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Velocity-resolved Laser-induced Desorption for Kinetics on Surface Adsorbates

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Most experimental methods for studying the kinetics of surface reactions – for example, temperature programmed desorption (TPD), molecular beam relaxation spectrometry (MBRS) and velocity-resolved kinetics (VRK) – employ detection schemes that require thermal desorption. However, many adsorbates – for example reaction intermediates – never leave the surface under reaction conditions. In this paper, we present a new method to measure adsorbate concentrations on catalytic surfaces and demonstrate its utility for studying thermal desorption kinetics. After a short-pulsed molecular beam deposits CO or NH_3 on Pt (111), the surface is irradiated with an ultrashort laser pulse that induces desorption. Another tightly focused ultrashort laser pulse ionizes the gas-phase molecules by a non-resonant multiphoton process and the ions are detected. This two-laser signal is then recorded as a function of time after the dosing molecular beam pulse and decays exponentially. First-order thermal desorption rate constants are obtained over a range of temperatures and found to be in good agreement with past reports. Ion detection is done mass selectively with ion-imaging, dispersing the gas phase molecules by their velocities. Since laser-induced desorption (LID) produces hyperthermal gas phase molecules, they can be detected with little or no background. This approach is highly surface-specific and exhibits sensitivity below 10^{-4} ML coverage. Because the signals are linearly proportional to adsorbate concentration, the method can be employed at lower temperatures than VRK, whose signal is proportional to reaction rate.

Introduction

The rates of chemical reactions can be dramatically accelerated by catalytically active surfaces; hence, reliable methods to measure the rates of surface reactions are of central importance to the field of heterogeneous catalysis.[1] Many experimental methods to measure surface reaction rates have been applied in the past and the field is still developing.[1a] Perhaps the simplest among these methods is temperature-programmed desorption (TPD), which provides rate information for non-reactive and reactive desorption. Here, desorbing molecules are detected by a mass spectrometer as the surface temperature is ramped upward. Molecular beam relaxation spectrometry (MBRS) has also been widely used to obtain rate constants for surface reactions. Here, a chopped molecular beam of reactants initiates a modulated surface reaction and the gas-phase product signal – again detected with a mass spectrometer – appears with a phase lag relative to the reactant. This phase lag is recorded with a lock-in amplifier and is related to the reaction time. Velocity-resolved kinetics (VRK) is a recently developed variant of MBRS that directly provides the flux of desorbing products as a function of reaction time at the surface, also known as the kinetic trace.[1b,2] This is accomplished with short gas pulses that initiate the reaction and time-resolved product detection that combines laser ionization of desorbing products with ion imaging. In this way, the product density and velocity are determined simultaneously. VRK is capable of providing surface site specific rate constants;[2b] for example, reactions at terraces may appear with different product-velocities than reactions at steps[3] and kinetic traces may depend dramatically on surface step-density.[2f] Taking advantage of its kinetic competition with desorption, adsorbate diffusion has also been detected with VRK.[2e,f] While TPD, MBRS and VRK have proven highly useful, they cannot be used to monitor the concentrations of surface adsorbates directly, as they rely on desorption for their signals. Of course, surface reactions often involve adsorbates that do not enter the gas-phase under the reaction conditions; consequently, other methods are needed to follow the kinetics of adsorbates directly.

In this work, we demonstrate laser-induced desorption velocity-resolved kinetics (LID-VRK), a new application of slice-ion imaging[4] combined with laser-ionization of laser-desorbed

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molecules. This takes advantage of the properties of laser induced desorption (LID),[5] where ultrashort light pulses heat the electrons of the solid to several thousand Kelvin[6] and molecules desorb within a few hundred fs with hyperthermal velocities. A second pulsed laser beam a few mm from the surface induces non-resonant multiphoton ionization (MPI) and ion-imaging provides the velocities of the desorbing molecules. The ion imaging separates the surface-sensitive LID signal in velocity space from background. We demonstrate this technique by following the kinetics of two simple molecules (CO and NH_3) desorbing from a Pt (111) surface. The LID ion-imaging-based detection produces a signal that is proportional to the adsorbate surface density, which decays exponentially after the molecular beam dosing pulse. The derived 1st order desorption rate constants are consistent with prior work,[2f,i] which, due to the advantages of LID, are easily extended to lower surface temperatures. This overcomes one of the limitations of VRK. We envision that LID-VRK will find many applications in surface chemistry, in particular regarding the detection of reaction intermediates.

Experimental Section

Figure 1 shows a schematic of the experimental apparatus used in this work. An ultra-high vacuum chamber holds a Pt crystal with a polished (111) surface that has been cleaned by cycles of Ar-ion sputtering and annealing. The crystallinity and cleanliness is controlled using LEED and AES. The experimental apparatus is equipped with a home-built Even–Lavie type nozzle (not used in this work) and a Parker Series 9 General valve. The molecular beam from the latter is used to dose the surface with a short (FWHM 250 µs) pulse of either neat CO or a mixture of 1.5 % NH_3 in helium, initiating the adsorption/desorption process. The repetition rate of the nozzle is adjusted to ensure that all molecules desorb before the next molecular beam pulse arrives. One laser pulse is used to induce desorption of molecules from the surface at a variable time delay after the molecular beam pulse has deposited molecules on the surface. The laser-desorbed molecules are then ionized by a second laser pulse ≈8 mm from surface that travels between two nickel grids – note that only one grid is shown in Figure 1. The delay between the two laser pulses is set to optimize sensitivity for hyperthermal laser-desorbed molecules. Ions are pulse-extracted 2.0 µs after the second laser pulse is fired, traveling downward in Figure 1 toward an ion-imaging camera detector[1b] employing ion slice imaging.[4]

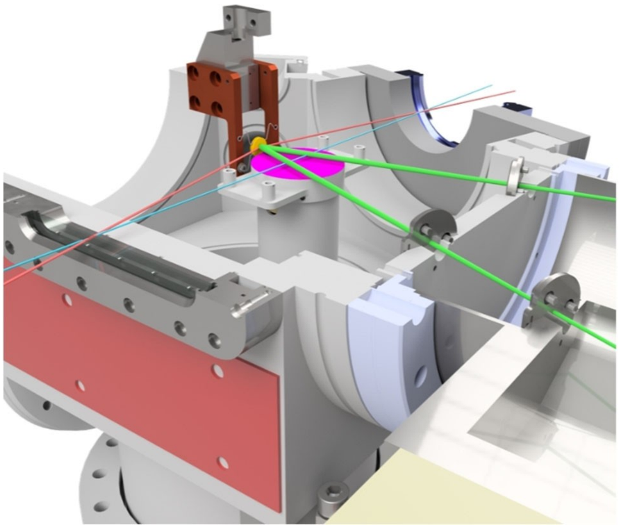

Figure 1. Cutaway of the instrument used in this work. The instrument is an UHV chamber equipped for preparation and manipulation of a clean single-crystal sample (yellow). A system of differential pumping chambers allows two molecular beams (green) to dose the surface. Only one beam is used in this work. A pulsed laser beam (red) is incident at glancing angle to the surface and is used to desorb molecules from the surface. A second pulsed laser beam (blue) ionizes molecules in the detection region of an ion imaging apparatus – the extractor grid is shown (magenta).The repeller grid is not shown to allow a clear view on the beam paths in front of the surface.

The light pulses used in this work come from a single Ti-sapphire oscillator seeding two regenerative amplifiers that produced two 800 nm laser pulses with a variable delay. The desorption laser with duration of 120 fs and a pulse energy of 200–300 µJ was mildly focused to ≈1 mm diameter at the surface. Great care was taken with the laser beam's spatial profile (typically $M^2 < 1.3$), as its quality is extremely important to achieve efficient desorption while avoiding surface damage. Non-resonant multiphoton ionization was accomplished in the beam focus (150 mm focal length lens) of the second amplifier (120 fs, 400–500 µJ). The repetition rate of both laser pulses is identical with the repetition rate of the molecular beam.

Results and Discussion

Figure 2 shows examples of the kind of velocity-resolved data that can be obtained in this experiment. The upper panel shows representative velocity distributions of laser desorbed molecules (circles) with the surface held at room temperature. LID produces hyperthermal velocities. For comparison, the grey lines show thermal Maxwell–Boltzmann-distributions. The lower panel of Figure 2 shows raw ion images (insets) obtained during the desorption-kinetics experiments and distributions of the normal velocity component derived from the images. Here the delay between molecular beam pulse and LID laser is fixed and the delay between the LID and detection laser pulses has been adjusted for maximum sensitivity to molecules with speeds of 1000 $m\,s^{-1}$. Note that the fixed delay between the two laser-pulses along with their fixed spatial separation acts as a velocity selector. The ion images exhibit a horizontal stripe at high velocities and a broad ion cloud at low velocities, cleanly separated from one another. The horizontal hyperthermal stripe disappears when either of the laser beams is blocked, whereas the slow cloud does not depend on the LID laser.

We next performed a velocity-resolved kinetic experiment, scanning the delay between the pulsed molecular beam and the desorption-laser pulse with the delay between the two laser pulses held constant. Figure 3 shows the signal dependence when integrating different velocity windows. For both thermal (open circles) and hyperthermal velocities (closed circles), similar exponential decays are seen. This is simply a result of the fact that these two kinetic traces follow the same desorption reaction – the thermal velocities detect gas-phase molecules (products) that have thermally desorbed, while the hyperthermal velocities report the adsorbate (reactants) surface concentrations. The solid black lines are fits to the LID-VRK data

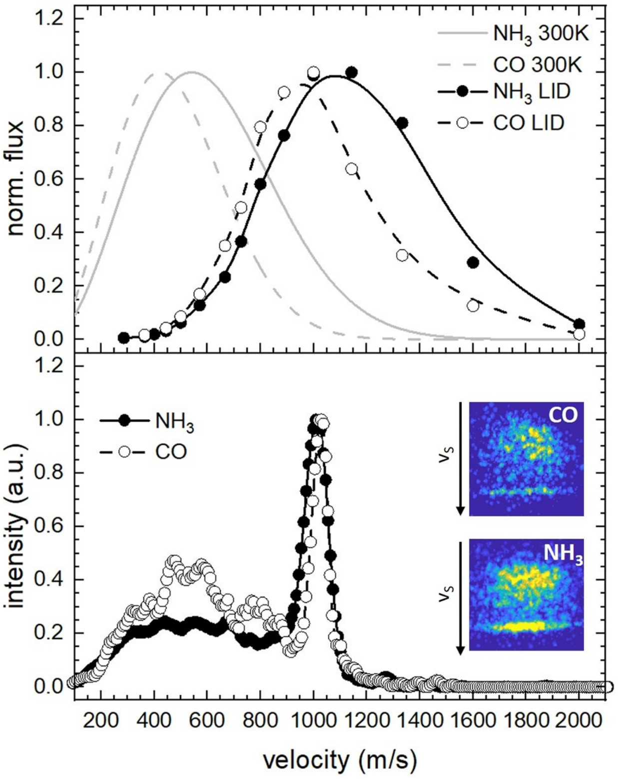

Figure 2. Examples for velocity distributions of CO (open symbols) and NH$_3$ (closed symbols) produced by LID from Pt (111). Upper panel: circles show the velocity distribution obtained by integrating LID signal in the ion image while scanning the delay between LID and MPI detection laser. The grey lines show the Maxwell–Boltzmann velocity distributions at the surface temperature of 300 K. Lower panel: scattered velocity normal to the Pt (111) crystal for a fixed LID-MPI laser delay set to detect 1000 m s^{-1} molecules. The insets show the corresponding ion images accumulated for CO and NH$_3$.

based on a 1st order model of the desorption kinetics, which includes a convolution over the shape of the molecular beam pulse, following Ref. [2i]. Optimized fits yield the first order desorption rate constants at various surface temperatures. These are shown in Figure 4 (closed black squares) with comparisons to results of prior work. The rate constants obtained with the newly developed LID approach agree well with the prior work using a variety of other methods.

The excellent agreement with previous results demonstrates that the LID-VRK method is a reliable way to monitor time-dependent adsorbate concentrations. The results also suggest that LID may be an attractive alternative to surface-sensitive spectroscopies like sum frequency generation (SFG), which has been widely used to monitor surface adsorbates. Like SFG, the LID-VRK method is non-destructive and highly surface-sensitive, while the kinetic traces of Figure 3 demonstrate a sensitivity that is better than $\approx 10^{-4}$ ML. Note that the initial dose from the CO molecular beam in Figure 3 is $\approx 0.3\%$ of a ML – this is based on the CO sticking probability (0.7) and measurements of the absolute flux of the molecular beam – yet we easily measure the adsorbate concentration at delays three times the desorption lifetime. For the NH$_3$ experiments, the sensitivity is even better as NH$_3$ is more efficiently ionized. It is also an advantage that LID-VRK signals are linearly proportional to adsorbate surface concentration, whereas SFG signals are proportional to the square of the surface concentration. The hyperthermal velocities produced in LID also allow the surface sensitive signal to be separated in velocity space from the background, whereas SFG backgrounds result from non-resonant processes that are not easily suppressed.

LID-VRK also exhibits advantages over conventional VRK. Specifically, the sensitivity of LID-VRK is not reduced at lower temperatures. Conventional VRK signals $S_{VRK}(t)$ are in general proportional to desorption flux $\Phi_{des}(t)$, which is the rate of desorption $d[A](t)/dt$. More accurately, $S_{VRK}(t)$ is proportional to the number of molecules that leave the surface in the time interval probed by the detection laser Δt_{MPI} in Equation (1):

$$S_{VRK}(t) \propto \int_{t}^{t+\Delta t_{MPI}} k_{des}(T)[A](t)dt \qquad (1)$$

Here, $[A]$ is the adsorbate's surface density, $k_{des}(T)$ is the thermal rate constant for desorption and Δt_{MPI} is the time slice of the thermal desorption flux that is detected in the experiment determined by the size of the MPI laser focus. Assuming, for example, an average velocity of the desorbing molecules of 600 m s^{-1} and a typical width of the ionization volume of 100 μm, Δt_{MPI} seen in VRK experiments is about 100–200 ns. At low temperatures T, the desorption rate becomes small and so does the VRK signal due to the constant value of Δt_{MPI}. The LID-VRK signal is, in contrast, proportional to the adsorbate surface density $[A](t)$. Consequently, the LID-VRK signal per laser shot is approximately independent of temperature. The advantage of LID-VRK at low surface temperatures is illustrated in the inset image of Figure 3, which shows the ion image intensity summed over all delay times in the kinetics experiment. The images show that the VRK signal (red rectangle) increases with increasing surface temperature, whereas the LID signal stays approximately constant. Another advantage becomes visible for the VRK signal of CO desorption from Pt (111). Especially at $T_S =$ 593 K, the VRK signal exhibits a prominent peak at about 300 μs, which results from the molecular beam dosing pulse – these are the molecules that did not stick to the surface but undergo direct scattering. This contribution is completely absent for the LID measurement.

We also note that LID is non-destructive. Experiments following the depletion of a full monolayer of CO from Pt (111) at room temperature showed that only about 1% of the adsorbate concentration is removed with each LID pulse. We point out that this fraction critically depends on the LID laser pulse energy and pulse duration as well as the type of adsorbate and the respective surface. Furthermore, the single crystal surface showed no visible damage nor did it exhibit changes in its LEED pattern. We also note that ion signals were only found at the parent mass-to-charge ratio (m/z = 28 for CO and 17 for NH$_3$). We found no indication of fragmentation due to the LID laser pulse. This feature is of great value as the m/z ratio can be used to assign the mass of the adsorbate.

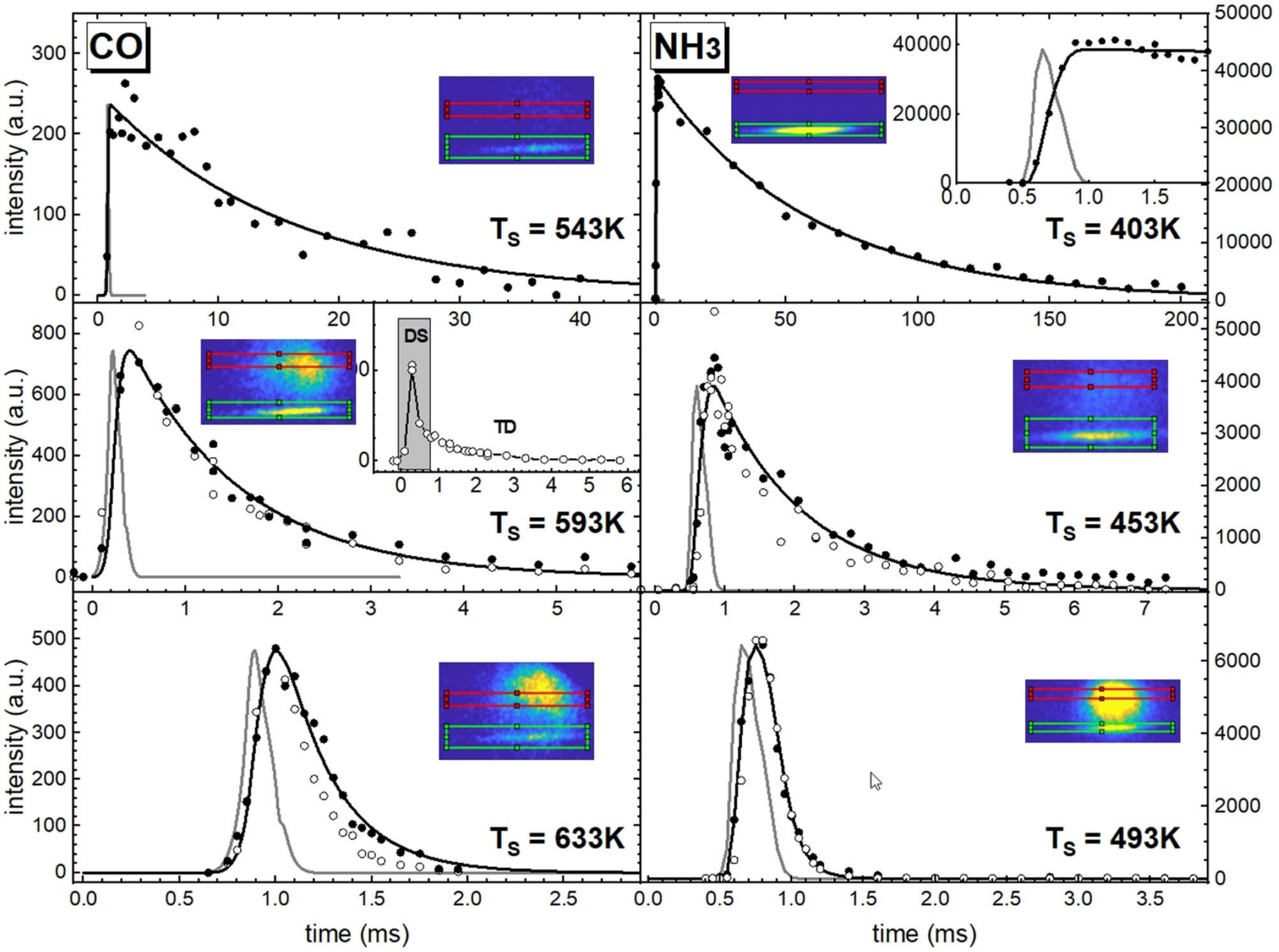

Figure 3. Laser-induced desorption signal measured as a function of time after the CO (left column) or NH_3 (right column) pulsed molecular beam (gray) has dosed a Pt (111) surface. The closed black circles show the velocity-resolved LID signal (selective integration of the green boxes in each ion image) fit to a first order kinetic model (black line). The open circles show thermally desorbed molecules (selective integration of the red boxes in each ion image) typically detected in VRK experiments. The open circle data has been scaled to the same amplitude as the LID data points. The images in each panel are the accumulated ion signal over all time delays detected in the kinetics measurements. Note that CO and NH_3 measurement we performed in separate experiments using the Parker Series 9 general valve nozzle.

Conclusion

While this work shows the successful application of non-resonant multiphoton ionization, which provided a quasi-universal detection scheme, more sensitive resonance-enhanced multiphoton ionization (REMPI) could obviously also be used. In fact, we have performed preliminary experiments of this kind that will be reported in a future publication. Past work has shown that LID produces molecules with high vibrational and rotational excitation.[8] REMPI allows detection of population in these energetic quantum states, which can be exploited to suppress background.

Future applications of LID-VRK will focus on detection of unstable atoms and radicals (e.g., O*, OH*), which are important intermediates in surface reactions. Monitoring the temporal evolution of these intermediates can be extremely valuable to identify the underlying reaction mechanisms in detail. For reaction intermediates, the non-destructiveness of LID-VRK will need to be evaluated again.

LID-VRK can also be applied for accurate measurements of adsorbate surface densities under equilibrium conditions, providing a new approach to Langmuir isotherms, from which important thermodynamics quantities like adsorbate binding energies are obtained.

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Writing – original draft: A. M. W., K. G.

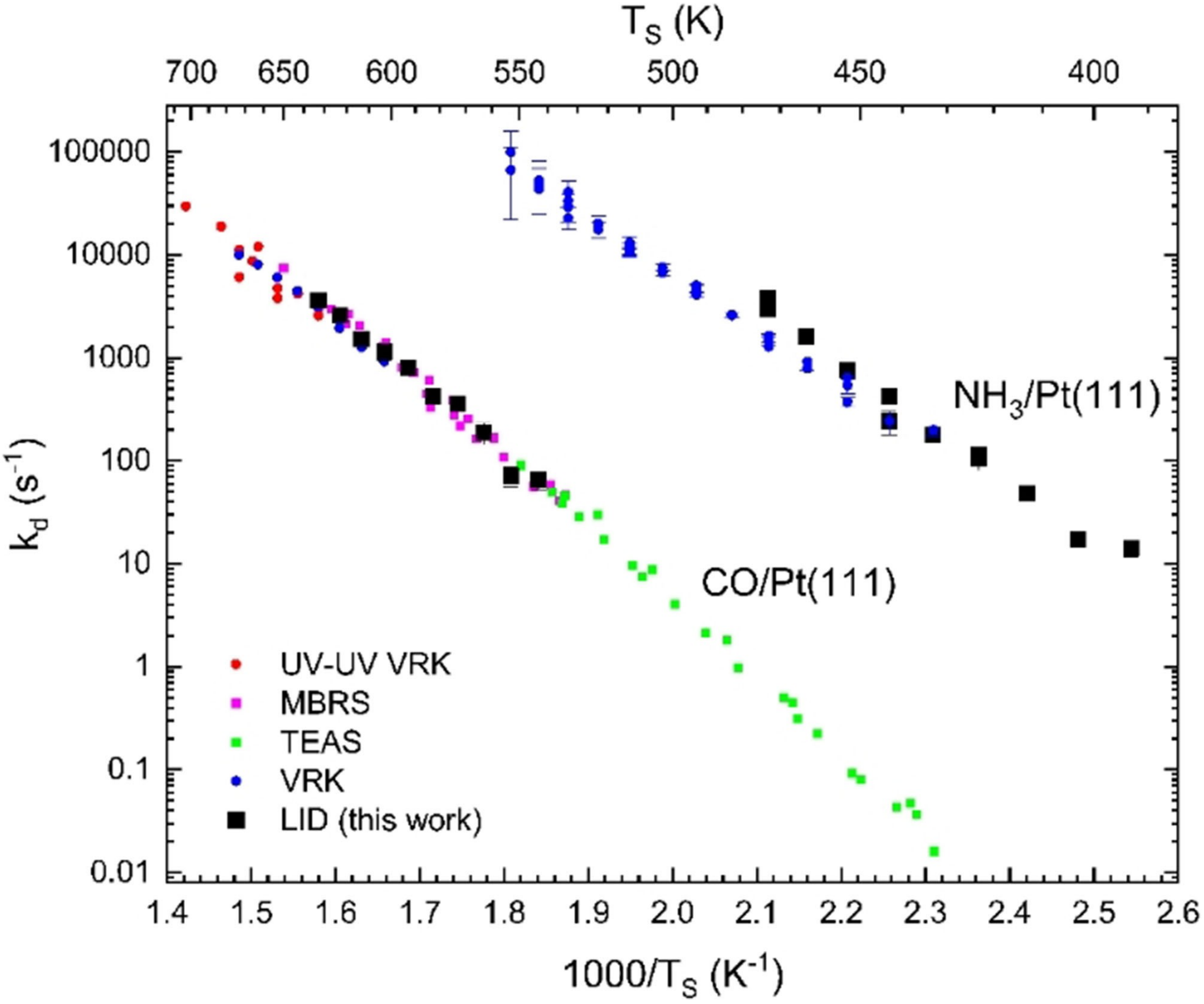

Figure 4. Rate constants obtained by monitoring the time-dependent adsorbate surface density with laser-induced desorption velocity-resolved kinetics (black squares) for CO and NH_3 desorption from Pt (111). The LID results are compared to previous work using conventional VRK (blue),[2b,f] UV-UV double resonance VRK (red),[2i] molecular beam relaxation spectroscopy (MBRS, magenta),[7] and thermal energy atom scattering (TEAS, green).[7]

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Conflict of Interest

Authors declare that they have no competing interests.

Data Availability Statement

All data that supports the findings of this study are available from the corresponding author, AMW, as well as KG upon request.

Keywords: adsorbate · ion imaging · laser-induced desorption · surface detection · velocity-resolved kinetics

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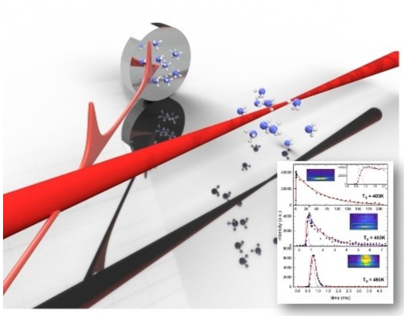
RESEARCH ARTICLE

Laser-induced desorption velocity-resolved kinetics (LID-VRK) as a highly surface sensitive detection method to study surface reaction kinetics are presented. The method is evaluated on the well-known desorption of CO and NH_3 from Pt (111). The measurements demonstrate the high sensitivity of LID-VRK of better than 10^{-4}. The LID-VRK signal is proportional to the adsorbate surface concentration, overcoming problems of conventional VRK due to low thermal desorption flux at low surface temperatures.



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