# Molecular Identification of Surface Adsorbates. Reactive Scattering of Hyperthermal Cs+ from a Ni(100) Surface Adsorbed with CO, C6H6, and H2O

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Identification of molecular species on solid substrate is an important issue in surface chemistry and mass spectrometric analysis. We report that molecular adsorption state can be identified by using hyperthermal Cs+−surface reactive scattering for the reactions of CO, C6H6, and H2O with a Ni(100) surface. It is demonstrated that the adsorption kinetics of these molecules can be monitored in real time.

Secondary ion mass spectrometry (SIMS) is a sensitive analytical tool for the detection of molecules on the surface.[1] Identification of molecular state from the mass spectral information, however, is a controversial issue associated with the mechanisms of secondary particle ionization and molecular ejection during kiloelectronvolt ion bombardment of a surface. When the beam energy is reduced to the hyperthermal regime (1−100 eV), the nature of ion−surface interaction becomes chemically more interesting. Recent investigations of this subject[2−10] have revealed a variety of reactions including molecular dissociation, reactive scattering, charge exchange, chemically induced desorption, and film deposition. Many of these reactive channels are expected to become suppressed by using Cs+ ion as a projectile, because it is chemically inert and undergoes little charge exchange on the surface.[11] Yet, we have found that Cs+ ions pick up surface atoms or molecules from a Si surface reacted with water.[12−14] In this communication, we demonstrate that the Cs+ reactive scattering method allows molecular identification of surface adsorbates and study of their adsorption kinetics.

The experimental setup was the ultrahigh vacuum (UHV) ion−surface scattering chamber[15] equipped with various surface spectroscopic tools. The low-energy ion beamline was used to generate energy-selected beams of Cs+ ions in the hyperthermal range. The typical current density of the Cs+ beam was 1−10 nA cm⁻². The Ni(100) sample was located inside a field-free region of the scattering chamber. The sample was cleaned with a standard method in UHV,[16] reacted with the gases, and then
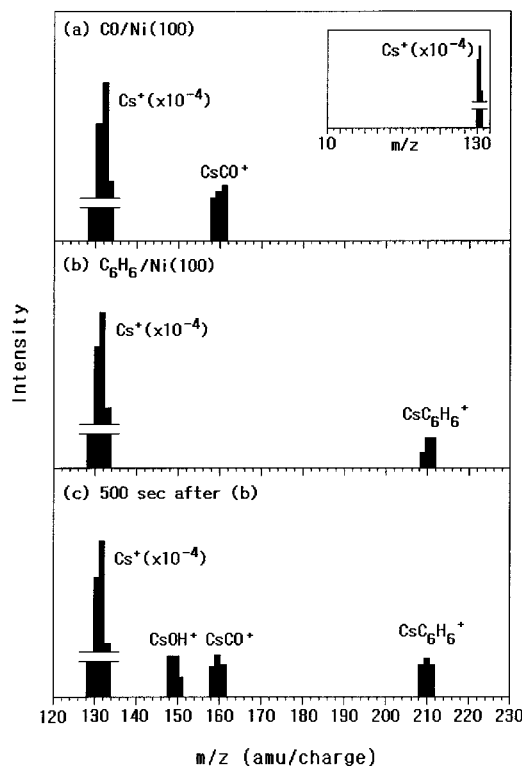


**Figure 1.** Mass spectra of the positive ions emitted upon 30 eV Cs+ collision of a Ni(100) surface reacted with CO, C6H6, and H2O. (a) CO-adsorbed surface. The inset shows a spectrum in the lower mass range. (b) C6H6-adsorbed surface. (c) A spectrum taken after reacting surface (b) with residual CO and H2O gases inside a vacuum chamber. The intensity of the Cs+ peak is reduced to a factor of $1 \times 10^{-4}$. The angles of an incident Cs+ beam and a detector are 45° to the surface normal. The mass peaks are broadened toward the low-mass side due to low resolution, but their exact positions are determined from high resolution spectra.

collided with the Cs+ beam. The product ions emanating from the surface were analyzed for their mass, using a quadrupole mass spectrometer operated in an ion transmission mode.

Figure 1a shows a positive ion mass spectrum of the scattered species upon Cs+ collision on a Ni(100) surface adsorbed with CO. The surface was prepared by CO adsorption at room temperature to a coverage of 0.5 monolayer,[17] and the molecular CO on the surface was identified by UV (He II) photoelectron spectroscopy.[18] The strongest peak at $m/z$ 133 amu/charge represents the scattered Cs+ ions. Another peak at 161 amu is assigned to CsCO+ formed via Cs+−CO association during the reactive scattering. Figure 1b shows a spectrum produced from a Ni surface covered with molecular benzene.[19] CsC6H6+ ($m/z$ 211 amu/charge) is the only cluster ion produced, again indicating a molecular pickup reaction of Cs+. In Figure 1c, this benzene-adsorbed surface is reacted with residual CO and H2O gases inside a vacuum chamber at a pressure of low 10⁻⁹ Torr. Two peaks additionally grow at 150 and 161 amu. The 161-amu peak is assigned to CsCO+ originating from CO adsorption. A control experiment with C6D6 reveals that it is not CsC2H4+ possibly produced via decomposition of benzene on the surface. The 150-amu peak represents CsOH+, and is attributed to the OH adspecies formed via H2O dissociation on a Cs-deposited Ni. This interpretation is made because CsOH+

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production becomes substantial only after $Cs^+$ beam exposure of the surface. While $H_2O$ does not chemisorb on clean Ni-(100) at room temperature,[20] dissociative chemisorption of $H_2O$ into OH has been well-known on metal surfaces in the presence of coadsorbed alkali metals, for example, on K/Ni(111),[21] Cs/Cu(110),[22] Na/Cu(111),[23] Na/Ru(001),[24] and K/Pt(111).[25] $CsOH^+$ emission is verified also from a separate experiment of $H_2O$ adsorption on Ni(100). Therefore, all of the $Cs^+$-bound clusters of Figure 1 reflect molecular identity of the adsorbates.

Figure 1 also indicates that molecular fragmentation or Ni sputtering does not occur to any significant degree by the $Cs^+$-collision. It is evidenced by the absence of possible dissociation products including $CsC^+$, $CsO^+$, $CsC_xH_y^+$ ($x, y < 6$), and $CsNi^+$. Adsorbate monomer or its fragmented ions are not ejected either, as exemplified by the inset of Figure 1a. Preferential ejection and detection of molecular species in the present work, compared to the results of SIMS[26,27] and laser induced thermal desorption,[13] is probably due to the soft-sputtering nature of hyperthermal $Cs^+$ collision as well as the fast time scale of reactive scattering. It has been addressed in our earlier study[13,14] that $Cs^+$ reactive scattering occurs in a subpicosecond time scale, which renders the $Cs^+$−molecule association to occur only with promptly desorbed molecular species.

The capability of $Cs^+$ reactive scattering for surface analysis is further examined. The yield for the scattering products is examined as functions of adsorbate coverage, $Cs^+$ beam energy, incidence angle, and dose. From these investigations the following observations have been made. The product intensity gives a quantitative measure of adsorbate concentration.[28] The probability for reactive scattering is on the order of $10^{-4}$, as exemplified by the peak intensity ratios of Figure 1. The reactive scattering process is composed of two steps, collisional desorption of adsorbate molecules and the subsequent $Cs^+$−molecule association, and these two events occur with the
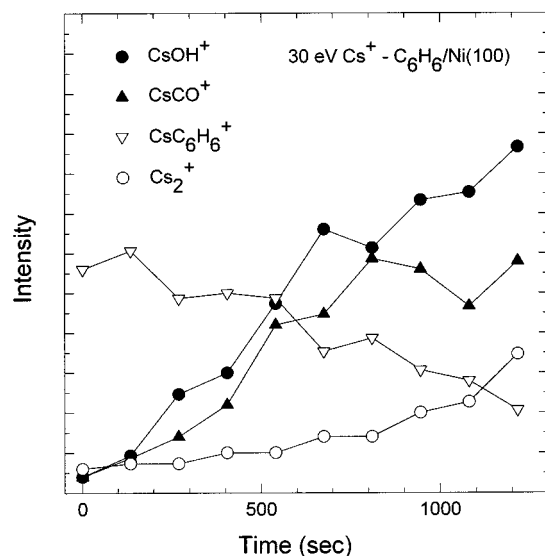
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**Figure 2.** Simultaneous monitoring of the product ions as a function of adsorption time. The initial surface is $C_6H_6$-adsorbed Ni(100), which then is reacted with CO and $H_2O$ gases. The $Cs^+$ beam energy is 30 eV.

probabilities of $10^{-1}$ and $10^{-3}$, respectively.[28] The latter step provides a means of cationizing the desorbed neutrals. With such detection sensitivity, real-time monitoring is possible for adsorption kinetics occurring in a few seconds. Figure 2 illustrates an example of kinetics study for a multiple adsorbate system. The Ni surface at initial time is covered only with molecular benzene, as is the case for Figure 1b. The benzene is slowly replaced with CO and OH by adsorption of residual CO and $H_2O$ gases, respectively. The increase in $Cs_2^+$ yield indicates concurrently growing concentration of Cs on the surface, deposited during the continuous $Cs^+$ beam exposures.[29]

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