Information Available: Film preparation details and Raman spectra (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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