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Absolute surface coverage measurement using a vibrational overtone

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Determination of absolute surface coverage with sub-monolayer sensitivity is demonstrated using evanescent-wave cavity ring-down spectroscopy (EW-CRDS) and conventional CRDS by employing conservation of the absolute integrated absorption intensity between gas and adsorbed phases. The first C–H stretching overtones of trichloroethylene (TCE), *cis*-dichloroethylene, and *trans*-dichloroethylene are probed using the idler of a seeded optical parametric amplifier having a 0.075 cm^{-1} line width. Polarized absolute adsorbate spectra are obtained by EW-CRDS using a fused-silica monolithic folded resonator having a finesse of 28 500 at 6050 cm^{-1} , while absolute absorption cross sections for the gas-phase species are determined by conventional CRDS. A measure of the average transition moment orientation on the surface, which is utilized for the coverage determination, is derived from the polarization anisotropy of the surface spectra. Coverage measurement by EW-CRDS is compared to a mass-spectrometer-based surface-uptake technique, which we also employ for coverage measurements of TCE on thermally grown SiO_2 surfaces. To assess the potential for environmental sensing, we also compare EW-CRDS to optical waveguide techniques developed previously for TCE detection. © 2004 American Institute of Physics.
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I. INTRODUCTION

High-finesse optical resonators significantly enhance spectroscopic sensitivity,^{1–7} providing new opportunities for novel fundamental studies and applications. Cavity ring-down spectroscopy (CRDS) is a prevalent resonator-enhanced technique that uses the photon decay rate of an ultra-low-loss resonator to probe weak absorptions or low number densities.^{5–7} In essentially all implementations of CRDS, a stable optical resonator is employed, supporting low-diffraction-loss, self-replicating optical modes. A laser light pulse with carrier frequency ω , is injected into the resonator to excite one or more modes that decay in intensity or “ring down” at a rate given by

$$\kappa(\omega) = \frac{1}{\tau(\omega)} = \frac{1}{t_r} \left[\sum_i \mathcal{L}_i(\omega) + \mathcal{L}_{\text{abs}}(\omega) \right], \quad (1)$$

where $\sum_i \mathcal{L}_i(\omega)$ is the sum of intrinsic resonator losses, $\mathcal{L}_{\text{abs}}(\omega)$ is *absolute* analyte extinction, and $t_r = n_c L/c$ is the per-pass light propagation time in the resonator of length L having refractive index n_c . In practice, the decay times with and without analyte, $\tau(\omega)$ and $\tau_o(\omega) = t_r(\sum_i \mathcal{L}_i(\omega))^{-1}$, respectively, are measured which determine $\mathcal{L}_{\text{abs}}(\omega)$ with a minimum of two laser pulses. CRDS provides a typical dynamic range of $10^{-7} \leq \mathcal{L}_{\text{abs}} \leq 10^{-3}$, where the detection limit

is determined by the product of the total intrinsic loss and the fractional uncertainty in $\tau_o(\omega)$. While CRDS provides a considerable gain in sensitivity, facile measurement of absolute optical loss is also a significant capability, yielding absolute absorption cross sections,^{8–13} number densities,^{14–17} and reaction rate constants.^{18–21} Here, we exploit the sensitivity and absolute measurement capability of CRDS to determine absolute sub-monolayer surface number densities using a vibrational overtone.

While most CRDS studies have probed gas-phase species using a conventional linear optical resonator, novel extensions of the technique have included studies of a sub-monolayer adsorbate,^{22–25} thin films,^{26–33} a thin liquid channel,³⁴ bulk liquids,^{35,36} fibers,^{37–40} and nanoparticles,⁴¹ often employing unconventional resonator configurations. Guided by the Fresnel equations, some configurations have utilized the Brewster angle^{24,26,27,36,41} or total-internal reflection (TIR)^{22–25,39,42} to admit intracavity elements or interfaces that facilitate sampling while maintaining a low intrinsic loss. In principal, the Brewster angle provides unit transmission through intracavity interfaces for modes with transverse magnetic (TM) polarization, although high losses are incurred for transverse electric (TE) modes, precluding determination of absorber orientation or absolute coverage on the element surface. Alternatively, TIR provides extremely low-loss ($\approx 10^{-6}$), broadband reflection for both TE and TM polarizations. Having an enhanced surface electric

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field with a tunable direction, the associated evanescent wave provides a well-suited probe of adsorbates, films, or particles as employed in evanescent-wave CRDS (EW-CRDS).^{22–25} EW-CRDS has been implemented through several resonator designs including direct extensions of the linear resonator with intracavity elements,^{24,25} a monolithic folded resonator,²² and a monolithic TIR-ring resonator,^{23,42} while whispering-gallery-mode spherical resonators³ could also be employed in a similar mode. Readily miniaturized with no intracavity interfaces, the monolithic resonators^{3,22,23,42} provide the lowest intrinsic loss (highest sensitivity), which is typically bulk-loss limited. Free of optical coatings that limit spectral bandwidth, the TIR-ring and spherical resonators are also broadband devices, although a comparatively complicated photon-tunneling mechanism is utilized for excitation. The monolithic folded resonator, which permits direct excitation of cavity modes through a coated surface as in conventional CRDS, provides a very stable and convenient design, despite the coating-limited bandwidth. As both TE and TM modes have high finesse for the monolithic resonators, adsorbate orientation and absolute coverage can be probed.

The measurement of absolute surface coverage is fundamental to surface science, providing key information for the elucidation of adsorption geometries and reaction stoichiometries.^{43–57} A variety of strategies have been employed to measure absolute coverage including several mass-spectrometer-based techniques,^{43–50} Rutherford back-scattering spectrometry (RBS),⁵¹ x-ray methods,^{52–55} and STM.^{56,57} Many strategies require UHV or provide an indirect or *ex situ* measurement. The development of an optical technique for absolute coverage measurement would eliminate the need for UHV and increase access to this often decisive information. In contrast to x-ray absorption cross sections, optical absorption cross sections typically show large changes at a given wavelength between different chemical environments. Yet the integrated absorption being proportional to the oscillator strength of a transition is essentially conserved, showing relatively small variations between different chemical environments, which can often be modeled.^{58,59} However, while optical absorption is readily used for relative coverage measurements,⁵⁴ determination of absolute coverage is complicated by baseline uncertainties and instrumental bandpass effects.⁶⁰ As CRDS-based methods provide the absolute loss directly, baseline subtraction uncertainties are essentially eliminated given an isolated absorption band that is contained within the high-finesse bandwidth of the resonator, although some residual error can be incurred from low-frequency noise sources.² CRDS also employs relatively narrow-band laser sources that eliminate complications arising from finite bandpass effects, which are a major consideration in the determination of absolute intensities by conventional absorption methods.⁶⁰ Therefore, the exploration of optical measurement of absolute coverage by CRDS-based techniques appears propitious with EW-CRDS in particular providing both sub-monolayer sensitivity and a requisite measure of surface orientation.^{22,23}

While for dipole-allowed electronic transitions sub-monolayer detection is readily achieved with EW-CRDS, sub-monolayer detection using most vibrational overtones is

more challenging due to their comparatively small absorption cross sections. Yet in the near IR where many vibrational overtones occur, the bulk attenuation of optical-communication-grade fused silica falls precipitously to achieve the well known minimum of $\approx 1 \times 10^{-6}$ loss/cm around ≈ 1550 nm, creating auspicious conditions for sub-monolayer detection by EW-CRDS. Further, in contrast to many electronic transitions, the absorption bandwidths of vibrational overtones for gas-, liquid-, and adsorbed-phases typically fit within the coating-limited bandwidth often encountered in CRDS measurements, allowing unambiguous baseline subtraction for all phases. Hence, conservation of the integrated band intensity can be readily implemented using vibrational overtones in the NIR to determine absolute sub-monolayer surface coverages. Furthermore, vibrational overtones provide a high degree of chemical specificity and increased conformational resolution,⁶¹ while NIR operation assures fiber-optic compatibility for chemical sensing applications.

In the following, we demonstrate the measurement of absolute surface coverage using a narrow-band, pulsed NIR source to probe the first C–H stretching overtones of trichloroethylene (TCE), *cis*-dichloroethylene (*c*-DCE), and *trans*-dichloroethylene (*t*-DCE). Conventional CRDS measurements provide absolute absorption cross sections for the overtone bands of the gas-phase species, which for *c*-DCE and *t*-DCE are compared to recent *ab initio* local mode calculations.⁶² Using a fused-silica monolithic folded resonator, EW-CRDS measurements provide polarized spectra for the adsorbed chloroethylenes. The absolute surface coverages are found from conservation of the integrated band intensities using average molecular tilt angles that are derived from the polarization anisotropies of the adsorbate spectra. To emphasize the unique capabilities and limitations of absolute coverage measurement by EW-CRDS, we contrast the technique with a mass-spectrometer-based uptake method, which is also employed here for absolute coverage measurements of TCE on thermally grown SiO₂ on Si(100). In addition, as TCE is a prevalent environmental contaminant, the sensitivity of EW-CRDS for detection of TCE in the NIR is compared to previous waveguide-attenuated-total-reflectance measurements.⁶³

II. EXPERIMENT

A schematic diagram of the experimental configuration used for both CRDS and EW-CRDS is shown in Fig. 1(a). The tunable NIR pulses are generated by an optical parametric amplifier (OPA) consisting of two beam-walk-compensating beta-barium-borate (BBO) crystals⁶⁴ pumped by a 10 Hz, frequency-tripled, injection-seeded-Nd:YAG laser, which also pumps a 0.075 cm^{-1} line width optical parametric oscillator (OPO) that seeds the OPA at the signal wavelength. Initial separation of idler from signal is accomplished with a dichroic beam splitter, while residual signal and pump-laser harmonics are extinguished beyond detection with glass filters. Polarization and pulse-energy control are provided by a pair of Glan-laser polarizing beam splitters with extinction ratios of 10^5 separated by a double Fresnel rhomb rotator. For both the CRDS and EW-CRDS measure-

FIG. 1. In (a) the optical configuration for CRDS and EW-CRDS measurements is shown (TP, GL, DFR, BD, DM, L, HR, TRP, DC, and DET correspond to turning prism, Glan-Laser polarizing beam splitter, double Fresnel rhomb, beam dump, dichroic mirror, lens, high reflectivity mirror, tilt-rotation platform, dosing cell, and detector, respectively). An optical parametric oscillator/amplifier (OPO/OPA) provides near-IR pulses for the CRDS measurements, which employ the intracavity flow cell, and the EW-CRDS measurements, which employ a monolithic folded resonator (MFR). In (b) the monolithic, folded resonator is shown in more detail. Two high-reflectivity-coated planar surfaces and a convex TIR surface form the stable resonator, which is fabricated from a single block of high-purity fused silica. Light is injected into one planar surface and the residual transmission is detected through the second planar surface. An evanescent wave emanates from the apex of the TIR surface to form the sensing region, which has dimensions defined by the resonator-mode spot size.

ments the NIR ring-down transients are free-space coupled to a high-speed, 125 MHz bandwidth, InGaAs detector with a 300 μm diameter. The output of the detector is digitized by a 12 bit, 50 MHz, PC-based data acquisition board. Individual ring-down times are extracted using a weighted least-squares fit and then averaged.

The gas-phase CRDS measurements are performed with a linear resonator and an intracavity double-Brewster-window flow cell, similar to that described elsewhere.⁴¹ Gimbal-mounted concave mirrors with a radius of curvature of 1 m and a maximum reflectivity specified as $R=99.997\%$ at 1650 nm are separated by 37 cm to form the linear reso-

nator. A mode-matching lens is employed to excite a small number of low-order modes. The intracavity flow cell consists of a pair of low-OH fused-silica optical flats (2.54 cm diameter $\times$ 0.635 cm) with surface roughness of <0.1 nm rms on one side and ≈ 0.4 nm rms on the other (WavePrecision, Moorpark, CA). The optical flats are gasket-sealed to a stainless-steel vacuum bellows with terminal flanges cut approximately at Brewster's angle ($\approx 55.4^\circ$). The modified flanges are supported by kinematic mounts to provide angular adjustment near Brewster's angle. To generate a known concentration of analyte, a gravimetrically calibrated diffusion vial (0.5 cm orifice; 2.54 cm neck length) is located inside a glass U-shaped tube having inlet and outlet ports, which is maintained at $(30.3 \pm 0.1)^\circ\text{C}$ in a temperature-controlled enclosure. A 250 liter liquid N_2 Dewar with a gas purifier ($[\text{H}_2\text{O}] \leq 10^{-10}$ mol/L) provides a dry nitrogen carrier gas stream through 1/4 in., electro-polished, stainless-steel tubing to a mass flow controller (10–1000 cm^3/min) which delivers a known flow through the U-tube and subsequently the intracavity cell.

For the EW-CRDS measurements, a fused-silica (Suprasil 311) monolithic folded resonator (REO, Boulder, CO) is employed similar to that described previously.^{22,65} As shown schematically in Fig. 1(b), the folded resonator has two high-reflectivity-coated planar surfaces and a convex TIR surface. The unfolded per-pass length, convex surface radius of curvature, and incident angle, at the TIR surface, are 3.0 cm, 7.5 cm, and 45.0° , respectively. The reflectivity of the two planar, coated surfaces is specified as $R=99.997\%$ at 1650 nm. The convex TIR and coated surfaces are polished to ≈ 0.05 nm rms surface roughness. The incident beam with typically 1–3 mJ per pulse is weakly focused on the coated surface, although no particular effort is made to mode match the spatially amorphous and temporally erratic idler beam. The minimum loss per pass is 1.1×10^{-4} , which provides an adequately long ring-down time of 1.3 μs . The resonator is mounted on a platform that provides control of all degrees of freedom relative to the incident laser beam. The weakly astigmatic Gaussian output beam of the resonator is collected with an anti-reflection-coated doublet lens and imaged onto the high-speed InGaAs detector. The detector is mounted on a subplatform that provides control of all degrees of freedom relative to the resonator. Gaussian beam calculations provide the initial cavity-to-lens and lens-to-detector distances for optimum signal collection at the 300 μm diameter detector. The TIR surface is dosed under equilibrium conditions at the room temperature ($22.0 \pm 0.5^\circ\text{C}$) vapor pressure of the haloethylenes (9.794×10^3 , 2.705×10^4 , and 4.443×10^4 Pa, for TCE, *c*-DCE, and *t*-DCE, respectively, at 25°C)⁶⁶ by employing a glass cell with a liquid reservoir that is gasket-sealed to the convex surface. For TCE, 18 TE-polarized spectra and 16 TM-polarized spectra were averaged, where each spectrum employed a 0.1 nm signal-wave step size and a 25 shot average/point. For *c*-DCE, 4 TE- and 4 TM-polarized spectra were averaged, while for *t*-DCE, 5 TE- and 3 TM-polarized spectra were averaged, both employing a 0.030 nm signal-wave step size and a 25 shot average/point.

The absolute surface coverage for TCE on an SiO_2 surface is also determined from mass-spectrometer-based up-

take measurements. The technique employed is similar to that described by Sanabia *et al.*,⁶⁷ which is based on previous work by Yates and co-workers.^{43–45} Although differences in dosing and surface conditions complicate a direct comparison of the coverage results with the EW-CRDS measurements, it is useful to contrast the two techniques. The samples are formed from Si (100) single crystals, which are cleaned by the low-temperature cleaning method of Ishizaka *et al.*⁶⁸ Oxidation of the Si surfaces is performed under the conditions reported by Watanabe *et al.*⁶⁹ to produce an oxide layer with an approximate thickness of 0.63 nm. The uptake measurements are conducted in a UHV system incorporating a temperature-controlled sample manipulator, a dosing system, and a quadrupole mass spectrometer. The dosing system consists of a gas manifold and injection system. The manifold contains a small, known volume (1.7 mL) which is pumped out by the UHV pumping system and then backfilled with sample vapor at a measured pressure (± 133 Pa) and temperature (25 ± 0.5 °C), thereby providing a known number of molecules, assuming ideal gas behavior. The known dose is then discharged through a stainless-steel (Type 316) nozzle with a $\frac{1}{16}$ in. inner diameter onto the sample located approximately 1 cm away in the UHV chamber at normal incidence. To obtain the absolute coverage, the time-integrated mass spectrometer response to a dose of N_o molecules is determined under two conditions: (1) for TCE-saturated conditions (sample and surroundings) where no net adsorption is expected, and (2) for a freshly cleaned sample surface. If the mass spectrometer response to dose N_o for a saturated-surface is $f_{\text{sat}}(t)$ and for a clean surface is $f_{\text{cln}}(t)$, then the absolute coverage is obtained from

$$N_{\text{ABS}} = \frac{N_o}{A_s} \left(1 - \frac{\int f_{\text{cln}}(t) dt}{\int f_{\text{sat}}(t) dt} \right), \quad (2)$$

where A_s is the sample area. In practice, the saturation response is determined for several dose sizes until a linear calibration curve is found, which indicates saturation is achieved. The slope of the calibration curve then provides $(1/N_o) \int f_{\text{sat}}(t) dt$. The clean surface response is obtained after heating the sample to 610 °C for 5 min in the UHV system, followed by cooling to room temperature. A potential determinant error in the measurement comes from adsorption to adjacent surfaces that are also heated during the cleaning cycle. To examine this effect, the sample cleaning step is accomplished with two heating systems having different dimensions. In one, a W filament (8 in. length, 0.008 in. diameter) with ceramic insulation is used as a radiative heat source. Located below the sample under a Mo heat shield, the W filament heater can achieve a 970 K sample temperature for an 80 W input power. The second system employs a UHV compatible “button” heater (HeatWave Labs, Inc., Model 101137), with a 0.5 in. diameter Mo body, which provides an upper limit of 940 °C. The sample sizes used with the W filament and button heater were 1.32×0.51 cm² and 0.89×0.89 cm², respectively. The relative standard deviation for a group of measurements using either heater is typically $\approx 20\%$ – 30% .

FIG. 2. The absolute cross-sections for the first C–H overtones of (a) TCE, (b) *cis*-DCE, and (c) *trans*-DCE are shown. The corresponding integrated cross sections are given in Table I. The inset in (b) shows the weak sideband occurring around 6010 cm^{−1} for *cis*-DCE, which appears to reproduce the main feature.

III. RESULTS AND DISCUSSION

Figure 2 shows the absolute cross sections for the first C–H stretching overtones of TCE, *c*-DCE, and *t*-DCE. In Fig. 2(a), the cross section for TCE reveals a peak value of 8.31×10^{-21} cm²/molecule at (6091.2 ± 0.2) cm^{−1} along with a secondary maximum at (6082.6 ± 0.2) cm^{−1}, though no rotational fine structure is observed. Using sub-Doppler optothermal spectroscopy (OTS), Platz and Demtröder⁷⁰ similarly observed two peaks for TCE at 6092 and 6084 cm^{−1} with line widths of ≈ 10 cm^{−1} possessing no rotational fine structure. Because the lack of fine structure observed in Fig. 2(a) is confirmed by sub-Doppler OTS, molecular physics accounts for the lack of structure, clearly indicating that the 0.075 cm^{−1} laser line width does not significantly affect the

TABLE I. Gas-phase integrated absolute cross sections.

	A_o^a	Γ_o^b	$A_{\text{calc}}^{a,c}$	ω_o^d
TCE	1.70	2.8	...	6091.1
<i>c</i> -DCE	2.50	4.11	3.10	6075.7
<i>t</i> -DCE	2.28	3.77	2.37	6077.3

^aUnits of 10^{-19} cm²/molecule.^bUnits of 10^{-23} cm²/molecule.^cFrom Ref. 62.^dPosition of band maximum in cm⁻¹.

band shape. Platz and Demtröder⁷⁰ tentatively assigned the peaks to P- and R-branches, while the suppression of rotational fine structure was explained by invoking a broad radiationless-transition line width relative to the small rotational level spacing arising from the heavy Cl atoms. In Fig. 2(b), the absolute cross section for *c*-DCE is shown, which also reveals a distinct lack of rotational structure, whereas in Fig. 2(c), the results for *t*-DCE show partially resolved, rather broad rotational lines. Although we have not found independent confirmation that the observed lack of rotational structure or broad rotational peaks for *c*-DCE and *t*-DCE, respectively, are free of laser line width effects, we nonetheless assume the 0.075 cm⁻¹ laser line width is sufficiently narrow for our purposes.

Table I shows the integrated absolute cross sections for TCE, *c*-DCE, and *t*-DCE as determined from the CRDS measurements in Fig. 2, along with calculated values for the DCE isomers taken from work of Takahashi *et al.*⁶² for comparison. From the CRDS measurements, the integrated absolute cross sections are determined by

$$A_o = \frac{1}{n_d l_c} \int \mathcal{L}_{\text{abs}}(\omega) d\omega \approx \omega_o \Gamma_o = \frac{\omega_o}{n_d l_c} \int \mathcal{L}_{\text{abs}}(\omega) \omega^{-1} d\omega, \quad (3)$$

where n_d , l_c , ω_o , and Γ_o are the number density, cell path length, wave number at band maximum, and the logarithmic integration of the absolute cross section, respectively. The integrated intensities can be determined by either integration with respect to frequency to yield A_o or by logarithmic integration to yield Γ_o . Although we provide A_o values for comparison to the calculations of Takahashi *et al.*,⁶² we use Γ_o to obtain absolute surface number densities for its theoretical advantages,⁷¹ although at high wavenumbers the difference is rather small. Takahashi *et al.*⁶² calculated the integrated cross sections for the C–H stretching overtones of *c*-DCE and *t*-DCE using a local mode model in which both the potential energy surface and the dipole moment function were determined from *ab initio* calculations. These authors sought to explain the deviation of the *t*-DCE cross section from the trend observed by Burberry *et al.*⁷² of a characteristic (molecule-independent) integrated cross section per C–H bond for the second through sixth overtones. Finding the vibrational wavefunctions for two DCE isomers to be essentially identical, Takahashi *et al.*⁶² explained the experimental discrepancy through a significant difference in the calculated dipole moment functions. While their calculated intensities were found to consistently overestimate the available liquid phase experimental data,⁷³ agreement improved considerably

above the first overtones. Comparing A_{calc} to A_o in Table I, we also note that the calculated values overestimate the experimental values for the first overtone in the gas phase. Furthermore, the *cis* and *trans* integrated cross sections measured by CRDS are not as disparate as reported for higher overtones,^{62,73} having the ratio $(A_o)^{\text{cis}}/(A_o)^{\text{trans}} = 1.09$, which is closer to the ratio for the fundamentals of ≈ 1 .^{74,75}

Figure 3 shows the absolute evanescent wave (EW) absorption spectra for the haloethylenes obtained with the folded resonator for TE and TM polarizations, after subtraction of the resonator intrinsic loss. The insets of Fig. 3(a) show the raw data for TCE and the baseline intrinsic loss, prior to subtraction. The baseline loss was established by fitting the average of multiple scans to a third-order polynomial. Small, constant baseline offsets as seen for TM polarization in the Fig. 3(a) inset, which likely arise from surface contamination, were removed. The EW spectra consist of contributions from both adsorbed species and gas-phase species. Superimposed on each EW spectrum in Fig. 3 is the estimated gas-phase contribution (gray lines) to the spectrum, which is determined using the peak absolute cross section for each species from Fig. 2 and the calculated effective thickness⁷⁶ for TM and TE evanescent waves. For the fused-silica folded resonator with a 45° angle of incidence at the TIR surface, the effective thickness for TM polarization is precisely twice the value for TE polarization. In Fig. 4, the gas phase contributions are subtracted from the EW spectra, revealing only the adsorbed-phase contribution. The subtraction was performed by aligning the relatively narrow gas phase peaks and applying minor adjustments to the estimated gas-phase signal magnitude while maintaining the $\times 2$ multiplier between the TE and TM polarizations. The minor adjustments to the wavelength axis of the gas-phase spectra used for subtraction arise mainly from the wavelength repeatability of the OPO and the scanning procedure, while intensity adjustments are likely required to correct for the actual versus calculated EW effective thicknesses and the actual partial pressure of haloethylene in the evanescent wave compared to the estimated ambient vapor pressure. Alignment of the rotational structure between the gas-phase and EW spectra for *t*-DCE is shown in the insets of Fig. 3(c), which aided the gas-phase subtraction in that case. In general, the adsorbed-phase spectra for the three haloethylenes in Figs. 4(a)–4(c) show single, symmetrical peaks which are shifted to lower wavenumbers relative to the gas-phase spectra with essentially identical peak positions for TE and TM within experimental error. Furthermore, there is a distinct polarization anisotropy for all three species as the TE polarizations show consistently stronger absorption compared to TM.

The polarization anisotropy of the adsorbed-phase spectra indicates a significant degree of orientation for the adsorbates, which must be considered to obtain the absolute coverage. Table II gives the integrated absolute intensities for the three adsorbed species and two polarizations. From the dichroic ratio of TE-to-TM-polarized intensities, $\rho = \Gamma_{\text{TE}}/\Gamma_{\text{TM}}$, a measure of the average orientation of the transition moment can be determined. A molecule in the evanescent field with a molecular transition moment given by

FIG. 3. The evanescent wave absorption spectra for (a) TCE, (b) *c*-DCE, and (c) *t*-DCE are shown as measured by EW-CRDS with the monolithic folded resonator. Both gas-phase and surface-bound species contribute to the spectra. The estimated gas-phase contributions (heavy solid lines) are superimposed on the EW spectra.

$\mu(\Theta, \phi) = |\mu| \{x \sin \Theta \cos \phi + y \sin \Theta \sin \phi + z \cos \Theta\}$ interacts with the surface electric field $\mathbf{E}(\Theta, \phi; \theta_i, n_c, n_o)$ according to $\Gamma_i \propto \langle [\mu(\Theta, \phi) \cdot \mathbf{E}(\Theta, \phi; \theta_i, n_c, n_o)]^2 \rangle$, where the angle brackets denote averaging over a distribution of orientations specified in the polar and azimuthal surface coordinates, Θ and ϕ , respectively (defined in the Fig. 5 inset). The surface electric field is assumed to be described by the Fresnel equations for a given polarization, angle of incidence θ_i , resonator refractive index n_c , and ambient refractive index n_o . If the distribution of orientations is assumed to be isotropic in ϕ , then the distribution function can be expanded in Legendre polynomials, P_n , according to

$$N(x) = \sum_{n=0}^{\infty} C_n P_n(x) = \sum_{n=0}^{\infty} \left(\int_0^1 N(\xi) P_n(\xi) d\xi \right) P_n(x) \quad (4)$$

where $x = \cos \Theta$ and $0 \leq \Theta \leq \pi/2$. Mirror symmetry about the equatorial surface plane requires all $C_n = 0$ for n odd, while absorption is further restricted to measurement of the “order parameter,” C_2 , only.^{77,78} If the distribution function is uni-

modal with a small angular dispersion, so that $N(\cos \Theta)$ can be approximated as $\delta(\cos \Theta - \cos \Theta_o)$, then $C_2 \approx P_2(\cos \Theta_o)$, which yields an average polar tilt angle $\Theta_o = \cos^{-1}[(2C_2 + 1)/3]^{1/2}$, as commonly used in studies of oriented polymer films⁷⁷ and adsorbed biomolecules.⁷⁸ Employing this assumption, the value of C_2 and Θ_o can be determined from ρ , which we find is given by

$$\rho = \frac{\Gamma_{TE}}{\Gamma_{TM}} = \frac{I_y[1 + C_2(\Theta_o)]}{(I_x + I_z) + (2I_z - I_x)C_2(\Theta_o)}, \quad (5)$$

where $I_i = |E_i|^2/|E_o|^2$, $i = x, y, z$, are the calculated electric field intensities at the TIR surface relative to the incident field intensity. Using $\theta_i = 45^\circ$ and $n_c(1640 \text{ nm}) = 1.442$ for the folded resonator, we find the relative field intensities to be $I_x = 0.28$, $I_y = 3.85$, and $I_z = 7.42$, which change negligibly over the absorption band. A plot of Θ_o versus ρ is shown in Fig. 5 along with the experimentally determined values of ρ for TCE, *c*-DCE, and *t*-DCE. Note that Θ_o remains relatively

FIG. 4. The TE- and TM-polarized evanescent wave absorption spectra for surface-adsorbed (a) TCE, (b) *c*-DCE, and (c) *t*-DCE are shown as obtained after subtraction of the gas-phase contributions from the EW-CRDS spectra shown in Fig. 3. The bars indicate the estimated full-width at half-maximum intensity.

constant over the interval $0 \leq \Theta_o \leq 60^\circ$, which leads to a relatively large error in Θ_o for a given error in ρ over this interval. Further, a given value of C_2 determined from ρ can correspond to a wide variety of distributions,⁷⁹ especially when C_2 is in the center of its range, which extends over the interval $[-0.5, 1]$. Indeed, for $C_2 = 0$, an assumed δ -function distribution leads to an orientation angle of $\Theta_o = 54.7^\circ$, while $C_2 = 0$ is also consistent with an isotropic distribution. However, the experimental data for the haloethylenes occur

around $C_2 \approx -0.4$, where $\Theta_o(\rho)$ levels off, which suggests the three adsorbates are distinctly oriented and a meaningful orientation angle can be determined with confidence, at least within the assumption of a unimodal distribution. The tran-

TABLE II. Integrated intensities, peak positions, and line widths for the adsorbed chloroethylenes.

	Γ_{TE}^a	Γ_{TM}^a	ρ	ω_o^b	$\Delta\omega_o^c$
TCE	2.92	2.41	1.21	6066.0	28.6
<i>c</i> -DCE	4.34	3.22	1.34	6053.1	30.0
<i>t</i> -DCE	4.47	3.55	1.26	6050.7	29.0

^aLogarithmic integration of the optical loss in units of 10^{-8} .

^bPosition of band maximum in cm^{-1} .

^cBandwidth in cm^{-1} of adsorbate spectrum after subtraction of gas-phase contribution.

FIG. 5. The average angle of orientation Θ_o for the transition moment is plotted as a function of the dichroic ratio, $\rho = \Gamma_{TE}/\Gamma_{TM}$. The experimental data points for the three haloethylenes are marked and defined in the legend.

sition moment tilt angles are found to be $\Theta_o = (74 \pm 2)^\circ$, $(75 \pm 2)^\circ$, and $(76 \pm 2)^\circ$ for TCE, *c*-DCE, and *t*-DCE, respectively, relative to the TIR-surface normal, where the error limits are estimated from the variability of the integrated intensities. The corresponding molecular orientations can be identified given the transition moment direction relative to a molecular axis. In the gas phase, TCE, *c*-DCE, and *t*-DCE have C_s , C_{2v} , and C_{2h} symmetries, respectively. For TCE, a normal coordinate perspective requires the transition moment to be in the molecular plane, since the transition operator must transform as A' to connect totally symmetric ground and excited states. The transition moments of the DCE isomers are also in-plane in the local mode model of Takahashi *et al.*⁶² Therefore, if the transition moments are all in-plane, the three haloethylenes have their molecular planes oriented on average nearly parallel to the mean plane of the ultra-smooth TIR surface. As the tilt angles are comparable for the three species, the different molecular symmetries apparently result in indistinguishable adsorption geometries within experimental error.

Given the integrated gas-phase cross sections, the adsorbed-phase integrated intensities, and the average orientations of the transition moments, absolute surface coverages can be obtained by invoking conservation of the integrated intensity with adsorption. Although the oscillator strength of a transition is conserved between gaseous and condensed phases, the integrated intensity is affected by changes in the local field. However, correction factors can be derived to account for local field effects,^{58,59} which predict the ratio of integrated gas-to-liquid phase cross sections to be <2 . As noted, here we assume the Fresnel equations describe the local electric field at the TIR surface, which neglects adsorbate coupling and surface image-dipole effects. Since the TE surface spectra have higher signal-to-noise ratio than the TM spectra, we employ these for the absolute coverage calculations. With $\mathbf{E}_{TE} = I_y \mathbf{y}$, we find the absolute number density of adsorbed molecules at the TIR surface to be given by

$$N_{\text{ABS}} = \frac{2 \cos \theta_i \int \mathcal{L}_{\text{abs}}^{\text{TE}}(\omega) \omega^{-1} d\omega}{3 I_y \sin^2(\Theta_o) \Gamma_0}, \quad (6)$$

where the factor of 3 in the denominator arises from orientation averaging of the gas phase absolute cross section and the factor of 2 in the numerator arises from azimuthal averaging over the surface distribution. Given spectra with sufficiently high signal-to-noise ratio, the major source of uncertainty in Eq. (6) lies in the evaluation of orientation, although as discussed above the uncertainty is smallest for highly oriented systems having C_2 near the periphery of its range $[-0.5, 1]$. Using Eq. (6), we find $N_{\text{ABS}} = 1.41 \times 10^{14}$, 1.40×10^{14} , and 1.59×10^{14} molecules/cm², for TCE, *c*-DCE, and *t*-DCE, respectively. If the underlying site density is defined by close-packed, planate TCE molecules ($N_0 \approx 1.23 \times 10^{15}$ sites/cm²), then the saturation coverages are found to be 11.5%, 11.4%, and 12.9% for TCE, *c*-DCE, and *t*-DCE, respectively.

For adsorbed TCE on oxidized Si(100) surfaces, the mass-spectrometer-based uptake measurements yielded absolute coverages of $(1.0 \pm 0.2) \times 10^{14}$ and $(0.4 \pm 0.1) \times 10^{14}$

molecules/cm² for the W filament and “button” heaters, respectively, where the quoted errors are standard deviations. As previously noted, the discrepancy between the results for the two heaters could arise from adsorption to adjacent, inadvertently cleaned surfaces, which could account for the larger coverage obtained for the larger W filament heater. Since the EW-CRDS measurements are performed under equilibrium conditions and ambient humidity where significant surface Si–OH formation and adsorbed water can be expected,⁸⁰ a direct comparison to the mass-spectrometer-based measurements is difficult. However, it is valuable to contrast the techniques. A key difference between the uptake measurements and EW-CRDS is the accessible pressure range, which is restricted to UHV in the former case and very broad in the latter case. The EW-CRDS approach also probes the species of interest directly at the surface within a spatial region that is precisely defined by the resonator properties, whereas the uptake approach infers the surface coverage from remote measurements in which the effective surface dimensions may be ill-defined by the cleaning step. However, an approach using EW-CRDS or some variation of CRDS requires the surface of interest to be integral to a resonator, while the uptake measurements can be applied to an arbitrary substrate. Furthermore, any approach based on conservation of integrated intensity requires an isolated absorption band and may require a local field correction.

Finally, we compare the detection capability of EW-CRDS to previous efforts in which evanescent wave NIR absorption was employed for TCE detection. Ache and co-workers^{63,81} explored extensively the detection of TCE with the first C–H overtone using a long-effective-path-length planar waveguide, which improved on the sensitivity of their previous optical-fiber sensor⁸² by a factor of 120. Polysiloxane coatings were employed with these devices to reversibly enrich the local concentration of TCE in the evanescent wave. The chemical composition of the polysiloxane polymers was also varied to identify optimal conditions for sensing as determined by the TCE partition coefficient and polymer refractive index.⁸³ Furthermore, it was shown that competing absorption from C–H groups of the polymer could be essentially eliminated through efficient deuteration.⁸³ The gas-phase detection limit for TCE obtained using the optimized planar waveguide with a polysiloxane coating was found to be ≈ 0.1 mmol/L or ≈ 2 parts-per-thousand in the gas phase at atmospheric pressure. By comparison, EW-CRDS also provides an equivalent detection limit determined by the minimum detectable absorption of 1×10^{-7} based on a 0.1% relative decay time precision (1σ for ensembles of 25 averaged laser shots per point) and a 1×10^{-4} /pass intrinsic loss. Yet this detection limit is obtained by EW-CRDS *without a TCE-enriching polymer*. As shown in Fig. 6, the EW-CRDS response to adsorption of TCE on the silica surface of the folded resonator is also reversible with a response time of <1 min. The addition of an enriching polymer layer to an EW-CRDS-based TCE detection scheme could lower detection limits significantly. The use of a low-scatter-loss, deuterated polysiloxane film should permit a low intrinsic loss to be maintained.⁸³ The polysiloxane layer, which can be thick relative to the evanescent wave

FIG. 6. Reversibility of the EW-CRDS measurement of TCE detection is demonstrated by modulating TCE exposure while monitoring the TE-polarized absorption.

decay length for an appropriate resonator design, should also serve to protect the sensing surface and eliminate interference from particulates. A significant additional improvement in sensitivity can be realized by reducing the resonator intrinsic loss relative to that found in the present work by the use of a smaller resonator that is fabricated from lower bulk-OH-content fused silica. Furthermore, it is worth noting that the monolithic resonator design improves in sensitivity through a reduction in size, whereas planar waveguides require an increase in length to increase sensitivity.

IV. CONCLUSIONS

This work is significant to both fundamental surface science and the development of chemical sensors. The measurement of the absolute surface coverage by EW-CRDS can potentially provide absolute reaction rates on films or particles, similar to gas-phase CRDS kinetics studies. Sub-monolayer coverages can be probed without the need for ultra-high vacuum as long as the total system intrinsic loss is sufficiently small. In connection with the development of new chemical sensors, EW-CRDS provides a significant advance in detection sensitivity in the NIR, along with comparable selectivity to the mid-IR. While further improvements appear feasible, the detection limit achieved in this initial effort using an unclad folded resonator is comparable to that obtained using an optimized planar waveguide with an analyte-enriching surface coating.

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dorsement by the NIST, nor does it imply that such products have necessarily been identified as the best available for the purpose.

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