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ABSTRACT

Chirality detection of gas-phase molecules at low concentrations is challenging as the molecular number density is usually too low to perform conventional circular dichroism absorption experiments. In recent years, new spectroscopic methods have been developed to detect chirality in the gas phase. In particular, the angular distribution of photoelectrons after multiphoton laser ionization of chiral molecules using circularly polarized light is highly sensitive to the enantiomeric form of the ionized molecule [multiphoton photoelectron circular dichroism (MP-PECD)]. In this paper, we employ the MP-PECD as an analytic tool for chirality detection of the bicyclic monoterpene fenchone desorbing from a Ag(111) crystal. We record velocity-resolved kinetics of fenchone desorption on Ag(111) using pulsed molecular beams with ion imaging techniques. In addition, we measure temperature-programmed desorption spectra of the same system. Both experiments indicate weak physisorption of fenchone on Ag(111). We combine both experimental techniques with enantiomer-specific detection by recording MP-PECD of desorbing molecules using photoelectron imaging spectroscopy. We can clearly assign the enantiomeric form of the desorption product fenchone in sub-monolayer concentration. The experiment demonstrates the combination of MP-PECD with surface science experiments, paving the way for enantiomer-specific detection of surface reaction products on heterogeneous catalysts for asymmetric synthesis.

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I. INTRODUCTION

A detailed and fundamental understanding of chiral reactions at surfaces is important due to the significance of enantioselective catalysis for the production of valuable chemical compounds in, for instance, the pharmaceutical industry.¹ Thus, chiral molecules and chiral reactions at surfaces have been studied extensively under ultra-high vacuum (UHV) conditions with experimental techniques such as circular dichroism in the angular distribution (CDAD) of adsorbates' photoelectrons, scanning tunneling microscopy (STM), atomic force microscopy (AFM), calorimetry, temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and low-energy electron diffraction (LEED).^{2–18} In general, different ways exist to introduce chirality to surfaces. Often, three categories are distinguished:¹⁹ naturally chiral surfaces, chirally templated surfaces, and one-to-one chiral modifiers. When investigating molecular adsorption, most studies probe the chirality at the surface either directly by using high-resolution microscopic imaging techniques like STM, AFM, and CDAD, or indirectly by measuring the molecule-surface interaction energies by techniques like TPD or calorimetry. Such studies provide information about intermediate species in a heterogeneously catalyzed reaction, namely the adsorbed reactants. To obtain chiral information about the final reaction products, it is necessary to probe the desorbed products in the gas phase in the vicinity of the surface. This is challenging as the molecular density is usually low in such experiments. Consider, for example, the desorption of a fenchone monolayer in a TPD experiment with 10¹⁵ molecules/cm², after which the number density 2 cm from the surface is in the range of 10^6 molecules/cm³.²⁰ Furthermore, this number density is only present for a short time during the monolayer desorption. At these concentrations, the optical density is so low that absorption experiments are impossible, and hence, conventional circular dichroism approaches

are infeasible. Alternative techniques are required for molecular chirality detection.

Recently, several promising approaches have been developed to identify the chirality of molecules in the gas phase at low concentrations.^{21–37} In particular, three-wave mixing schemes in microwave spectroscopy^{21,22} and multiphoton photoelectron circular dichroism (MP-PECD) spectroscopy^{32-35,37} have been demonstrated as effective tools for detection of enantiomeric excess in the gas phase with better than 1% sensitivity. In microwave three-wave mixing experiments, two orthogonally polarized resonant applied electric fields are used to induce a third mutually orthogonal field in a sumfrequency generation process. The induced free induction decay is collected by a microwave horn antenna and recorded on an oscilloscope, and the field's phase is rotated by 180° with the enantiomeric form of the molecule. A typical high-gain microwave horn antenna has an acceptance width of 10 cm. Hence, the detection region for the macroscopic free induction decay is in the range of ~1000 cm³. Also, the lower detection limit of microwave spectroscopy is typically ~109 molecules/cm3. Both constraints make this technique impractical for surface science experiments, in which the number density of desorbed molecules is low (~10⁶/cm³) after desorption and spatial resolution is important to construct, for instance, angular distributions of the desorbing molecules. In contrast, for MP-PECD measurements, photoelectrons are recorded after photoionization with focused laser pulses.³⁷ Hence, the detection region of chiral molecules is confined by the laser focus and is usually in the sub-mm³ range. Chiral molecules are photoionized using circularly polarized light, and photoelectron angular distributions (PADs) are recorded by imaging techniques.^{38,39} The PAD exhibits a significant forward/backward asymmetry with respect to the light propagation axis that changes sign when the molecular chirality or light helicity is reversed.⁴⁰ The amount of this asymmetry can be used as an analytic tool to determine the enantiomeric excess in gas-phase mixtures.⁴¹ Due to its high sensitivity and spatial resolution, this technique is well suited for surface desorption experiments.

Initially, PECD measurements were performed on synchrotron sources using single-photon ionization.³¹ In the last years, the MP-PECD has also been performed using multiphoton ionization schemes via resonant electronically excited states, allowing the technique to be performed with table-top laser systems available in typical physical chemistry laboratories.^{32,33,42,43} Both femtosecond and nanosecond laser systems have been employed for MP-PECD experiments. The MP-PECD depends on the excitation wavelength, laser pulse duration, intermediate electronic state, and molecule.^{36,44} If all these parameters stay fixed and are well known, the MP-PECD can be used as an analytic tool to determine the concentration of enantiomers in gas-phase mixtures.

In this paper, we combine MP-PECD spectroscopy with surface science experiments and demonstrate the feasibility of chirality detection in molecular desorption processes as has been suggested in previous studies.⁴² In the tradition of the terpene chemistry founder Otto Wallach, who worked also in Göttingen, we study the interaction of the bicyclic monoterpene fenchone with a Ag(111) crystal. We chose fenchone as a well-studied benchmark molecule from MP-PECD spectroscopy and investigated the desorption from an achiral Ag(111) surface to keep the system as simple as possible for this proof-of-concept study. Fenchone physisorbs on Ag(111) with a binding energy of 0.52 eV. It does not react, so that the molecules maintain their chirality after desorption. Due to the high sensitivity of MP-PECD spectroscopy, we can determine the chirality of desorbing molecules in the gas phase even for sub-monolayer coverages.

II. EXPERIMENTAL

A. Experimental setup

The experiments were performed in a differentially pumped molecular beam surface science apparatus shown in Fig. 1.

Enantiopure fenchone (S)-(+)- and (R)-(-) samples were purchased from Sigma-Aldrich (99.2% purity) and were used without further purification. The enantiomeric excess (e.e.) was 99.9% for (S)-(+)-fenchone and 84% for (R)-(-) fenchone. Figure 2 shows the structure of both enantiomers.

Liquid fenchone was soaked into a cotton wad and placed in a reservoir attached upstream from the nozzle. The pulsed, homebuilt solenoid valve nozzles were based on the Even-Lavie design and have been described in detail before.⁴⁵ By heating the sample reservoir to 350 K, fenchone was evaporated into the gas phase. Water was removed by passing the carrier gas through a sample of MgSO₄ (99% purity). We used 2 bars of helium or argon as backing gas to generate a pulsed molecular beam. For fast switching between experiments with S-(+)-fenchone and R-(-)-fenchone, nozzle 1 and nozzle 2 were filled up with respective enantiopure samples. Nozzle 1 and nozzle 2 share a common source chamber. The beams each passed through a skimmer (Ni Model 2, Beam Dynamics, Inc.) and entered the surface chamber after passing a differentially pumped chamber. The intersection point of the molecular beams was located at the Ag surface. The Ag(111) surface was cleaned by cycles of Ar ion sputtering (Staib Instruments, IG-5-C) and annealing to 820 K. The surface temperature was monitored by a K-type thermocouple and could be temperature controlled between 1235 K and 110 K by resistive heating and liquid nitrogen cooling. Surface cleanliness was monitored by Auger electron spectroscopy (CMA-2000, LKTech). Fenchone was ionized using the frequency-doubled output of a Ti:Sa regenerative amplifier (35 fs, 400 nm, 10 μ J, Solstice, Spectra-Physics) in a 2 + 1 resonance-enhanced multiphoton ionization (REMPI) process via the 3s Rydberg state. The laser beam was focused with a f = 300 mmplano-convex quartz lens into the interaction region as depicted in Fig. 1(b). For velocity map imaging, we used the ion lens setup as described by Eppink and Parker.³⁹ Ions were accelerated onto an imaging detector consisting of microchannel plates (MCPs, Topag, MCP 56-15) and phosphor screen (ProxiVision). The detector could be used in two different modes. First, for photoelectron detection, the repeller and extractor were set to negative voltages (-2000 V, -1370 V, respectively), accelerating electrons toward the detector. Second, for ion detection, the polarity was switched and ions were recorded at the detector. In this mode, ToF mass spectra of the ions could be obtained. To record a single mass at the phosphor screen, the MCP voltage was pulsed at a gate timed to the arrival time of the respective ion. The apparatus has been used for two different types of experiments, namely temperature-programmed desorption (TPD) and velocity-resolved desorption kinetics experiments.



FIG. 1. (a) Molecular beam surface science apparatus for dosing chiral molecules at surfaces. Molecular beams are generated in pulsed nozzles mounted in the source chamber. After passing skimmer and differentially pumped chamber, the molecular beams enter the surface chamber and impinge upon the surface. Two nozzles are available for dosing the surface with different molecules. Nozzle 1 is mounted parallel to the surface normal. The molecular beam originating from nozzle 2 is tilted by 26° with respect to the surface normal. Molecules are ionized by laser radiation and detected in a velocity map imaging (VMI) setup, which is mounted next to the sample holder. Charged particles are accelerated and focused by VMI electrodes and are recorded on microchannel plates (MCPs) and a phosphor screen after 20 cm flight distance. (b) Ionization region of the VMI setup. Ions and electrons are generated between repeller and extractor electrodes and focused through the apertures onto the detector. The design is adapted from Eppink and Parker.³

For velocity-resolved desorption kinetics experiments, we followed the experimental means developed previously in Göttingen.^{46–49} Briefly, the adsorption of the fenchone beam pulse serves as time zero for the experiment (equivalent to the pump pulse in laser pump-probe experiments). Subsequently, the delayed ionization laser probes desorbing fenchone with respect to time zero by recording the parent ion mass signal (152 amu) at the VMI detector. As the VMI detector allows for velocity detection of desorption products, the fenchone residence time on Ag(111) can be calculated and desorption kinetic traces are obtained. An Arrhenius plot is constructed by measuring desorption kinetics at different surface temperatures. We also implemented chiral sensitivity to the experiment by recording the MP-PECD of desorbing fenchone. For this, we changed the polarity of the VMI electrodes and recorded



FIG. 2. Structural formulas of S-(+)-fenchone (left) and R-(-)-fenchone (right).

the projection of three-dimensional photoelectron angular distributions (PADs) onto the VMI spectrometer obtained after ionizing fenchone with left circularly polarized (LCP) light and right circularly polarized (RCP) light. We created LCP light and RCP light by passing linearly polarized light through an achromatic quarter waveplate (Thorlabs WPQ10M-405). The quality of polarization was checked by determining the Stokes S3 parameter using a Glan-Laser polarizer (Thorlabs GT10-A) and a power meter (Gentec-EO, MAESTRO 206300, PH100-Si). S3 is for all presented measurements well above 98%, and no correction with respect to S3 has been performed. PAD images were recorded with a 1024 \times 768 pixel CCD camera (Sony XCD-X710) and averaged for 10 000 laser shots for each polarization. The MP-PECD image was calculated by subtracting the averaged RCP PAD image from the averaged LCP PAD image and subsequent antisymmetrization. The velocityresolved desorption experiments were repeated at the 200 Hz repetition rate of the nozzle, and the PAD was averaged for 10000 laser shots.

In a second approach, we performed temperature-programmed desorption (TPD) experiments. Here, the molecular beam was used for dosing the surface with little spatial spread and large control over the incident translational energy while the surface was kept at cryogenic temperatures. After dosing the surface for a defined time with fenchone seeded in argon, the surface temperature was ramped linearly with a heating rate of 2 K/s and desorbing products were

ionized. REMPI-time-of-flight-mass spectra (REMPI-ToF-MS) were recorded as a function of surface temperature using the femtosecond laser as the ionization source. We implemented chiral sensitivity to the TPD experiments by measuring the MP-PECD instead of mass spectra while heating up the sample. We recorded MP-PECD images similar to the time-resolved desorption kinetics experiments. However, in contrast to velocity-resolved desorption kinetics experiments, TPD experiments cannot be performed at high repetition rates. Hence, only molecules that were previously adsorbed at cryogenic temperatures at the surface can be ionized while heating the surface up on a 10 min timescale. We recorded two separate TPD spectra ionizing with either LCP light or RCP light. Afterward, we averaged PADs emitted at certain desorption peaks and calculated corresponding MP-PECD images. The image was calculated by subtracting the averaged RCP PAD image from the averaged LCP PAD image and subsequent antisymmetrization.

B. Data evaluation

We employ two approaches to calculate the MP-PECD of fenchone. First, we directly use the experimental data without Abel inversion and calculate MP-PECD values following the approach developed previously,⁴²

$$MP-PECD = \frac{I_{RCP,f} - I_{LCP,f}}{0.5} - \frac{I_{RCP,b} - I_{LCP,b}}{0.5}.$$
 (1)

Here, $I_{p,f}$ and $I_{p,b}$ denote the integrated intensity in forward and backward directions, respectively. *p* denotes the polarization of the laser. The MP-PECD value depends on the intermediate REMPI state. Hence, MP-PECD calculations from the raw data only yield accurate values as long as not more than one intermediate state is involved in the REMPI scheme. This way, the PES is composed of only one contribution and overlapping of different spectral features will not blur the MP-PECD. For excitation energies of 400 nm, this is the case for fenchone.

In a second approach, we calculate MP-PECD from Abelinverted images. The originally three-dimensional photoelectron angular distributions obtained after ionization with LCP light and RCP light are each reconstructed using the MaxEntropie algorithm developed by Dick.⁵⁰ We use Legendre polynomial basis functions up to the sixth order following Yang's theorem.⁵¹ The chiral signature is contained in the odd-order Legendre polynomial coefficients. The multiphoton PECD can be calculated as sum over the odd-order coefficients c_i normalized to the total signal c_0^{37}

MP-PECD =
$$\frac{1}{c_0} \left(2 c_1 - \frac{1}{2} c_3 + \frac{1}{4} c_5 \right).$$
 (2)

We calculate the MP-PECD value within the full width of half maximum (FWHM) of the peak signal using a weighted average to take into account the peak intensity variation. Within the absolute experimental MP-PECD error of $\pm 3\%$, we obtain identical values for both approaches.

III. RESULTS AND DISCUSSION

A. Velocity-resolved desorption kinetics

We first recorded photoelectron angular distributions (PADs) after ionizing fenchone in the incident molecular beam originating

from nozzle 1. Figure 3 shows the ion yield of the incident molecular beam after 2 + 1 REMPI for S-(+)-fenchone and R-(–)-fenchone seeded in He as function of the molecular beam-laser delay. The FWHM of the incident molecular beam pulse is in the order of 40 μ s.

At the maximum of the incident molecular beam, we recorded the PAD and calculated the MP-PECD image by subtracting the averaged RCP PAD image from the averaged LCP PAD image and subsequent antisymmetrization. See images in Fig. 3. The forward/backward asymmetry with respect to the light propagation axis is obvious and changes sign with the enantiomeric form. We calculate the MP-PECD using Eq. (1). In accordance with earlier studies, we calculate MP-PECD values of -15% and +13% for S-(+)fenchone and R-(-)-fenchone, respectively.³⁶ The PECD value of R-(-)-fenchone has been corrected for its enantiomeric excess value of 84%. Calculating the MP-PECD value from the Abel inversion



FIG. 3. (a) Ionization yield as function of the delay between nozzle opening and laser ionization of the incident beam of S-(+)-fenchone seeded in He. We record the ionization yield by measuring the total ion signal after REMPI ionization with linearly polarized light at 400 nm. The incident beam has a FWHM of ca. 40 μ s. At the maximum of the incident beam pulse, we record angular distributions of photoelectrons after ionization with left and right circularly polarized (LCP and RCP, respectively) light. The inset shows the MP-PECD image, which is created by subtracting the photoelectron angular distributions produced by LCP light and RCP light. The lower half shows the antisymmetrized experimental data, and the upper half shows the Abel-inverted image. (b) Same measurements performed with R-(-)-fenchone. The PECD changes sign.

Legendre polynomial coefficients following Eq. (2) yields identical values within the absolute MP-PECD error of $\pm 3\%$.

We used the molecular beam pulse to record desorption kinetics traces as explained in detail in Ref. 46 and in the experimental section. We obtain kinetic desorption traces by detecting positively charged ions on the ion imaging detector shown in Fig. 1. Running the imaging detector in velocity map imaging (VMI) mode allows us to determine the translational energy of desorbing molecules and to calculate corresponding flux as function of the residence times as the surface ionization distance is known. Figure 4 shows the velocity distribution of S-(+)-fenchone desorbing from Ag(111) at two different temperatures. Distributions are extracted from raw velocity map images displayed as inset in Fig. 4 by taking a narrow, 10 pixel wide, slice through the center of the feature, subtracting the background, and performing a density to flux correction. The image is a sum over all molecular beam-laser delays. The distribution is shifted toward higher velocities at higher surface temperatures, indicating thermalization of adsorbed fenchone molecules.

We determine velocity distributions as described above for each individual velocity map image as we scan the delay time between molecular beam and ionization laser. We then calculate residence times of fenchone on the silver surface from the total ion signal on the detector taking into account the distance between surface and ionization region and the velocities of desorbing molecules. Figure 5 shows desorption kinetic traces of S-(+)-fenchone from Ag(111) at different surface temperatures. The residence times are significantly shorter at elevated temperatures. We do not observe any contributions from directly scattered fenchone in the signal.



FIG. 4. Velocity distributions of S-(+)-fenchone desorbing from Ag(111) at $T_{\rm S}$ = 323 K and $T_{\rm S}$ = 363 K summed over the full range of molecular beam-laser delays. The distribution is shifted toward larger velocities at a higher surface temperature. The inset shows the raw velocity map image at a surface temperature of 363 K. We extract the distribution from the raw velocity map image by taking a narrow, 10 pixel wide, slice through the center of the feature, subtracting the background, and preforming a density to flux correction. Note that the maximum of the distribution is shifted toward higher velocities compared to the raw image due to the density to flux conversion.



FIG. 5. Kinetic desorption traces of S-(+)-fenchone desorbing from Ag(111) at different temperatures. The dashed line shows the incident molecular beam, and the inset displays an Arrhenius plot for the system. We deduce an activation energy of 0.52 eV for the desorption process and an Arrhenius prefactor of $1.5 \times 10^{11} \text{ s}^{-1}$.

We fit the kinetic traces at each temperature with a function formed by a convolution of the incident molecular beam and an exponential decay to extract first-order rate constants as explained in previous studies.^{46,49} The inset in Fig. 5 shows an Arrhenius plot using the first-order rate constants from which we deduce a desorption activation energy of 0.52 eV and an Arrhenius prefactor of 1.5 $\times 10^{11}$ s⁻¹. The value of the desorption activation energy is typical for polyatomic organic molecules physisorbed at non-reactive surfaces. However, the Arrhenius prefactor is surprisingly low for large molecules.^{52–55} In transition state theory (TST), the desorption reaction prefactor is related to the increase of entropy between adsorbed state and transition state to desorption. For polyatomic molecules, this increase is mostly attributed to translational, rotational, and torsional degrees of freedom.⁵⁵ However, fenchone is a rigid bicyclic terpene with only three attached methyl groups. See Fig. 2. In contrast to, for instance, long-chain alkanes, significantly less torsional modes are available, so that the entropy difference between adsorbed state and gas phase is expected to be less pronounced. This holds, in particular, for adsorbate states, for which the torsional modes of the methyl groups are non-hindered. In addition, the molecule might go through different intermediate states during desorption, which could also influence the experimentally measured prefactor.

We performed the same experiments with the other enantiomeric form R-(–)-fenchone and measured a desorption activation energy of 0.51 eV. This value is identical within the error of the experiment as the adsorption/desorption occurs on an achiral surface. A discrimination of both enantiomeric forms by the desorption dynamics is impossible on an achiral surface. However, measuring the MP-PECD of the desorbing molecules after desorption in the gas phase allows molecules of different chirality to be distinguished easily. For these experiments, we detected the MP-PECD of the desorption products 500 μ s after the adsorption of the incident beam to avoid interference due to photoelectrons produced from the tail of the incident molecular beam. Figure 6 shows desorption kinetic traces of S-(+)-fenchone and R-(–)-fenchone for the same surface



FIG. 6. Kinetic desorption traces of R-(–)-fenchone and S-(+)-fenchone for a Ag(111) surface temperature of 333 K. Kinetic traces have been constructed from photoion signal as shown in Fig. 5. We distinguish different enantiomers after desorption by recording respective MP-PECD for molecules with a surface residence time of 500 μ s. MP-PECD values are calculated using Eq. (1). The MP-PECD value of R-(–)-fenchone is corrected for its enantiomeric excess of 0.84. The MP-PECD is –17% and 14% for S-(+)-fenchone and R-(–)-fenchone, respectively.

temperature of 333 K. Corresponding MP-PECD images are displayed in the insets. As in the MP-PECD images of the incident beam shown in Fig. 3, the forward/backward asymmetry with respect to the light propagation axis is evident and changes sign with the enantiomeric form. From the MP-PECD images, we calculate MP-PECD values using Eq. (1), which are -17% and 14% for S-(+)-fenchone and R-(-)-fenchone, respectively. Within the error of the experiments of ±3%, these values are identical to the MP-PECD of the incident beam as fenchone does not react on Ag(111). Any enhancement or reduction of the MP-PECD due to vibrational excitation of desorbing fenchone compared to vibrationally cooled incident fenchone cannot be resolved in this experiment. In general, the vibrational character of the intermediate level of the REMPI scheme has only a minor influence on the PECD.⁴³ From TPD experiments, we can estimate the coverage achieved with one molecular beam pulse to be 0.01% of a monolayer. After desorption, this corresponds to a molecular density of 8×10^6 molecules/cm³ at 2 cm distance to the surface or a local pressure of 2×10^{-10} Torr at 300 K for a desorption lifetime of 500 μ s. These experiments demonstrate that even at such low molecular densities, the two different enantiomeric forms of fenchone can easily be distinguished after surface desorption.

We also observe the excitation of vibrational modes after desorption in the photoelectron spectrum (PES) of fenchone. In Fig. 7, we show the PES for fenchone in the incident beam and after desorption from a Ag(111) crystal with temperatures of 423 K, 623 K, and 673 K. We observe a single peak in the spectrum, which we assign to the 3s \leftarrow S₀ transition. The PES is extracted from the photoelectron angular distributions after ionizing with linearly polarized light of 400 nm using a polar onion peeling algorithm written in MATLAB.⁵⁶ The algorithm reconstructs the original three-dimensional photoelectron distribution from the two-dimensional



FIG. 7. Photoelectron spectrum of S-(+)-fenchone in a cold molecular beam (blue curve) and after desorption from a Ag(111) surface temperature stabilized to 423 K (green), 623 K (orange), and 673 K (black). The peak arises from 2 + 1 REMPI via the 3s \leftarrow S₀ transition. The dashed line shows the linewidth of the ionization laser. The excitation of vibrational modes in fenchone by thermalization with the surface temperature leads to a broadening of the peak at the low-energy tail. The inset shows the 2 + 1 REMPI excitation scheme of fenctione via the 3s Rydberg state. Excess energy is converted to photoelectron energy.

velocity map image using an Abel inversion routine. When adsorbed at the surface, fenchone thermalizes and vibrational degrees of freedom get excited. As a consequence, the PES changes depending on the Franck-Condon overlap between vibrational modes in the electronic ground state and in the electronically excited state. We observe a broadening of the 3s peak in the spectrum at lower photoelectron energies. See Fig. 7. Even though the spectrum of the excitation laser pulse exhibits a FWHM of 30 meV, we observe a slight dependence of the peak's low-energy tail on the surface temperature. The hotter the surface, the more the tail is broadened toward lower photoelectron energies. This dependence could be a promising approach to evaluate the vibrational energy of polyatomic molecules in surface collision experiments using ionization lasers with narrower frequency bandwidth. Of course, careful calibration for each molecule would be necessary for such experiments.

B. Temperature-programmed desorption

In a second approach, we investigated the desorption kinetics of fenchone and Ag(111) using temperature-programmed desorption (TPD) experiments. For this, we used the pulsed molecular beam with argon as seeding gas for controlled surface dosing at cryogenic temperatures with a translational energy of 280 meV. Figure 8 shows TPD curves for the S-(+)-fenchone/Ag(111) system for different surface coverages.

We employed REMPI-ToF-mass spectrometry (REMPI-ToF-MS) to identify the desorption products while heating up the surface and construct TPD curves by plotting the parent ion mass of 152 amu as function of the surface temperature. We observe two peaks at 224 K (α) and 248 K (β), respectively, when dosing the surface at 195 K. When dosing at 150 K, we observe a third peak



FIG. 8. Temperature-programmed desorption curves of S-(+)-fenchone desorbing from Ag(111) for different fenchone dosages using REMPI-ToF-MS with the femtosecond laser as ionization source. The TPD curves are shown for the parent ion mass of 152 amu. The surface temperature was ramped linearly with a heating rate of 2 K/s. We observe two desorption peaks at 224 K (α) and 248 K (β) when dosing at a surface temperature of 193 K. When we dose at 153 K, we detect the multilayer peak, which is non-saturable at higher dosages. The inset shows mass spectra recorded at the different desorption peaks. The black curve shows a simulation of the TPD spectra using parameters obtained with velocity-resolved desorption kinetics experiments described previously. The simulated desorption rate has been multiplied by -1 for ease of presentation.

at 191 K, which does not saturate at higher dosages, and which we assign to multilayer desorption. In particular, the shape of this peak indicates zero-order desorption kinetics, which supports this assignment. Mass spectra for the three desorption peaks are shown as insets in Fig. 8. The fragmentation patterns are characteristic of fenchone and are identical for different desorption peaks. No reaction at the surface is observed. The temperatures at which S-(+)fenchone desorbs from Ag(111) indicate physisorption for both the α -peak and the β -peak. Possible explanations for the observation of two nearby desorption peaks are, among others, the adsorption on different surface sites, different desorption channels with different probabilities of intermediate steps, dimer formation, adsorption on edges, and different adsorption geometries. Further experiments using experimental techniques like reflection-absorption infrared spectroscopy (RAIRS), x-ray photoelectron spectroscopy (XPS), or high-resolution electron energy loss spectroscopy (HREELS) are needed for further analysis but are not the focus of this study. From the desorption parameters obtained in velocity-resolved desorption kinetics experiments described above, we simulate the TPD spectrum. See the black curve in Fig. 8. The simulated peak overlaps with the experimentally measured a-peak. Considering the uncertainty in the kinetic parameters, we calculate an error of the TPD maximum of ±10 K. In the velocity-resolved desorption kinetics experiments, we do not observe any hints of a second desorption component as we observe in the TPD experiments.

We measured the chirality of desorption products by combining TPD with MP-PECD measurements. In a proof-of-concept experiment, we first dosed one monolayer of S-(+)-fenchone at a surface temperature of 195 K using nozzle 2 as depicted in Fig. 1. Afterward, we cooled the surface to 150 K and dosed with R-(–)-fenchone using nozzle 1. With this approach, we prepared a layer of R-(–)-fenchone adsorbed on a monolayer of S-(+)-fenchone as the molecular beams intersect at the surface. In the subsequent TPD experiment, we detected photoelectron angular distributions (PADs) while heating up the surface and ionizing desorbing fenchone with either LCP or RCP in separate scans. PADs were recorded with a frequency of 10 Hz, which yielded ~100 images per desorption peak at a heating rate of 2 K/s. We sum all PADs associated with each desorption peak and construct MP-PECD images by subtracting PADs recorded in LCP and RCP scans, respectively. MP-PECD values are calculated from the raw images as described previously.

In Fig. 9, we present the corresponding MP-PECD images associated with the TPD spectrum of fenchone. The two enantiomers can clearly be distinguished and assigned to separate peaks as expected from the preparation procedure, indicating that molecules from the first monolayer do not exchange with molecules from the overlayers at temperatures below 200 K. MP-PECD images obtained with TPD experiments cannot be averaged extensively like those obtained in velocity-resolved desorption kinetics experiments. Instead, averaging is limited to the number of molecules that are adsorbed at the surface at cryogenic temperatures before starting the heating ramp, which is at maximum one monolayer. The images are therefore significantly noisier. Nevertheless, the measured MP-PECD values are identical to those obtained in velocity-resolved desorption kinetics experiments to within the experimental uncertainty, revealing the potential of this technique for enantioselective surface reaction experiments in the future.



FIG. 9. TPD of a S-(+)-fenchone/R-(-)-fenchone mixture desorbing from Ag(111). We dosed the surface such that S-(+)-fenchone forms the monolayer and R-(-)-fenchone the multilayer. During the heat ramp, we recorded photoelectron angular distributions at a frequency of 10 Hz. This yields ~100 images per desorption peak at a heating rate of 2 K/s. We averaged all images associated with a certain desorption peak and constructed MP-PECD images from which we calculated the MP-PECD value. The TPD curve (black line) is deduced from photoions as shown in Fig. 8. We can clearly assign the chirality to distinct desorption peaks.

IV. CONCLUSION

In this study, we combined multiphoton photoelectron circular dichroism (MP-PECD) measurements with surface desorption experiments of the bicyclic monoterpene fenchone from a Ag(111) surface. We used pulsed beam velocity-resolved desorption kinetics and temperature-programmed desorption (TPD) experiments to investigate the interaction of fenchone with Ag(111). Fenchone physisorbs on Ag(111) and does not react. We combined both experimental techniques with enantiomer-specific detection by measuring photoelectron angular distributions after ionizing fenchone with circularly polarized light to obtain the MP-PECD. This way, we can clearly assign the enantiomeric form of desorbing molecules even at molecular densities of 8×10^6 molecules/cm³, which corresponds to the desorption of 0.01% of a monolayer. The proof-of-concept experiments illustrate the potential of this technique for future studies on enantioselective surface reactions.

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The authors declare no competing financial interests.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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