

Orientation of 1- and 2-Methylimidazole on Silver Electrodes Determined with Surface-Enhanced Raman Scattering

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Surface-enhanced Raman scattering is used to determine the potential-dependent orientation of 1- and 2-methylimidazole on Ag electrodes. Frequency shifts resulting from adsorption and potential changes suggest adsorption of these molecules through the pyridine nitrogen at positively charged surfaces. Unique $\nu(\text{CH}_3)$ features appear in the SERS spectra of 1-methylimidazole at neutral and negatively charged surfaces which suggest direct interaction of the methyl group with the surface. SERS surface selection rules are applied to three carefully selected groups of vibrational modes. The comparison of in-plane and out-of-plane ring modes is used to determine the orientations of the imidazole ring planes relative to the surface. The orientations of the methyl groups relative to the surface are elucidated by comparing the $\nu_{\text{sym}}(\text{CH}_3)$ and $\nu_{\text{asym}}(\text{CH}_3)$ modes. Finally, comparison of the $\nu(\text{N}-\text{CH}_3)$ to the $\delta_{\text{sym}}(\text{N}-\text{CH}_3)$ of 1-methylimidazole and the $\nu(\text{C}-\text{CH}_3)$ to the $\delta_{\text{sym}}(\text{C}-\text{CH}_3)$ of 2-methylimidazole provides information on the “side-to-side” tilting of these molecules. The orientation information thus obtained suggests that the methylimidazoles are attached to the electrode in a tilted orientation at potentials positive of the potential of zero charge (PZC), become more vertical as the potential approaches the PZC, and then are attached to the electrode primarily through the interaction of the methyl group at the most negative potentials. Pronounced “butterfly” waves in the cyclic voltammetry of these systems are interpreted in terms of adsorbate layer rearrangement. The potentials at which these processes occur are consistent with those at which spectral changes are observed.

Introduction

The surface-enhanced Raman scattering (SERS) of imidazole (Im) at Ag electrodes was recently studied in this laboratory, and the potential-dependent orientation of Im was estimated.¹ Adsorption-induced frequency shifts observed were concluded to be consistent with adsorption of Im through the “pyridine N” (hereafter referred to as “N₃”) lone pair of electrons as opposed to the “pyrrole N”, (hereafter referred to as “N₁”). The application of Raman surface selection rules to relative intensities of in-plane and out-of-plane ring modes indicate that Im is tilted relative to the electrode surface at potentials positive of the potential of zero charge (PZC), becoming more vertical at potentials near the PZC. This previous study was limited to a comparison of in-plane and out-of-plane ring modes by our inability to assign Im bands to specific localized vibrational modes. Raman spectral assignments for Im distinguish type of vibration (γ , δ , and ν) and bond (ring, CH, or NH), but few bands are assigned to specific bonds or functional groups. Therefore, information for Im is limited to orientation of the ring-plane.

Concomitant with past work involving Im, this laboratory was also successful in using SERS to estimate methyl group orientation for adsorbed alcohols and alkanethiols on Ag and Au surfaces.² In this work, the orientation of an isolated part of the molecule (the methyl group) was used as an indicator of orientation for the entire molecule. In the present study, a similar approach is applied to understand the orientation of two isomers of methylimidazole (MeIm), 1-methylimidazole (1-

MeIm), and 2-methylimidazole (2-MeIm), at Ag electrodes. The addition of the methyl group to the Im ring introduces localized methyl group modes that yield additional information about adsorbate orientation.

Thus, the present study was motivated by two goals. First, it was undertaken to verify the adsorption behavior of Im on Ag electrodes through use of the methyl group in these molecules as a SERS orientation indicator. Secondly, we hypothesized that this study would provide further verification of the effectiveness of the methyl group as a SERS orientation indicator.

Experimental Section

Materials. 1-MeIm (Aldrich, 99+%) was used as received. 2-MeIm (Aldrich, 99%) was purified by recrystallization from benzene prior to use. Mallinckrodt AR grade KCl was used as received. Solutions used for the SERS studies were 0.050 M in MeIm and 0.100 M in KCl and were prepared using water that was deionized and then doubly distilled from a permanganate solution. All solutions were deaerated by bubbling with nitrogen immediately prior to use in a SERS experiment.

Electrochemistry. Ag electrodes for cyclic voltammetry and differential capacitance measurements were prepared according to standard metallographic procedures. After polishing, the electrodes were degreased with ethanol in a Soxhlet extractor for at least 24 h prior to use. Final cleaning was accomplished by H₂ evolution for ca. 3 min prior to use.

All electrochemical measurements were made and are reported versus a Ag/AgCl reference electrode. Capacitance measurements were performed on a system designed and built in-house.³ Cyclic voltammetry was performed on a BAS100W electrochemical workstation.

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Raman Spectroscopy. The Raman system used in this study was equipped with a Photometrics PM512 charge-coupled device (CCD) detector and a Spex 1877 Triplemate spectrograph. A camera lens (Minolta, $f/1.2$, 50 mm dia) was used for collection. This system has been previously described.⁴

Laser excitation at 600 nm for these studies was provided by a Coherent Radiation 599 tunable dye laser containing rhodamine 6G dye pumped by a Coherent Radiation Innova 90-5 Ar⁺ laser. Laser powers used to obtain SERS spectra ranged from 160 to 220 mW at the sample. This excitation wavelength was used to minimize photodecomposition of adsorbed MeIm.¹ At this excitation wavelength, SERS spectra of adsorbed molecules are also enhanced relative to the broad background features reported in earlier work.² Thus, the signal-to-noise ratios of MeIm spectra obtained at 600 nm are significantly improved over those obtained with 514.5 nm excitation. Spectra covering the regions from 150 to 1800 cm⁻¹ and from 2550 to 3450 cm⁻¹ were obtained over a wide range of electrode potentials (at -0.25 V, at 0.05 V increments from -0.40 to -0.80 V, and at 0.10 V increments from -0.90 to -1.20 V).

For 600 nm excitation, the CCD spectrometer system provides a spectral window of ca. 350 cm⁻¹. To obtain the entire spectral coverage indicated above, 11 spectral regions were acquired separately and subsequently spliced together. Thus, acquisition of one entire data set required a total of up to 10 h under the conditions of this study. However, it was necessary to limit spectral acquisition time to no more than two hours after performance of an oxidation-reduction cycle (ORC) pretreatment of the Ag electrode because of the instability of the SERS-active Ag surface. Therefore, data for each MeIm were collected using three separate runs; each run consisted of the preparation of a fresh SERS-active Ag electrode surface followed by acquisition of spectra from four or five spectral regions at all desired potentials. Spectra from different regions were acquired in each run, except for the ca. 990–1330 cm⁻¹ "reference region," which was acquired in all runs for normalization purposes. Intensities were normalized to the peaks in this reference region and to the same integration time and laser power to permit direct comparison of intensities between spectra acquired from different runs.

Intensity corrections were made to account for differences in the rate of decay of active sites between runs. These corrections were accomplished by acquisition of SERS spectra of the "reference region" noted above (centered at ca. 1150 cm⁻¹) at three potentials, -0.25, -0.6, and -0.9 V, in all runs. For each MeIm, these reference spectra were used to normalize the remaining experimental spectra in a given series at these potentials, thereby allowing normalization of all spectra in each series. Time-dependent and potential-dependent changes in surface enhancement due to loss of active sites were addressed in the following manner. The first and last spectra collected at each potential were of the same spectral region. Differences in spectral intensities were used to estimate time-dependent decay of active sites at that potential. In addition, after reaching -1.2 V, the potential was returned to -0.25 V and a spectrum was recorded to document the degree of irreversible loss of SERS that occurred over the entire run. Using this total decrease in conjunction with the decreases observed at each potential, the fractional decrease of the intensity with time associated with each potential could be determined. Thus, each spectrum was divided by this fractional surface enhancement reduction resulting in SERS intensities that are normalized to the surface enhancement present for the first spectrum of each run. This

procedure was found to result in intensities between runs that were reproducible to within ca. $\pm 20\%$.

Spectra were calibrated using procedures described previously.^{4,5} The accuracy of frequencies obtained in this fashion have been estimated⁴ as ± 4 cm⁻¹ for bands below 500 cm⁻¹, ± 3 cm⁻¹ for bands between 500 and 1000 cm⁻¹, ± 2 cm⁻¹ for bands between 1000 and 1350 cm⁻¹, and ± 3 –4 cm⁻¹ for bands above 1350 cm⁻¹. These accuracy estimates limit the comparison of SERS band frequencies with those from solution Raman spectra. However, frequency shifts between bands measured at different potentials are limited only by the precision of the SERS spectra, which is ± 2 cm⁻¹ or better for all regions.

SERS measurements were carried out in a previously described spectroelectrochemical cell.⁶ The working electrode was a 7 mm dia Ag disk (99.99%, Johnson Matthey) which was first freshly polished before each experiment with successively finer grades of alumina (Buehler) down to 0.05 μm and then sonicated to remove any traces of alumina. The counter electrode was a Pt wire. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials associated with SERS are reported versus this electrode.

Roughening of Ag electrodes to obtain SERS-active surfaces was accomplished by a single ORC by scanning the applied potential positive from -0.25 V at 10 mV/s. The scan was reversed when 25–40 mC/cm² of anodic charge had been passed, and scanned at the same rate back to -0.25 V. The total charge passed was between 50–90 mC/cm². Variation in the total charge passed within these limits did not noticeably affect the SERS intensities. The ORC was performed in the same MeIm-containing solution in which the SERS spectra were acquired. Potentials were controlled with an IBM Instruments EC/225 voltammetric analyzer. Charge was measured with a Princeton Applied Research Model 379 digital coulometer.

SERS intensities were obtained from peak areas obtained by curve fitting the spectra. The spectral background was fit to a polynomial and subtracted prior to curve fitting. Curve fitting was accomplished using a mixed Gaussian-Lorentzian band shape derived from several spectrally isolated peaks. As a starting point for peak identification in the $\nu(\text{C-H})$ region, spectra of pure 1- and 2-MeIm were acquired using s- and p-polarization. The number, positions, and widths of $\nu(\text{C-H})$ bands identified for the pure compounds were used as a starting point for curve fitting of SERS spectra. A minimum number of additional peaks, also constrained in position and width, were added to the fit as necessary. Goodness-of-fit criteria included physical meaning of the number and positions of peaks and magnitude of the χ^2 residuals from the fit.

Results and Discussion

Cyclic Voltammetry. The electrochemistry of 1-MeIm and 2-MeIm was investigated using cyclic voltammetry, coulometry, and differential capacitance measurements to establish the presence or absence of bulk Faradaic processes of these molecules. These studies reveal no Faradaic processes of either molecule within a potential window of 0.0 to -1.5 V; however, a relatively complex series of capacitive processes are observed which indicate strong interactions between the Ag surface and the MeIm species and specifically adsorbed Cl⁻. The discussion presented here outlines the essential features of the electrochemistry necessary for support of the conclusions drawn from the spectroscopic results. A more detailed description of the electrochemistry of these systems will be reported elsewhere.⁷

Figure 1a shows the cyclic voltammetry of a solution of 0.05 M 1-MeIm/0.1 M KCl at two sweep rates. A series of

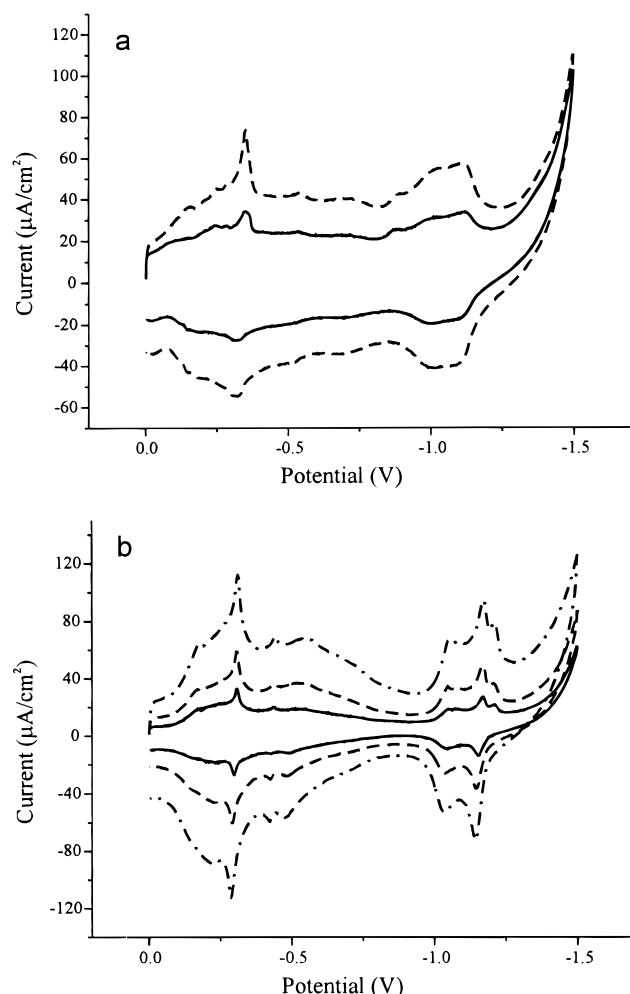


Figure 1. Cyclic voltammetry for (a) 0.05 M 1-MeIm/0.1 M KCl and (b) 0.05 M 2-MeIm/0.1 M KCl at Ag. Sweep rates: (a) — 100 mV/s. — — 200 mV/s. (b) — 100 mV/s. — — 200 mV/s. - · - 400 mV/s.

symmetrical “butterfly” peaks are observed in these voltammograms typical of surface-confined processes. The linearity of the peak currents of these waves with potential sweep rate further confirms that they originate from surface processes. The differential capacitance behavior of this system exhibits capacitance maxima at potentials corresponding to peaks in these voltammograms. This correlation implicates adsorption/desorption processes and phenomena involving ion movement upon adsorbate layer reorientation. This hypothesis is also consistent with the small currents associated with these peaks. Finally, the reversibility of these processes indicates reversibility in the adsorption/desorption and adsorbate reorientation phenomena.

Consistent with the spectroscopy to be presented below, the voltammetric waves between 0.0 and -0.5 V are attributed to desorption of Cl^- from the surface with concomitant rearrangement of the 1-MeIm adlayer. The peaks in the region between -1.0 and -1.2 V are proposed to be due to partial desorption of 1-MeIm with subsequent rearrangement of the remaining surface-bound 1-MeIm. This electrochemical behavior correlates well with the SERS measurements which indicate the greatest changes in spectral intensity, band shape, and peak frequencies beginning at potentials negative of ca. -0.6 V.

The cyclic voltammetry for 2-MeIm is equally compelling as shown in Figure 1b. In this case, the “butterfly” waves are more pronounced and better defined in all potential regions.

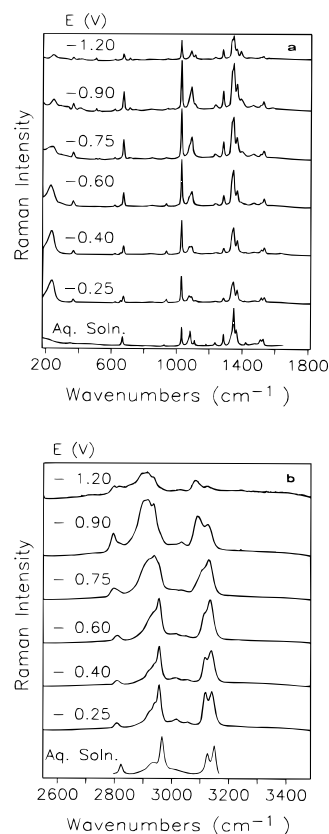


Figure 2. SERS spectra as a function of potential for 0.05 M 1-MeIm/0.1 M KCl with normal Raman spectrum of 1.0 M aqueous 1-MeIm for reference for (a) 200–1800 cm^{-1} and (b) 2600–3400 cm^{-1} regions.

These voltammetric waves are again reversible and linear in magnitude with potential sweep rate. The differential capacitance behavior of this system indicates processes associated with adsorption/desorption and adlayer reorientation processes. It is interesting to note that the minimum in the capacitance associated with the PZC is more pronounced for 2-MeIm than that for 1-MeIm. The cyclic voltammetry of the 2-MeIm system also corresponds well with the SERS results, with the greatest spectral changes occurring at potentials negative of -0.9 V.

A more detailed discussion of the electrochemical phenomena associated with these systems is reserved for a future publication.⁷ However, the electrochemical results presented here indicate the inability of both adsorbates to undergo bulk Faradaic redox processes within the potential region spanned by the SERS studies described below.

Vibrational Frequency Shifts. The SERS spectra of 1-MeIm are shown in Figure 2, and those of 2-MeIm are shown in Figure 3. The SERS and normal Raman (aqueous) frequencies of these two compounds are presented and compared in Tables 1 and 2; vibrational assignments are included from ref 8. A cursory examination of the frequencies of the MeIm species adsorbed to Ag electrodes demonstrates a similarity with those of adsorbed Im.¹

The frequency shifts between the SERS spectra at -0.25 V and normal Raman spectra of 1.0 M solutions are presented in Tables 1 and 2 as $\Delta\nu_{\text{SERS}}$ values where

$$\Delta\nu_{\text{SERS}} = \nu_{\text{SERS}} - \nu_{\text{Soln}}$$

The majority of the modes of both molecules, and a large majority of the Im ring modes, have positive $\Delta\nu_{\text{SERS}}$ values. Under the conditions employed in this study (initial adsorption

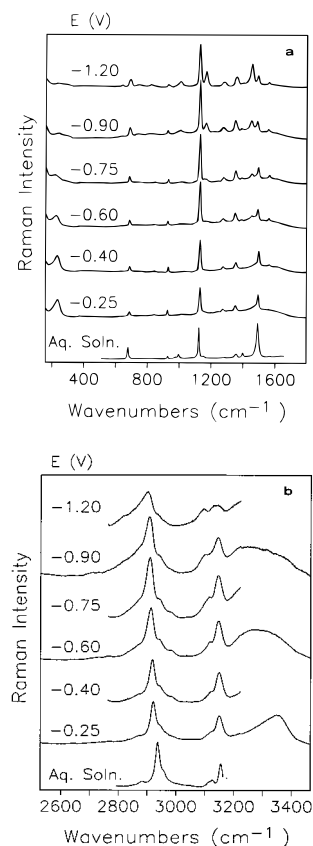


Figure 3. SERS spectra as a function of potential for 0.05 M 2-MeIm/0.1 M KCl with normal Raman spectrum of 1.0 M aqueous 2-MeIm for reference for (a) 200–1800 cm^{-1} and (b) 2600–3400.

at positively charged surfaces), frequency shifts to higher frequencies (positive $\Delta\nu_{\text{SERS}}$ values), especially of ring modes, are characteristic of “N₃”-adsorption.¹

Frequency changes with potential were examined by calculating $\Delta\nu_E$ for separate bands according to:

$$\Delta\nu_E = \Delta\nu_{-1.20 \text{ V}} - \nu_{-0.25 \text{ V}}$$

Negative $\Delta\nu_E$ values are observed for almost every 1-MeIm and 2-MeIm band. Thus, the frequencies are shifting to lower values with increasingly negative potential; this attribute is also characteristic of N-adsorption and was observed for Im adsorption at Ag.¹ Thus, by analogy to the behavior noted for Im, the frequency behavior of these two MeIm isomers strongly suggests that these molecules are predominantly adsorbed to the Ag electrode through the “N₃” lone pair electrons at potentials positive of the PZC. Interaction of “N₁” with the electrode may be ruled out,¹ because the “N₁” atom is sp² hybridized with the lone pair of electrons located in a p-orbital overlapping with the two π -bonds to form a conjugated system. Adsorption through “N₁” would most likely involve the entire conjugated ring system as it does for pyrrole⁹ resulting in a flat orientation. Such an orientation is inconsistent with the spectral data for Im,¹ and as will be shown below, for the MeIm molecules.

Tables 1 and 2 also contain the frequencies of a number of bands, labeled “negative potential species”, whose intensities become substantial, and in some cases, are only present at the most negative potentials studied. The appearance of these bands is accompanied by the reduction in intensities, and in some cases, the disappearance of bands with the same assignment

TABLE 1: Frequencies and $\Delta\nu$ Values for 1-MeIm

vibrational assignments ref 8	Raman shift (cm ⁻¹)		negative potential species ^a	$\Delta\nu_{\text{SERS}}^b$	$\Delta\nu_{\text{E}}^b$
	SERS				
	aqueous (ref 8)	−0.25 V			
$\gamma(\text{NCH}_3)_{\text{op}}$	222		242		
$\delta(\text{NCH}_3)$	350	366		17	−4
$\gamma(\text{R})$	619	621		2	−3
$\nu(\text{NCH}_3)$	668	673		6	−3
$\gamma(\text{CH})_{\text{op}}$			712		
$\gamma(\text{CH})$	855	852		−3	−4
$\gamma(\text{CH})_{\text{op}}$	922	936	951 ^c	14	−8
$\delta(\text{R})$	1031	1029		−2	−4
$\rho(\text{CH}_3)_{\text{ip}}$	1075	1077		2	−2
$\delta(\text{CH})$	1084	1093		9	−6
$\rho(\text{CH}_3)_{\text{op}}$	1110	1116	1109 ^d	6	
combo	1235	1240		5	−6
$\delta(\text{CH})$	1288	1287		−1	−6
$\nu(\text{R})$	1335	1335		0	−2
$\nu(\text{R})$	1350	1347		−3	−2
$\nu(\text{R})$	1367	1370		3	−7
$\delta_{\text{sym}}(\text{CH}_3)_{\text{op}}$	1422	1417	1395	−5	−8
$\delta_{\text{asym}}(\text{CH}_3)$	1475	1472		−3	−4
$\nu(\text{R})$	1512	1517		5	−6
$\nu(\text{R})$	1528	1535		7	−9
$2\nu(\text{R})$	2822	2807	{ 2796		−11
			{ 2816 ^d	−15	9
	2896	2896	{ 2830	0	−66
$\nu_{\text{sym}}(\text{CH}_3)$			{ 2846		−81
			{ 2868 ^d	−5	−59
			{ 2894		−63
$\nu_{\text{sym}}(\text{CH}_3)_{\text{FR}}$			{ 2910 ^d	−10	−47
			{ 2935		−79
			{ 2948 ^d	5	−67
$\nu_{\text{asym}}(\text{CH}_3)$			{ 3003		−47
			{ 3027	18	−23
			{ 3086	9	−35
$\nu(\text{CH})_{\text{C2 atom}}$	3032	3050			
$\nu_{\text{asym}}(\text{HCCH})$	3126	3118	3086	9	−23
$\nu_{\text{sym}}(\text{HCCH})$	3149	3141	3124	6	−15

^a Bands that are distinct from those observed at −0.25 V and characteristic of 1-MeIm orientation at negative potentials. ^b $\Delta\nu_{\text{SERS}} = \nu_{-0.25 \text{ V}} - \nu_{\text{soln}}$ and $\Delta\nu_E = \nu_{-1.20 \text{ V}} - \nu_{-0.25 \text{ V}}$. ^c Appears at −0.60 V. ^d Appears at −0.75 V.

that are observed at −0.25 V. These bands result from splitting of the modes to which they are assigned and indicate significant differences in the orientations and surface interactions of the molecules at the two ends of the potential region studied. The bands that split in this manner are primarily out-of-plane ring modes or methyl modes. The bands belonging to the “negative potential species” generally appear at ca. −0.60 V and frequently replace their positive potential counterparts by −0.90 V. The most striking example of this behavior is the growth of new $\nu(\text{CH}_3)$ features between 2800 and 2950 cm^{-1} in the 1-MeIm SERS spectra. Understanding the significance of these low-frequency features is key to understanding the remainder of the SERS data. Therefore, it is addressed in a general sense in the next section.

Methyl Stretching Region. As shown in Figure 2b, the low-frequency $\nu(\text{CH}_3)$ modes are first noticeable in the 1-MeIm SERS spectrum at ca. −0.60 V as a generalized increase in intensity of the shoulder on the low-frequency side of the $\nu(\text{CH}_3)$ band. They emerge between −0.60 and −0.75 V and dominate the $\nu(\text{CH}_3)$ region at −1.20 V. The gradual disappearance of the bands observed at −0.25 V and the growth of the low-frequency $\nu(\text{CH}_3)$ features are proposed to be due to changes in the relative populations of two distinct 1-MeIm surface populations.

TABLE 2: Frequencies and $\Delta\nu$ Values for 2-MeIm

vibrational assignments (ref 8)	Raman shifts (cm ⁻¹)		negative potential species ^a	$\Delta\nu_{\text{SERS}}^b$	$\Delta\nu_E^b$
	aqueous (ref 8)	SERS (−0.25 V)			
$\nu(\text{CCH}_3)$	272				
$\delta(\text{CCH}_3)_{\text{op}}$			287		
$\delta(\text{CCH}_3)$	367	372		5	0
$\nu(\text{R})$	628	625	640 ^c	−3	−1
$\nu(\text{CCH}_3)$	678	684	689	8	−4
$\delta(\text{CH}_3)_{\text{op}}$			742		
$\nu(\text{CH})$	856	845	816 ^d	−10	−1
$\nu(\text{NH})$	928	928	1003	0	−5
$\nu(\text{R})$ or $\delta(\text{CH})$	996	1009		13	
$\delta(\text{CH})$	1123	1129		6	−2
$\rho(\text{CH}_3)_{\text{op}}$	1153	1153	1166	0	1
$\delta(\text{NH})$	1282	1275		−7	2
$\nu(\text{R})$	1351	1353		2	2
$\nu(\text{R})$	1398	1393		−5	−2
$\delta_{\text{sym}}(\text{CH}_3)$	1398				
$\delta_{\text{asym}}(\text{CH}_3)$	1480	1480	1455	1	1
$\nu(\text{R})$	1492	1497		5	−6
$2\nu(\text{R})$	2882	2880		−2	
$\nu_{\text{sym}}(\text{CH}_3)$	2936	2921		−15	−16
$\nu_{\text{sym}}(\text{CH}_3)_{\text{FR}}$	2959	2944		−15	−14
$\nu_{\text{asym}}(\text{CH}_3)$	2979	2979		0	−17
$\nu_{\text{asym}}(\text{CH}_3)$	3010	3007		3	−21
$\nu_{\text{sym}}(\text{HCCH})$	3128	3118		−10	−27
$\nu_{\text{sym}}(\text{HCCH})$	3156	3151		−5	−15

^a Bands that are distinct from those observed at −0.25 V and characteristic of 2-MeIm orientation at negative potentials. ^b $\Delta\nu_{\text{SERS}} = \nu_{-0.25\text{ V}} - \nu_{\text{soln}}$ and $\Delta\nu_E = \nu_{-1.20\text{ V}} - \nu_{-0.25\text{ V}}$. ^c Appears at −0.60 V. ^d Appears at −0.90 V. ^e Appears at −0.75 V.

In contrast, the general shape of the $\nu(\text{CH}_3)$ region in the 2-MeIm SERS spectrum is relatively less affected by potential as seen in Figure 3b. Although a significant intensity increase on the low energy side of the $\nu(\text{CH}_3)$ band is observed at the most negative potentials, this feature is impossible to assign to individual bands.

Distinct SERS $\nu(\text{CH}_3)$ bands at negative potentials have also been observed for other methyl-containing molecules at Ag electrodes. Molecules for which this behavior has been observed in this laboratory include a series of normal alcohols,^{10–14} a series of methylpyridines,¹⁵ and dimethylsulfide.¹⁶ As in the current study, new low-frequency $\nu(\text{CH}_3)$ features appear for these molecules at negative potentials. Furthermore, the assignment of these “soft” $\nu(\text{CH})$ modes has precedence in the surface science literature. In previous work by Demuth, Ibach, and Lehwald¹⁷ and Hoffman and Upton,¹⁸ similar “soft” $\nu(\text{CH})$ modes were observed for alkyl species adsorbed to metal surfaces in UHV. Remarkably, in the work of these researchers, shifts of the fundamental $\nu(\text{CH})$ modes as large as 200–300 cm⁻¹ to lower frequencies were observed^{17,18} and attributed to attractive “hydrogen-bonding-like” interactions between the C–H and the metal surface.¹⁷ We attribute the broadening and lowering in frequency of $\nu(\text{CH})$ modes for alkyl-containing molecules at negatively charged electrodes to be a manifestation of similar alkyl–metal interactions.

Orientation models for the MeIm molecules begin to emerge from consideration of the differences between the 1-MeIm and 2-MeIm SERS spectra. For “N₃”-bound 1-MeIm at positive potentials, the methyl group of this vertical or tilted molecule is oriented away from and unable to interact with the electrode surface. At negative potentials, the emergence of the low-frequency features is proposed to result from methyl group interaction with the surface. Recent studies in this laboratory have suggested that such methyl group–surface interactions are

quite strong at negatively charged surfaces, often dictating the orientation of solvent molecules or adsorbates at potentials close to or negative of the PZC.^{11,16} Interaction between the π -system of the Im ring and the surface is also possible, but is proposed to play less of a role than “N₃” and methyl group interactions.

The emergence of relatively distinct $\nu(\text{CH}_3)$ bands for two orientations of 1-MeIm results from a transition from predominantly one orientation to the other. At positive potentials, 1-MeIm interacts with the surface through the “N₃” lone pair electrons placing the methyl group on the opposite side of the ring where it is physically unable to interact with the surface. As the potential becomes more negative, interaction between the methyl group and the negatively charged surface becomes increasingly favored, and some of the molecules change orientation. At the most negative potentials, the strength of this methyl group–surface interaction dominates, and the population of molecules interacting through the methyl group is very large. A transition in which methyl-bound 1-MeIm becomes dominant occurs around the PZC (estimated to be at ca. −0.9 V in this medium.¹⁹)

In contrast, the methyl group of 2-MeIm is in close proximity to the surface over the entire potential range studied. At positively charged surfaces, the orientation required for interaction of the “N₃” lone pair electrons with the surface places the methyl group very near the surface, although the strength of the chemical interaction is apparently weak at these potentials based on the lack of spectral perturbation observed. At more negative potentials, the methyl group–surface interaction increases and the “N₃”-surface interaction decreases leading to growth of the low-frequency $\nu(\text{CH}_3)$ modes. Furthermore, a continual shift of the 2-MeIm $\nu_{\text{sym}}(\text{CH}_3)$ mode to lower frequency with increasing negative potential results from an increasing methyl group–surface interaction. This shift and the general broadening of the 2-MeIm $\nu_{\text{sym}}(\text{CH}_3)$ feature are indicative of methyl group–surface interaction.

It should be noted that the potential dependence of the spectra of both MeIm molecules is completely reversible as shown by the data in Figure 4. Although the absolute intensities of the spectra of both species decrease irreversibly after exposure to the most negative potentials studied, presumably as a result of the irreversible loss of atomic scale roughness features, the spectra at the more positive potentials (e.g., −0.25 V) can be regenerated after exposing an electrode to even the most negative potentials (e.g., −1.20 V) studied. This reversibility is consistent with the reversibility observed in the cyclic voltammetry of these systems described above.

The general models that emerge from qualitative consideration of the $\nu(\text{CH}_3)$ region of these spectra are, in fact, confirmed by a more quantitative assessment of features in all spectral regions. After an introduction to the quantitative approach taken in analyzing these data in the next section, the remainder of this paper details the arguments which support the general models of the potential-dependent orientations of 1- and 2-MeIm developed in this section.

Relative SERS Enhancement Factors. In order to eliminate the need to determine absolute SERS enhancement factors for individual Raman bands and to account for changes in adsorbate surface coverage that occur as a function of potential, it is useful to calculate a relative enhancement factor (R_{EF}) for a particular Raman band:

$$R_{\text{EF}} = \left(\frac{I}{I_{\text{ref}}} \right)_{\text{SERS}} / \left(\frac{I}{I_{\text{ref}}} \right)_{\text{Raman}}$$

where I represents the intensity (normal Raman and SERS) of

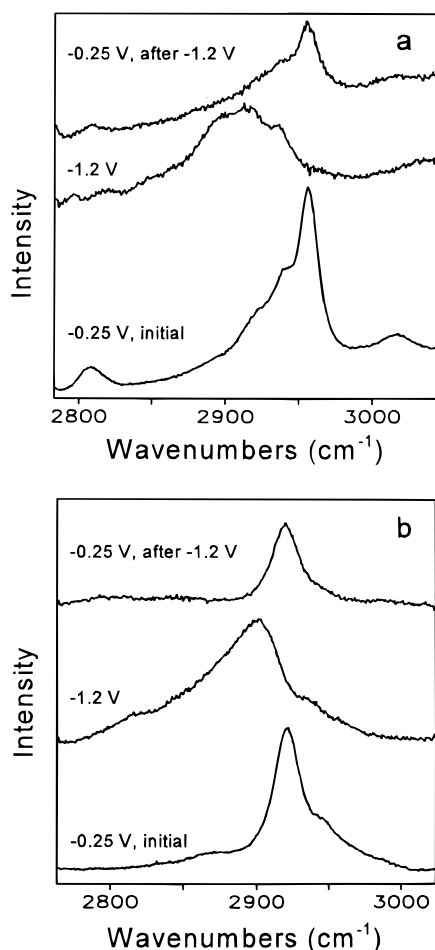


Figure 4. SERS spectra indicating reversibility of potential-dependent response. (a) 0.05 M 1-MeIm/0.1 M KCl and (b) 0.05 M 2-MeIm/0.1 M KCl.

the band of interest and I_{ref} represents the intensity (normal Raman and SERS) of a reference band. R_{EF} describes changes in intensity of the band of interest relative to the reference band and infers a corresponding difference in the SERS enhancement of the two bands. Identical SERS enhancement of the two bands occurs for $R_{\text{EF}} = 1$, less enhancement of the band of interest compared to the reference band occurs for $R_{\text{EF}} < 1$, and greater enhancement of the band of interest occurs for $R_{\text{EF}} > 1$.

For this study, SERS bands were compared to their aqueous solution normal Raman counterparts. Thus, R_{EF} becomes

$$R_{\text{EF}} = \left(\frac{I}{I_{\text{ref}}} \right)_{\text{SERS}} \left/ \left(\frac{I}{I_{\text{ref}}} \right)_{\text{soln}} \right.$$

One problem with using this approach is the need to use a reference band which may itself be subject to changes in SERS enhancement. The symmetric ring-breathing modes of the MeIm molecules were used to calculate R_{EF} values based on our previous work with Im.¹ As a result, R_{EF} values reflect the convolved behavior of the two bands.

A related method for estimating the orientation of specific functional groups relative to the surface has been devised by calculating R_{EF} -like ratios relating two modes of the functional group having different spatial orientations. This approach for the methyl group as an orientation indicator has been successfully used in past SERS studies in this laboratory.^{2,11–15} In this method, the intensity ratio of the $\nu_{\text{sym}}(\text{CH}_3)$ and $\nu_{\text{asym}}(\text{CH}_3)$

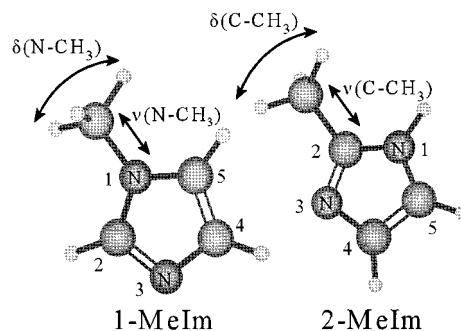


Figure 5. Vibrational modes used in computation of R_{NC} for 1-MeIm and R_{CC} for 2-MeIm.

modes from both SERS and solution spectra are compared through the overall ratio R_{Me}^2

$$R_{\text{Me}} = \left[\frac{I_{\nu_{\text{sym}}(\text{CH}_3)}}{I_{\nu_{\text{asym}}(\text{CH}_3)}} \right]_{\text{SERS}} \left/ \left[\frac{I_{\nu_{\text{sym}}(\text{CH}_3)}}{I_{\nu_{\text{asym}}(\text{CH}_3)}} \right]_{\text{soln}} \right.$$

Values of R_{Me} vary with the angle θ between the bond connecting the methyl group to the molecule and the surface normal. R_{Me} values are predicted² to range from 0.1 ($\theta = 90^\circ$) to 10 ($\theta = 0^\circ$) and will be 1 when $\theta = 45^\circ$, assuming the electric field normal to the surface is exactly 1 order of magnitude greater than that parallel to the surface.

For the MeIm species, other modes which involve the methyl group are valuable in interpreting the SERS results using a similar approach. Coupled pairs of vibrational modes analogous to the $\nu_{\text{sym}}(\text{CH}_3)$ and $\nu_{\text{asym}}(\text{CH}_3)$ pair of the methyl group used to calculate R_{Me} values can be identified for each of the MeIm molecules: the $\delta(\text{N}-\text{CH}_3)$ and $\nu(\text{N}-\text{CH}_3)$ modes for 1-MeIm, as well as the $\delta(\text{C}-\text{CH}_3)$ and $\nu(\text{C}-\text{CH}_3)$ modes for 2-MeIm. These modes have two features in common with the methyl stretch modes used to calculate R_{Me} : (1) they appear in the spectra at unique frequencies, and (2) their motions are spatially orthogonal such that variations in their relative intensities provide information about the orientation of one mode relative to the other.

One mode in each pair involves motion of the methyl group relative to the ring, and one mode involves motion of the bonds connecting the methyl group to the rings. These motions are illustrated in Figure 5. The change in SERS intensity of these modes, relative to the same modes, in the solution spectra, can be evaluated by calculating the following ratios: for 1-MeIm,

$$R_{\text{NC}} = \left(\frac{I_{\delta(\text{N}-\text{CH}_3)}}{I_{\nu(\text{N}-\text{CH}_3)}} \right)_{\text{SERS}} \left/ \left(\frac{I_{\delta(\text{N}-\text{CH}_3)}}{I_{\nu(\text{N}-\text{CH}_3)}} \right)_{\text{soln}} \right.$$

and for 2-MeIm,

$$R_{\text{CC}} = \left(\frac{I_{\delta(\text{C}-\text{CH}_3)}}{I_{\nu(\text{C}-\text{CH}_3)}} \right)_{\text{SERS}} \left/ \left(\frac{I_{\delta(\text{C}-\text{CH}_3)}}{I_{\nu(\text{C}-\text{CH}_3)}} \right)_{\text{soln}} \right.$$

Unlike R_{Me} , R_{NC} and R_{CC} are not directly related to angles between the N–C or C–C bonds and the surface normal; however, they can be used to determine which of the two modes is oriented more normal to the surface. The modes used to determine R_{NC} and R_{CC} are in-plane modes, and as a result, the SERS enhancements of the two modes (δ and ν) are affected equally by tilting of the Im ring plane. Thus, R_{NC} and R_{CC} are unaffected by changes in *only* the angle of the ring plane relative to the surface. However, if the molecule is tilted “side-to-side”

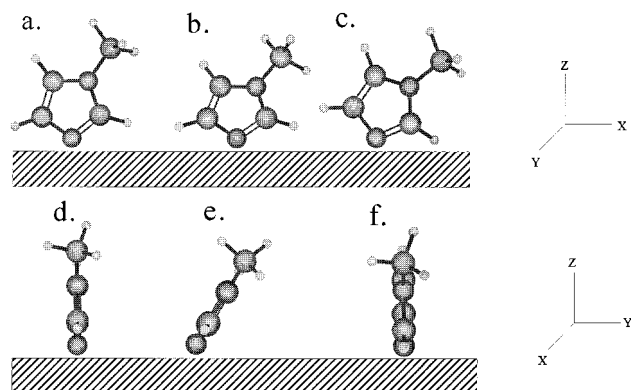


Figure 6. Comparison of molecular-plane tilting and “side-to-side” tilting of 1-MeIm. (a–c) Face-view, (d–f) Side-view, (a and d) perfectly vertical 1-MeIm. (b and e) Molecular-plane tilt only; (c and f) “side-to-side” tilt only.

the enhancements of these modes change in opposite directions, and R_{NC} and R_{CC} are affected. The “side-to-side” tilt (as opposed to tilting of the ring plane) can be better understood by considering Figure 6.

Two molecular views of 1-MeIm are presented in Figure 6. In the “side-view” (d–f), the molecule is viewed with the plane of the ring (in the xz plane) perpendicular to the page permitting the reader to view the tilting of the molecular plane relative to the surface in the yz plane. The “face-view” (a–c) is rotated 90° from the side-view, and shows “side-to-side” tilting of the molecule in the xz plane. “Side-to-side” tilting of the molecule is most easily noted in the “face-view” as a change either in the *relative* distances of atoms from the surface or by the change in angle of the N–CH₃ bond relative to the surface normal in the xz plane in Figure 6. Orientations will be discussed relative to “perfectly vertical” “N₃”-bound 1-MeIm (Figure 6a and d).

Figures 6b and e portray a tilting of the molecule in the yz plane. The C₂ and C₄ atoms are equidistant from the surface in the orientations shown in Figures 6a,b and d,e. In this case, the orientations in Figures 6a and b can be considered to have similar “side-to-side” tilts and R_{NC} should be approximately the same for both orientations. Only “side-to-side” tilting *in addition to molecular plane tilting* will change R_{NC} .

“Side-to-side” tilt in the xz plane is portrayed by Figures 6c and f. Note that the molecular-plane tilt in the yz plane is identical to that in the perfectly vertical orientation (Figure 6d). However, the C₂ atom is nearer the surface than the C₄, and the angle between the N–CH₃ bond and the surface normal in the xz plane is greater than in Figure 6a and b. Thus, R_{NC} would be greater for this orientation. For a given “side-to-side” tilt, if the molecular-plane of the 1-MeIm represented by Figures 6c and f was also tilted in the yz plane (as in Figure 6e), R_{NC} would not change further.

By analogy with the behavior of the two $\nu(\text{CH}_3)$ modes,² and considering the simplest case of only the xz plane, if the angle of the N–CH₃ or C–CH₃ bond is 45° with respect to the surface normal, R_{NC} or R_{CC} should be equal to one. If the angle is greater than 45°, the stretching mode is enhanced less than the bending mode, and R_{NC} or R_{CC} would be greater than one, and if the angle is less than 45°, the ratio is expected to be less than one. It should be noted, however, that these simple situations do not allow for the more complex case of rotation of the ring plane about the N–C bond (a combination of “side-to-side” tilt plus molecular plane tilt.) Such rotation adds additional complexity to this analysis and causes deviation of R_{NC} from these ideal values. Nonetheless, it is a useful starting point for

TABLE 3: Ratio Values for 2-MeIm

E (V vs SCE)	2-MeIm R_{Me}^a	2-MeIm R_{CC}^b
–0.25	0.5	2.8
–0.40	0.5	3.3
–0.60	0.4	2.7
–0.75	0.4	2.2
–0.90	0.5	1.7
–1.20	0.4	1.2

^a Aqueous value calculated using 2979 and 2959 cm^{–1} bands.

^b Calculated using the combined R_{EF} values of 684 and 689 cm^{–1} bands.

analysis, since rotation of the ring-plane will affect the enhancement of all in-plane modes equally.

In the following sections, the use of these ratios for the determination of potential-dependent MeIm orientations is discussed separately for each molecule.

2-Methylimidazole

2-MeIm Methyl Modes. R_{Me} values for 2-MeIm are reported in Table 3. These values are relatively constant at ca. 0.4–0.5 across the entire potential region studied suggesting that the angle of the axis of the methyl group relative to the surface normal is greater than 45°. Assuming the electric field normal to the surface is between 5 and 10 times greater than that parallel to the surface,² the angle of this axis with respect to the surface normal can be estimated to range between ca. 80° and 74°, respectively.²⁰ The data suggest that this angle decreases slightly as the potential is made more negative with the transition beginning at ca. –0.60 V. For the most part, however, the angle between the axis of the methyl group and the surface normal is almost invariant with changes in potential.

The $\nu(\text{C–CH}_3)$ band splits into two bands in the SERS spectra at ca. 684 and 689 cm^{–1}. The 684 cm^{–1} band is prevalent at more positive potentials, and the 689 cm^{–1} band dominates at the most negative potentials. The relative intensities of the δ -(C–CH₃) and the ν (C–CH₃) bands are compared using R_{CC} values in Table 3. R_{CC} values, calculated using the integrated intensities of the envelope of both ν (C–CH₃) bands, are greater than one between –0.25 and –0.75 V. Although more complicated to interpret than R_{Me} values, large R_{CC} values are generally consistent with the δ (C–CH₃) mode (i.e., ring plane) being slightly more perpendicular to the surface than the ν (C–CH₃) mode (i.e., C–C bond) to an extent that varies with potential. In order for these modes to be oriented in this fashion, the methyl group axis must be largely parallel to the surface (consistent with the R_{Me} values), and the ring plane must be greater than 45° with respect to the surface normal. At the most negative potentials, the R_{CC} values decrease and approach one at –1.20 V. This decrease in R_{CC} requires an increase in angle between the surface normal and the molecular plane.

2-MeIm In-plane/Out-of-plane Modes. Examination of variations in the R_{EF} values of in-plane and out-of-plane modes with potential should provide additional insight into the behavior of the ring plane. The relatively unchanging orientation of the methyl group makes the ν (C–CH₃) band a useful reference band. The essentially invariant orientation of this band with potential implies an equally stable enhancement factor making it the ideal reference band for determining R_{EF} values.

Figure 7 shows R_{EF} values for six 2-MeIm in-plane modes relative to the ν (C–CH₃) band at 684 cm^{–1}. When analyzed in this fashion, these bands all exhibit similar potential dependence. The R_{EF} values of the in-plane modes shown in Figure 7 generally increase from an intermediate value at –0.25 V to a maximum at ca. –0.60 to –0.75 V and then decrease to

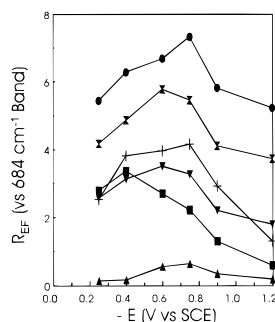


Figure 7. R_{EF} values for 2-MeIm in-plane modes relative to 684 cm^{-1} mode. (shaded dot) 1275 cm^{-1} , (shaded hourglass) 1353 cm^{-1} , (plus) 3118 cm^{-1} , (shaded upside down triangle) 1129 cm^{-1} , (shaded box) 372 cm^{-1} , and (shaded upright triangle) 1393 cm^{-1} .

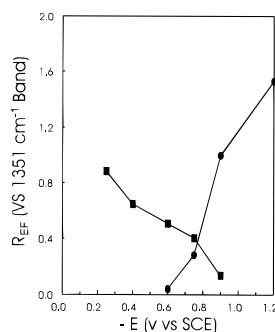


Figure 8. R_{EF} values for 2-MeIm out-of-plane $\gamma(R)$ modes at (shaded box) 625 cm^{-1} and (shaded dot) 640 cm^{-1} .

a minimum value at -1.20 V. This clearly indicates that the ring plane of 2-MeIm is initially tilted at -0.25 V and assumes an orientation more normal to the surface as the potential approaches -0.6 to -0.8 V. At the most negative potentials, the ring again tilts, eventually assuming an angle with respect to the surface which is smaller than observed at -0.25 V.

Two trends are observed for out-of-plane modes. First, two out-of-plane bands, the $\delta(\text{C}-\text{CH}_3)$ at 287 cm^{-1} and the $\delta(\text{CH}_3)$ at 742 cm^{-1} which are absent at more positive potentials, appear as the potential is made more negative. Due to the small angle between the 2-MeIm molecular plane and the surface at more negative potentials, these modes are significantly enhanced such that they are observed.

The second trend is that several out-of-plane modes split into two bands, with each one of the split bands dominating the spectrum at opposite ends of the potential range. The $\gamma(R)$ band (628 cm^{-1} in aqueous solution) is a typical example producing two bands at ca. 625 and 640 cm^{-1} . The 625 cm^{-1} band dominates the spectrum at positive potentials, and the 640 cm^{-1} band dominates at negative potentials. The R_{EF} values for these two bands are plotted as a function of potential in Figure 8. The combined behavior of these two bands is essentially opposite to the behavior described above for the in-plane modes in that they exhibit intermediate values at -0.25 V, decrease to minimum values at ca. -0.6 to -0.8 V, and then finally increase to their maximum values at the most negative potentials. These variations in R_{EF} value are consistent with the ring plane going from a slightly tilted orientation at positive potentials to near-vertical at intermediate potentials to near-parallel at negative potentials. Other bands that behave in a similar manner are the $\gamma(\text{CH})$ band, which splits into bands at 816 and 845 cm^{-1} , the $\gamma(\text{NH})$ band, which splits into bands at 928 and 1003 cm^{-1} , the out-of-plane $\rho(\text{CH}_3)$ at 1153 cm^{-1} , and the $\delta_{\text{asym}}(\text{CH}_3)$ band at 1480 cm^{-1} . The large shift of the $\gamma(\text{NH})$ band to higher frequencies at negative potentials is significant and indicates

that there may be an interaction of the NH bond with the surface at the most negative potentials. In fact, we speculate that such H-surface interactions for slightly acidic or polarizable hydrogens, including those on the methyl group and the “N₁” atom, are responsible for the almost parallel molecular plane orientation of 2-MeIm at negative potentials.

The 1398 cm^{-1} band of aqueous 2-MeIm has been assigned to a coincidental degeneracy of the $\nu(R)$ and the $\delta_{\text{sym}}(\text{CH}_3)$ modes. The corresponding SERS band (1393 cm^{-1}) is enhanced significantly less than the $\nu(\text{C}-\text{CH}_3)$ reference band, and its potential dependence suggests in-plane behavior. The observed SERS intensity must result from the $\nu(R)$ mode, because the $\delta_{\text{sym}}(\text{CH}_3)$ mode will be nearly parallel to the surface at all orientations. Small R_{EF} values for this band result from the absence of a significant contribution from the $\delta_{\text{sym}}(\text{CH}_3)$. The potential dependence of the R_{EF} values is also explained by a minimal contribution from the $\delta_{\text{sym}}(\text{CH}_3)$ band. Thus, even though both modes are present in solution, the observed SERS behavior is attributable only to the $\nu(R)$ mode.

The two $\nu(\text{HCCH})$ modes at 3118 and 3151 cm^{-1} are also largely normal to each other, and a comparison of their SERS intensities should provide additional orientation insight. The intensities of the $\nu_{\text{asym}}(\text{HCCH})$ mode (3151 cm^{-1}) relative to the $\nu_{\text{sym}}(\text{HCCH})$ mode (3118 cm^{-1}) are less in the SERS spectra than in the aqueous spectrum at all potentials. This difference is small at -0.25 V, but increases over the entire potential range, and is quite marked at -1.20 V. This trend implies that the $\nu_{\text{asym}}(\text{HCCH})$ mode is more normal to the surface than the $\nu_{\text{sym}}(\text{HCCH})$, marginally at more positive potentials and drastically at -1.20 V, consistent with the proposed orientation for 2-MeIm.

1-Methylimidazole

1-MeIm Methyl Modes. In analyzing the $\nu(\text{CH}_3)$ vibrations of 1-MeIm, it will be necessary to address the behavior of the two orientations which are indicated by splitting of the $\nu(\text{CH}_3)$ bands.

The curve-fit spectrum of 1-MeIm adsorbed at a Ag electrode at -0.25 V in Figure 9a highlights the characteristic bands of “N₃”-adsorbed 1-MeIm in the $\nu(\text{CH}_3)$ region. R_{Me} values for “N₃”-adsorbed 1-MeIm were determined using the 2957 cm^{-1} $\nu_{\text{sym}}(\text{CH}_3)$ and 3015 cm^{-1} $\nu_{\text{asym}}(\text{CH}_3)$ bands and are presented in Table 4. Initial R_{Me} values of “N₃”-adsorbed 1-MeIm are slightly less than one indicating that the methyl group angle relative to the surface is close to although slightly greater than ca. 45° with respect to the surface normal. The angle between the methyl group of perfectly vertical “N₃”-bound 1-MeIm and the surface normal is 36° . Thus, the observed angle requires the molecular-plane to be tilted, or the C₂ atom to be nearer the surface than the C₄ atom (“side-to-side” tilt), or both; evidence presented below demonstrates that both factors contribute to the observed methyl group orientation. The R_{Me} values increase slightly to a value greater than one prior to the disappearance of the 3015 cm^{-1} $\nu_{\text{asym}}(\text{CH}_3)$ band at -0.90 V. Thus, assuming that the out-of-plane component of the $\nu_{\text{asym}}(\text{CH}_3)$ is being observed, the molecular plane must be oriented more normal to the surface as the potential is varied from -0.25 to -0.75 V, approaching the behavior expected for vertically-oriented, “N₃”-adsorbed 1-MeIm. Interestingly, the $\nu_{\text{asym}}(\text{CH}_3)$ band is absent or significantly shifted in frequency at -0.90 and -1.20 V, suggesting that the species (“N₃”-adsorbed) associated with this band must be absent from the surface or present at coverages below the detection limit of these SERS experiments. Further information about orientation of the methyl group at potentials negative of the PZC must be obtained by considering the entire $\nu(\text{C}-\text{H})$ envelope.

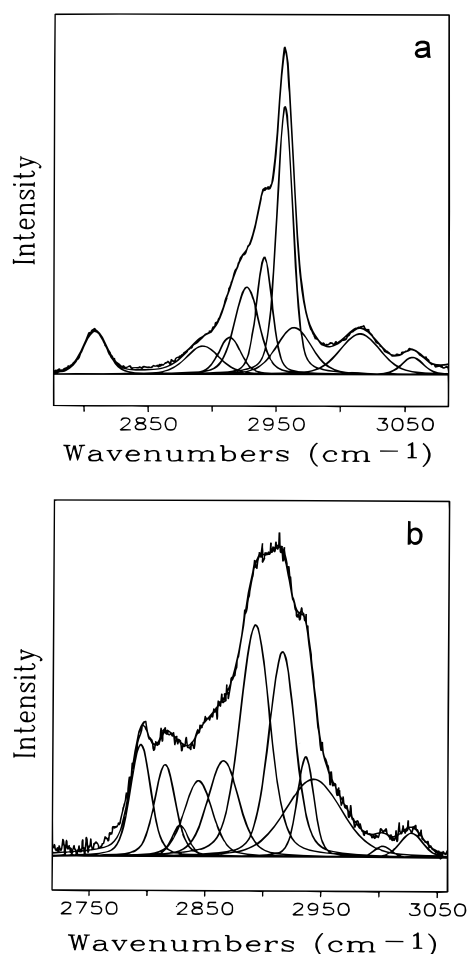


Figure 9. Curvefit SERS spectra of 1-MeIm $\nu(\text{CH}_3)$ region at (a) -0.25 V and (b) -1.20 V.

TABLE 4: Ratio Values for 1-MeIm

E (V vs SCE)	R_{Me}^a (N-adsorbed species)	R_{Me}^b (π -adsorbed species)	1-MeIm (R_{NC})
-0.25	0.8		1.5
-0.40	0.9	0.1	1.3
-0.60	1.1	0.4	1.2
-0.75	1.1	0.4	1.0
-0.90		0.4	0.9
-1.20		0.5	1.1

^a Calculated using 3015 and 2957 cm^{-1} bands. ^b Calculated using 2948 and 2894 cm^{-1} bands.

The curve-fit spectrum of 1-MeIm adsorbed at Ag electrodes at -1.20 V is shown in Figure 9b. The broad band at 2948 cm^{-1} is assigned to the $\nu_{\text{asym}}(\text{CH}_3)$ mode of a new surface species. The bands at 2868 and 2894 cm^{-1} are assigned to the two Fermi resonance bands of the $\nu_{\text{sym}}(\text{CH}_3)$ mode. These frequencies are significantly lower than their “N₃”-bound counterparts suggesting significant perturbation of the methyl group for this surface species. In fact, similar low-frequency $\nu(\text{CH}_3)$ modes have been observed previously for species in which the methyl group is in direct contact with the metal surface.^{10–18} As in the case of 2-MeIm discussed above and these previously studied systems, methyl group–surface interactions occur primarily on negatively charged electrode surfaces. Thus, we propose that 1-MeIm is oriented in a fashion that promotes substantial interaction between the methyl group and the surface at these negative potentials. This species is referred to here as the methyl-bound 1-MeIm species. Additional ν -

(CH) modes at 2846, 2816, and 2796 cm^{-1} are observed which correspond to the 2927, 2896, and 2807 cm^{-1} bands at -0.25 V.

R_{Me} values for methyl-bound 1-MeIm determined using the 2948 cm^{-1} $\nu_{\text{asym}}(\text{CH}_3)$ and 2894 cm^{-1} $\nu_{\text{sym}}(\text{CH}_3)_{\text{FR}}$ bands are also presented in Table 4. R_{Me} values at the most negative potentials based on these assignments are ca. one-half the values observed for “N₃”-adsorbed and aqueous 1-MeIm. Thus, the angle of the methyl group relative to the surface is significantly greater than 45° . The small angle between the methyl group and the surface places the Im ring in close proximity to the surface suggesting that, in addition to the methyl group, the Im ring or its hydrogen atoms may interact with the surface as well.

The variation of the R_{NC} ratio of the 1-MeIm $\nu(\text{N}-\text{CH}_3)$ and $\delta(\text{N}-\text{CH}_3)$ bands suggests changes in the “side-to-side” tilt of the 1-MeIm molecule with changes in potential. This behavior is analogous to that observed for 2-MeIm as indicated by the R_{CC} ratio. Initially, at the more positive potentials, R_{NC} values are greater than one. The C₂ atom of the “N₃”-adsorbed 1-MeIm must be nearer the surface than the C₄ atom to obtain this value. In this orientation, the N=C π -bond is near the electrode surface and probably contributes to the interaction of this molecule with the surface. As the potential approaches the PZC, R_{NC} decreases to a value close to one. Thus, the angle of the methyl group with the surface nears 45° , approaching the angle expected for the perfectly erect “N₃”-adsorbed molecule (36°). It is notable that both R_{Me} and R_{NC} values near the PZC are close to what is expected for perfectly vertical, “N₃”-adsorbed 1-MeIm.

At the most negative potentials where R_{Me} suggests that methyl-bound 1-MeIm dominates, the R_{NC} value increases to 1.1, suggesting that the angles relative to the surface of both the $\delta(\text{NCH}_3)$ and the $\nu(\text{NCH}_3)$ modes are nearly the same. Given the small methyl group-surface angles of methyl-adsorbed 1-MeIm indicated by the R_{Me} values, the equivalency of the angles between these two vibrational modes and the surface leads to two conclusions. The angle between both of these modes, and thus the ring-plane, and the surface must be less than 45° . Secondly, C₂ and C₅ are different distances from the surface. Two orientations meet these criteria involving interaction of either the C₂ hydrogen atom or the C₅ hydrogen atom with the surface. The $\nu(\text{CH})$ SERS data can be used to distinguish between these two options.

Two ring $\nu(\text{CH})$ bands are observed in the 1-MeIm aqueous Raman and SERS spectra. Both bands broaden and shift to significantly lower frequencies at potentials between -0.60 and -1.20 V. This behavior is reminiscent of that of the methyl group, and confirms the conclusion made above that ring hydrogens also interact with the surface. The band at 3141 cm^{-1} is assigned to the $\nu_{\text{sym}}(\text{HCCH})$ mode and the 3118 cm^{-1} band is assigned to the $\nu_{\text{asym}}(\text{HCCH})$ mode. The broadening and shift to lower frequency of both bands establishes the involvement of the H-C=C-H group in the surface interaction. Thus, the methyl group and the C₄ and C₅ hydrogen atoms are proposed to interact with the surface at negative potentials.

1-MeIm In-plane/Out-of-plane Modes. Unlike 2-MeIm, no 1-MeIm band is identifiable which has the same surface orientation at all potentials. Thus, R_{EF} values were calculated relative to the three $\nu(\text{R})$ modes at 1335, 1347, and 1370 cm^{-1} . Rather than choose between one of these modes, the average intensity of all three was used to calculate R_{EF} values in order that variations in the behavior of the individual ring modes might be averaged out. Figure 10 shows the R_{EF} values of in-plane modes which demonstrate the same general behavior as was observed for 2-MeIm in-plane modes, first increasing as the

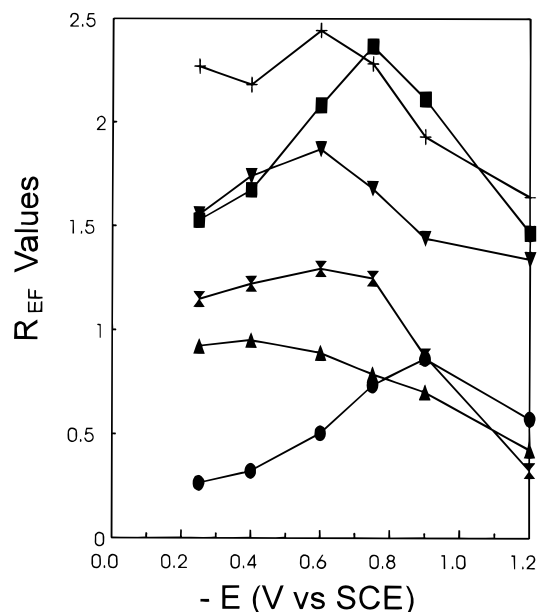


Figure 10. R_{EF} values for 1-MeIm in-plane modes. (plus) 366 cm^{-1} , (shaded box) 673 cm^{-1} , (shaded upside down triangle) 1029 cm^{-1} , (shaded hourglass) 1077 cm^{-1} , (shaded upright triangle) 1535 cm^{-1} , and (shaded dot) 1093 cm^{-1} .

potential is made negative before decreasing at the most negative potentials studied.

As with 2-MeIm (Figure 8), a number of out-of-plane bands are split. One branch, due to "N₃"-adsorbed 1-MeIm, is present at more positive potentials and decreases in intensity as potential is made more negative. The second branch, due to methyl-adsorbed 1-MeIm, is weak or absent at -0.25 V and increases in intensity as the potential is made more negative. The split out-of-plane bands observed in the 1-MeIm spectra belong to the $\gamma(\text{CH})$ modes at 936 and 951 cm^{-1} , the out-of-plane $\rho(\text{CH}_3)$ modes at 1109 and 1116 cm^{-1} , and the out-of-plane $\delta_{\text{asym}}(\text{CH}_3)$ modes at 1395 and 1417 cm^{-1} .

Two out-of-plane bands are observed only at the most negative potentials: the 712 cm^{-1} $\gamma(\text{CH})$ mode and the 242 cm^{-1} $\gamma(\text{N}-\text{CH}_3)$ mode. No band is observed near 712 cm^{-1} in the aqueous 1-MeIm Raman spectrum,¹ but in the IR spectroscopy of a CS₂ solution, a band at 728 cm^{-1} has been assigned to a $\gamma(\text{CH})$ mode. It is possible that the 712 cm^{-1} SERS band belongs to the same mode as a result of increased enhancement of out-of-plane modes due to the ring-plane being almost parallel to the surface at the most negative potentials. The SERS behavior of the $\gamma(\text{N}-\text{CH}_3)$ mode is complicated by its proximity to the $\nu(\text{AgCl})$ stretching vibration, and both of these bands are superimposed on the intense Raleigh line tail. The band at ca. 235 cm^{-1} observed at positive potentials is due to the $\nu(\text{Ag}-\text{Cl})$ mode. This band decreases in intensity and shifts to lower frequency with increasing negative potential, as expected. At more negative potentials, a band appears at ca. 242 cm^{-1} . No band of this intensity is observed in the SERS spectra of Im.¹ Thus, this band is assigned to the $\gamma(\text{N}-\text{CH}_3)$ mode. The greater intensity of this out-of-plane band in the SERS spectra at negative potentials compared with the solution spectrum is consistent with a ring plane that is largely parallel to the surface.

These data clearly suggest that the behavior of R_{EF} values of the in-plane and out-of-plane modes for both 1-MeIm and 2-MeIm are identical. Therefore, the changes in 1-MeIm ring-plane orientation with potential mirror those observed for 2-MeIm: tilted initially at -0.25 V, becoming near normal close

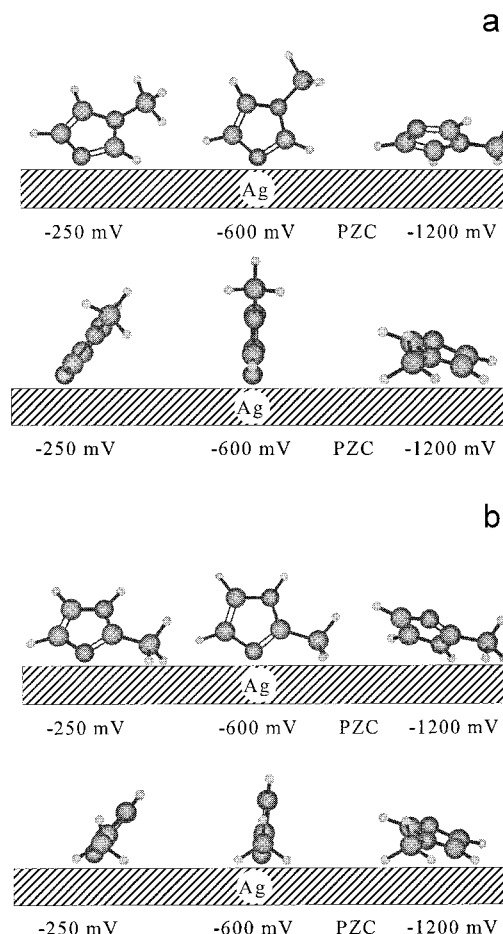


Figure 11. Models for (a) 1-MeIm and (b) 2-MeIm adsorption to Ag electrodes.

to the PZC, and at the most negative potentials, tilted with the ring plane largely parallel to the surface.

Adsorption Models

Models for the potential-dependent adsorption of 1-MeIm and 2-MeIm at Ag electrodes are presented in Figures 11a and b, respectively. These models are based on the SERS results and the principles of electrosorption. As in Figure 6, two views are presented in this figure, each rotated by 90°. Three potential regions (-0.25 , -0.60 , and -1.20 V) are shown and the approximate location of the PZC is included for reference. The general behavior of the two molecules is the same and they will be discussed together.

Following the ORC, the potential is at -0.25 V which is positive of the PZC. MeIm species (and Im¹) in this region interact with the electrode through the "N₃" lone pair of electrons. The plane of the molecule is tilted (not normal to the surface) at the most positive potentials and the C₂ atom is nearer the surface than the C₄ atom (i.e., the molecule is tilted "side-to-side"). Because of steric interactions between the methyl group and the surface, the C₂ atom of 2-MeIm is not as close to the surface as that of 1-MeIm. However, it is probably nearer to the surface than the ball-and-stick model of Figure 11 portrays. This initial orientation directs the N=C π -bond toward the surface, suggesting that the π -orbital interacts with the surface in addition to the "N₃" lone pair.

As the potential is changed towards the PZC, the MeIm molecules assume a position more vertical to the surface, shown for example at -0.60 V. The N=C bond also moves away

from the surface weakening any π -orbital interactions with the surface such that C_2 and C_4 are about the same distance from the surface. Because surface coverage of an adsorbate is typically highest for neutral organic molecules near the PZC, it is reasonable that the surface coverage at -0.25 V is lower than that at -0.60 V, and increases further as the PZC is approached. It is typical for flat or tilted molecules at surfaces to take on a more vertical orientation when conditions favor higher surface coverages. For MeIm molecules, this would result in a decrease in the tilt of the molecular plane with respect to the surface normal lessening the interaction of the π orbital with the surface. The increased number of " N_3 "-surface interactions resulting from an increased surface coverage must make up for the weakening of the π -orbital-surface interactions.

Finally, data in this report support methyl group-surface interactions at negatively charged electrodes. The transition to the methyl-adsorbed state begins at potentials negative of ca. -0.60 V. Recent semiempirical theoretical calculations reported by Romanowski et al.²¹ predict adsorption of alcohol molecules to Hg clusters through methyl group interactions with a noncharged (i.e., at the PZC) metal cluster. Methyl group interactions with a negatively charged surface can be understood as an extension of this behavior as electric field-induced dipole interactions between the surface and the methyl group. However, the presence of methyl-adsorbed MeIm before and near the PZC further suggests that the hydrophobic methyl group interacts with a Ag electrode surface which is increasingly hydrophobic due to the loss of specifically adsorbed Cl^- . This proposal is in harmony with the cyclic voltammetry shown in Figure 1 if the "butterfly" waves centered at ca. -0.3 V for both MeIm species are due to desorption of specifically adsorbed Cl^- .

Finally, the small angles between the ring-planes and the surface are indicative of Im ring interaction with the surface. The broadening and shifting in the $\nu(CH)$ and the $\delta(NH)$ modes point to interactions of the $H-C\equiv C-H$ group of the 1-MeIm and the $N-H$ group of 2-MeIm with the surface.

These models, albeit perhaps counterintuitive at first glance, are the only orientations consistent with the SERS data. Moreover, the SERS data in *all* spectral regions are self-consistent in their predictions of the orientations shown in Figure 11. Three independent orientation indicators were assessed for each of these molecules: (1) ring plane tilt from in-plane/out-of-plane mode data, (2) methyl group orientation from R_{Me} values, and (3) "side-to-side" tilt from R_{NC} and R_{CC} values. Any two of these indicators provide enough information to deduce the orientation of the MeIm molecules; the third provides an independent check of the orientation. These results are also consistent with the results from our earlier Im SERS work.¹ However, more details about the orientations of 1-MeIm and 2-MeIm (presented as ring-plane and side-to-side tilting) could be extracted here due to the additional insight provided by the presence of the methyl group.

Conclusions

The utility of using relative SERS enhancement factors has been clearly demonstrated by the overall success in analyzing

ring tilt, side-to-side tilt, and methyl group orientation from R_{EF} , R_{CC} , and R_{NC} , and R_{Me} values. Analysis of R_{EF} values is complicated by potential-induced changes in reference band enhancement. However, this problem can be minimized by careful selection of reference bands used in calculating these values. Detailed orientations of these molecules as a function of potential were obtained from the SERS data. In general, the resulting molecular pictures are consistent with previous work on Im at positively charged surfaces. At positive potentials, both Im and the MeIm isomers are adsorbed to the surface through the " N_3 " lone pair electrons in a tilted orientation, which is suggestive of $C\equiv N$ π -orbital interaction with the surface. These molecules become more vertical as the potential is made more negative. The behavior of Im and the MeIm isomers diverge at negative potentials due to methyl group interactions with the surface in the latter molecules, which dominate at negative potentials.

The addition of a methyl group to Im achieved the desired effect of increasing the amount and specificity of the orientation information obtainable from SERS data. The observation that this functional group interacts with uncharged and negatively charged electrodes is equally important in providing additional insight into mechanisms of organic molecule adsorption. This combination, the simultaneous presence of functional groups providing characteristic SERS orientation information and functional groups having different adsorption characteristics, is effective in the elucidation of adsorption models.

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