I. INTRODUCTION

Studies on cluster-surface interactions are frequently motivated either by the need to deposit clusters from the gas phase on a solid surface as inert as possible to allow further investigations of their geometric, electronic, magnetic, or optical properties or by the goal to use energetic cluster ion beams as a tool for the growth of high-quality thin films, the smoothing of the surface, or the control and modification of material properties. For us, the intermediate “hyperthermal” energy range from about 0.01–100 eV is especially interesting because it allows to address a large variety of fascinating processes such as fragmentation phenomena and phase transitions in finite systems, electron-transfer processes, and both chemical reactions within the cluster and between the cluster and the target surface. Here our focus is on “small” cluster sizes with a few up to about a hundred molecules where physical and chemical properties vary with every molecule added to the molecular aggregate.

To address the many fascinating questions of cluster impact chemistry, we have designed and built a new, specialized experimental setup capable of studying both intrACLUSTER reactions initiated by the collision of size-selected molecular cluster ions with a chemically inert surface and chemical processes occurring between neutral clusters and a well-defined surface of catalytic interest. Carbon monoxide presents an excellent model system for the investigation of both aspects: Firstly, CO is a simple and reactive organic molecule of significant industrial relevance and is thus one of the most widely studied molecules in catalytic processes and surface reactions. Secondly, because the binding energy between two carbon monoxide molecules in a molecular aggregate is small it allows easy fragmentation on surface impact, providing high local molecule abundance.

II. EXPERIMENTAL SETUP

Figure 1 schematically depicts our newly built experimental instrumentation for the systematic study of cluster-surface interactions. The setup consists of a spherical vacuum chamber (with a diameter of 400 mm) with a pulsed supersonic jet source for cluster generation and a variable-energy electron gun for optional ionization. A second differentially pumped chamber provides a reflectron-type time-of-flight mass spectrometer, a pulsed mass gate, a target surface, and a bipolar ion detector with postacceleration capabilities for reactive intrACLUSTER studies of size-selected cluster ions (1–100 eV/molecule). The third chamber is equipped with a cryogenically shielded, high-performance quadrupole mass analyzer for angular-, time-, and velocity-resolved collision experiments of neutral molecular aggregates. It offers thermal desorption spectroscopy (TDS) and is connected to an analysis and preparation chamber (different working plane, not shown) with basic surface science techniques [Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED)].

Because a meaningful investigation of reactive surface processes of molecules and clusters of organic substances requires well-defined target surfaces, suitable ultrahigh-vacuum (UHV) conditions are achieved by completely hydrocarbon-free pumping stages consisting of corrosion-resistant, magnetically levitated turbomolecular drag pumps (Pfeiffer TMU 400MPH and TMU 1000MPCT) and chemically persistent diaphragm pumps (Vacuubrand MD 4BRL).
A home-built control electronics (based on the Siemens S7-200 PLC system) automates and monitors vacuum operation.

In our experimental setup a cold jet of molecular clusters is efficiently generated by pulsed supersonic expansion of the gaseous substance such as CO, CO2, O2, C2H4, C2H6, C2H8, and SF6 seeded in a rare gas at high pressures (1–130 bars).

Cluster growth is governed by the degree of supersaturation of the expanded gas and by the total number of collisions. Thus, increasing the stagnation pressure \( p_0 \) and/or reducing the gas temperature \( T_0 \) can significantly enhance cluster size and beam intensity. Due to the generally small binding energies of molecular clusters (of the order of approximately 10–100 meV) as compared to metal clusters or \( C_{60} \), the experimental capability to adjust stagnation pressure and temperature in a wide range is of great value. On the...
other hand, ultrahigh-vacuum conditions demand a very limited gas load, and the common approach is to use a pulsed nozzle with a short opening time.\textsuperscript{15}

Basis of our cluster source is the novel design of a miniaturized pulsed valve\textsuperscript{16} for supersonic expansion,\textsuperscript{16} which is depicted in Fig. 2. It consists of a conical nozzle with a hole diameter of 0.3 mm and facilitates ultracold temperatures in the expanding jet\textsuperscript{17} by the use of high stagnation pressures of up to 130 bars. Moreover, high stagnation pressures permit an increased beam intensity and thus a significantly enhanced signal-to-noise ratio. Due to the short opening time of the pulsed valve of less than 20\textsuperscript{s}, roughly a factor of 20 less than other commercially available nozzles, the resulting gas load is reduced accordingly and allows the compact, cost-efficient coupling of an intense source of molecular clusters to a UHV chamber. Clean operation conditions are further supported by the use of chemically resistant materials--stainless-steel alloys, ceramics, and polyimides--and the possibility to bake the valve up to 435 K.

To optimize cluster growth, avoid gas condensation already in the valve, and accurately define the mean velocity of...
TABLE I. Comparison of the relevant parameters in the two experimental configurations.

<table>
<thead>
<tr>
<th>Configuration 1</th>
<th>Configuration 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic energy of molecular clusters</td>
<td>Accelerated ions: 1–100 eV/molecule</td>
</tr>
<tr>
<td>Size of molecular clusters</td>
<td>Size selected: 1–100 molecules/cluster</td>
</tr>
<tr>
<td>Electric charge of molecular clusters</td>
<td>Singly positive or singly negative</td>
</tr>
<tr>
<td>Electric charge of reaction products</td>
<td>Same as charge of incoming parent clusters</td>
</tr>
<tr>
<td>Product detection</td>
<td>• Angle integrated • Energy resolved</td>
</tr>
<tr>
<td>Relevance of solid surface</td>
<td>Chemically inert: Used for efficient and fast conversion of translational energy into internal cluster excitations</td>
</tr>
<tr>
<td>• Velocity resolved</td>
<td>• Local particle density • Adsorbate coverage • Geometric structure • Surface temperature</td>
</tr>
</tbody>
</table>

the supersonic beam, the valve temperature is continuously regulated using a thermal liquid (Julabo Thermal HL80) together with a computer-controlled external circulator (Julabo Presto LH85), providing excellent temperature stability ($\Delta T \leq 0.03$ K) in the range of $T = 220–435$ K. Temperature is measured using a NiCr/Ni thermocouple spot-welded directly to the valve body. Even lower temperatures can be achieved using liquid nitrogen as coolant. Besides the option to choose a feasible cluster source temperature, the coexpansion of the gaseous substance together with rare gases (He, Ne, Ar, and Xe) provides the possibility to continuously adjust the mean size $\bar{n}$ and kinetic energy $E_{\text{kin}}$ of neutral molecular clusters in the range of $\bar{n} = 1–1000$ and $E_{\text{kin}} = 0.01–1.0$ eV/molecule. The cluster source is mounted on a $xyz$-translator stage (Pink, $xy$ motion: $\pm 12.5$ mm, $z$ travel: 200 mm) to properly align it to the beam axis defined by two skimmers (Fig. 1) and to adjust the distance to the first skimmer. Especially for high-pressure expansions the latter ability is extremely important to minimize skimmer interference effects leading to reduced cluster intensity and increased beam temperature.

Another extremely valuable feature of the presented cluster source is its unsurpassed pulse-to-pulse stability with a standard deviation of less than 1%, as demonstrated in Fig. 3. The visible scatter of the peak amplitudes is entirely caused by the resolution of the digital oscilloscope. The evaluation of a single pressure pulse reveals the amount of gaseous substance fed into vacuum. For the depicted measurement it results in approximately $10^{-11}$ mol/pulse, underlining the very economical use of expanded substances. The emerging jet gas pulse (with a maximum repetition rate of 25 Hz) can be ionized by electron attachment or electron impact close to the nozzle exit. For this purpose a compact, shielded electron gun (see Fig. 4 for details) mounted on the valve body is used. It features an electron beam with a kinetic energy spread of $\Delta E < 1$ eV. Space-charge effects are minimized by operating the output electrode in a pulsed mode with typical on times of 10–20 $\mu$s, leading to increased ion currents. The emission current (several milliamperes) can be monitored with a collector electrode located opposite of the beam axis. Currents and voltages are provided by computer-controlled power supplies (Delta Elektronika ES150). Proper timing of all pulses is achieved by two synchronized pulse/delay generators (Stanford Research DG535).

The conical skimmers with a typical length of 20 mm are machined from stainless steel and further polished. They are mounted electrically isolated using Vespel® gaskets, allowing optional biasing voltages.

An overall analysis of the pulsed cluster beam with respect to velocity and cluster size distribution is available using an on-axis retarding-field ion-energy analyzer in combination with a shielded Faraday cup detector. Resulting electron signals are amplified with a low-noise, ultrasensitive current amplifier with a transimpedance of $10^7$ V/A (Femto LCA-4K-1G). Due to its reduced upper cutoff frequency (4 kHz), its response function has been determined experimentally.

For investigations of surface-impact phenomena of size-selected molecular cluster ions, acceleration to high kinetic energies up to 6 keV is available by pulsed ion extraction perpendicular to the axis of the neutral beam using a com-
pact, high-resolution time-of-flight mass spectrometer. It consists of three acceleration stages, the first two (each 12 mm long) are in the shape of pot electrodes, while the last one (27 mm long) is composed of 27 equally spaced field rings of 0.5 mm thickness each. This design results in a mass resolution $m/\Delta m > 500$ already for the linear configuration (total length $\approx 730$ mm). Figure 5 depicts sample mass spectra of $(\text{CO})_n^+$ clusters measured in this linear configuration for three different source temperatures. For lower stagnation temperatures the shift to larger cluster sizes can be clearly observed.

The acceleration stage of the time-of-flight mass spectrometer is complemented by a set of parallel shielded deflection plates to compensate the transversal velocity component of the cluster beam. An improved design of a Bradbury-Nielson-type ion gate,\textsuperscript{18–20} which is depicted in Fig. 6 and located in the first focal plane of the time-of-flight mass spectrometer, enables the size selection of cluster ions prior to their interaction with a polycrystalline diamond surface, which is located in the ion reflector. A high-speed bipolar time-of-flight detector (Burle) with a sensitive area of 25 mm diameter is placed in the second focal plane of the time-of-flight mass spectrometer. It features a postacceleration of positive and negative ions up to 10 keV for enhanced detection efficiency of high mass ions and a rise time of the output signal below 500 ps. Ion signals can be directly recorded in high voltages that can be accurately set programmatically to within $\pm 40$ mV (seg NHQ). Detailed descriptions of mass filter and mass spectrometer are published separately.

In addition to the study of intrachannel reactions of size-selected positively or negatively charged cluster ions in the energy range of 1–100 eV/molecule, a complementary setup is provided in a further UHV scattering chamber. This second configuration is equipped with a high-performance quadrupole mass analyzer (Hiden HAL 3F) with 10 $\mu$s time resolution, 500 amu mass range, and single-ion counting capabilities allowing time-resolved scattering studies of neutral clusters with kinetic energies of 0.01–1 eV/molecule. A translator stage provides the possibility to sample the incoming beam (target surface retracted) and to measure the velocity distribution of scattered particles. Angular information can be accessed by rotating the target surface ($\theta_{\text{scatter}} = \theta_{\text{in}} + \theta_{\text{out}}$) and by changing the total scattering angle $\theta_{\text{scatter}}$ from 22.5° to 157.5° in steps of 22.5° by using different flange positions for the mass spectrometer. Basic surface science techniques for sample preparation and characterization (AES, LEED) are available in a separate UHV chamber.

III. SUMMARY

We have built a versatile setup for the investigation of a multitude of fascinating questions and phenomena in cluster science and surface reactions. Its main capabilities are summarized in Table I.

ACKNOWLEDGMENTS

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