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High-resolution laser spectroscopy between 0.9 and 14.3 THz in a supersonic beam: Rydberg-Rydberg transitions of atomic Xe at intermediate n values

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A laser-based, pulsed, narrow-band source of submillimeter-wave radiation has been developed that is continuously tunable from 0.1 THz to 14.3 THz. The source is based on difference-frequency mixing in the nonlinear crystal DAST. By varying the pulse length, the bandwidth of the submillimeter-wave radiation can be adjusted between 85 MHz and 2.8 MHz. This new radiation source has been integrated in a vacuum-ultraviolet(VUV)-submillimeter double-resonance spectrometer, with which low-frequency transitions of atoms and molecules in supersonic beams can be detected mass-selectively by photoionization and time-of-flight mass spectrometry. The properties of the radiation source and spectrometer are demonstrated in a study of $33f \leftarrow nd$ Rydberg-Rydberg transitions in Xe with n in the range 16 – 31. The frequency calibration of the submillimeter-wave radiation was performed with an accuracy of 2.8 MHz. The narrowest lines observed experimentally have a full-width at half-maximum of ~ 3 MHz, which is sufficient to fully resolve the hyperfine structure of the Rydberg-Rydberg transitions of ^{129}Xe and ^{131}Xe . A total of 72 transitions were measured in the range between 0.937 THz and 14.245 THz and their frequencies are compared with frequencies calculated by multichannel quantum defect theory (MQDT).

I. INTRODUCTION

Electromagnetic radiation with frequencies in the range between 0.1 THz (3.3 cm^{-1}) and 30 THz (1000 cm^{-1}) can be regarded as being part of the far-infrared and of the submillimeter-wave ranges of the electromagnetic spectrum. This region is now often referred to as the “THz frequency range”. This range provides access to studies of the rotational spectra of light molecules of relevance to astrophysics, among other applications, and of the low-frequency vibrational spectra of molecular clusters and of polyatomic molecules subject to large-amplitude motion. High-resolution spectroscopic data in this frequency range are much more limited than below 0.1 THz (microwave region of the electromagnetic spectrum) where powerful, broadly tunable and narrow-bandwidth sources have been commercially available for a long time, and above 30 THz, where coherent, narrow-bandwidth, broadly tunable, laser-based radiation sources are routinely used in laboratory investigations. A combination of several factors renders high-resolution spectroscopy in the THz range challenging: i) Available narrow-bandwidth sources in this range are usually of limited tunability; ii) the sensitive detection of the THz radiation necessitates more efforts than in neighboring frequency ranges; iii) the abundance of H_2O lines throughout the THz range makes it necessary to carry out spectroscopic experiments under conditions where the partial pressure of water is strongly reduced. In the realm of high-resolution spectroscopy, experiments on samples in cold, pulsed, supersonic beams, which permit the study of clusters and a wide range of reactive species under conditions where Doppler and pressure broadenings are negligible, are complicated by the fact that most narrow-bandwidth THz radiation sources operate in a continuous-wave mode. The sensitivity of the measurements is therefore reduced by the unfavorable duty cycle: a typical pulsed nozzle delivers $200\text{ }\mu\text{s}$ -long gas pulses at repetition rates below 100 Hz, which reduces the available radiation power by a factor of more than 50.

Despite these difficulties, considerable progress has been made in recent years in the development and use of narrow-bandwidth THz radiation in high-resolution molecular spectroscopy. Nonlinear frequency upconversion¹ of backward-wave oscillators²⁻⁵ and Gunn oscillators⁶ can be used to access the range up to about 3 THz at a resolution of better than 1 kHz. Broad tunability and narrow bandwidth (below 1 MHz) can be reached in the range below 4 THz by difference-frequency generation using photoconductive antennas^{7,8} and

by difference-frequency mixing in nonlinear crystals (i.e., GaSe, quartz, LiNbO₃, GaP, ZnTe, DAST...) ⁹. Quantum-cascade lasers are increasingly used as high-power narrow-bandwidth laser sources in the THz-frequency range but are not yet commercially available ^{10,11}. High resolution throughout the entire THz range can be achieved using synchrotron radiation in combination with Fourier-Transform (FT) spectrometers (Ref. 12 and references therein), the resolution being currently limited to $\sim 0.0007 \text{ cm}^{-1}$ (21 MHz) by the path length of the moving mirror in the Michelson interferometer ^{13,14}. FT spectroscopy in the THz range further offers the multiplex advantage ¹⁵ and represents one of the most attractive ways of performing high-resolution molecular spectroscopy in the THz range, the only drawback being that the experiments require large synchrotron facilities with limited access.

In this article, we present an extension of a pulsed, laser-based THz radiation source described in Ref. 16 and its integration into a vacuum-ultraviolet-THz (VUV-THz) double-resonance spectrometer that can be used to study transitions between 0.9 to 14.3 THz with a resolution adjustable between 2.8 and 85 MHz. The source is based on difference-frequency mixing in the nonlinear crystal DAST ^{17,18}. THz generation takes place in a DAST crystal placed in vacuum, which eliminates the problem of power reduction by water vapor absorption. The combination of our THz source with VUV radiation enables THz studies of high Rydberg states, and opens up the possibility of photoionization-detected rotational and vibrational spectroscopy. A special feature of the THz-radiation source is the ability to adjust the pulse length, and thus the spectral resolution: Short pulses ($\sim 10 \text{ ns}$) with a larger bandwidth ($\sim 85 \text{ MHz}$) can be used to record spectra over broad regions, whereas long pulses ($\sim 400 \text{ ns}$) with a narrow bandwidth ($\sim 3 \text{ MHz}$) are suited to study selected regions at high resolution. In addition to the broad tunability and narrow bandwidth of the THz radiation, the spectrometer therefore also offers the advantage of high sensitivity (background-free detection with single-ion sensitivity) and mass-selectivity because the transitions are detected by photoionization or pulsed-field ionization.

The spectrometer was developed in the realm of our studies of atomic and molecular Rydberg states. Broadly tunable radiation in the range of 0.9-14.3 THz indeed enables the investigation of transitions between Rydberg states in the range of principal quantum number n between 10 and 40. High-resolution spectroscopic data on Rydberg states in this range of principal quantum number is scarce but is ideally suited to derive information on the energy-dependence of the quantum defects and is needed as input data in our global

FIG. 1. Excitation scheme used to measure spectra of $33f \leftarrow nd$ Rydberg-Rydberg transitions of Xe. The transitions were detected by selective field ionization of the final $33f$ level. The figure illustrates the range of initial states corresponding to the frequency range from 0.9 THz ($n = 31$) to 14.3 THz ($n = 16$).

analyses of the Rydberg spectra of rare-gas atoms^{19,20} and molecular hydrogen²¹ using multichannel quantum defect theory (MQDT). At a resolution of ~ 3 MHz, the hyperfine structure of atomic and molecular Rydberg states can be resolved and the analysis of the spectra using MQDT provides information on the role of nuclear spins in atomic and molecular photoionization^{21–23}.

In this article, we demonstrate the high sensitivity and resolution as well as the mass-selectivity of our experimental approach and its power to study Rydberg-Rydberg transitions with an investigation of the Rydberg states of atomic Xe. Without modification, our spectrometer can also be used to study Rydberg transitions in molecules as well as the rotational and vibrational spectra of molecules and clusters in the THz frequency range.

II. EXPERIMENTAL

A. Excitation Sequence and Generation of THz Radiation

Rydberg states of effective principal quantum number n^* in the range of $13.8 - 28.8$ were prepared by irradiation of a supersonic beam of Xe with VUV radiation. Tuning the frequency of the VUV radiation provided access from the 1S_0 ground state to $16d - 31d$ Rydberg states belonging to series converging on the $^2P_{3/2}$ ground state of Xe^+ . The THz radiation source was used to record spectra of transitions from these Rydberg states to higher-lying Rydberg states. The excitation scheme is presented in Figure 1 and the schematic optical layout used in the experiment is depicted in Fig. 2. In the experiments described in this article, we chose $33f$ as the final state of all transitions, which enabled us to study the d Rydberg states in the intermediate range of principal quantum number between 16 and 31. The transitions were detected by selective field ionization and recording either the electrons or ions, the latter offering the advantage of mass selectivity.

The pulsed VUV radiation of wave number $\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_{\text{UV}} + \tilde{\nu}_{\text{VIS}}$ was generated by resonance-enhanced sum-frequency mixing in Xe as described in Ref. 24. The frequency-doubled output (wave number ν_{UV}) of a dye laser was used to access the $(5p)^5(^2P_{3/2})6p[1/2](J=0) \leftarrow (5p)^6(^1S_0)$ two-photon resonance of atomic Xe at $2\tilde{\nu}_{\text{UV}} = 80118.97 \text{ cm}^{-1}$. The output ($\tilde{\nu}_{\text{VIS}}$) of a second, tunable dye laser was used to generate tunable VUV radiation at wave numbers around 97700 cm^{-1} .

The basic principle of THz generation is similar to that described in Ref. 16 and relies on difference-frequency mixing using two pulsed near-infrared (NIR) lasers, one of which is kept fixed in frequency while the other is tuned, resulting in tunable THz radiation. Narrow-bandwidth NIR radiation is produced by two titanium-doped sapphire (Ti:Sa) ring lasers, the cw outputs of which are converted into pulses using two acousto-optical modulators (AOMs) and subsequently pulse-amplified in a bow-tie configuration²⁵ as shown in Fig. 2. The same bow-tie is used for amplification of the two NIR lasers so that the frequency shifts and chirps occurring in the amplification process are identical for both. The amplified NIR pulses are directed into a vacuum chamber where difference-frequency generation takes place in a *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST) crystal (details on the crystal and the cut used for optimal generation of THz radiation are given in Ref. 16).

FIG. 2. Schematic optical layout of the spectrometer used to record VUV-THz double-resonance spectra. AOM: acousto-optical modulator; FR: Fresnel rhomb; PBS: Polarization beamsplitter; OF: optical fiber; OI: optical isolator; DAST: *trans*-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate crystal; OAPM: off-axis parabolic mirror; PE: polyethylene window.

The THz spectrometer is depicted in Fig. 3 and is described in detail below.

B. VUV-THz Double-Resonance Spectrometer

The VUV-THz double-resonance spectrometer has been designed in such a way as to be able to: (i) easily adjust the frequency across the range from 0.1 – 14.3 THz, (ii) avoid reduction of THz power caused by water absorption, and (iii) easily optimize the interaction volume between the molecular beam and the THz and VUV-radiation beams. In order to avoid losses, only two gold-coated, off-axis parabolic mirrors (OAPMs) have been used as optical elements. Such mirrors have very high reflectivities across the entire above-mentioned

FIG. 3. Spectrometer used to record VUV-THz double resonance spectra of Xe in a supersonic expansion. A: Entrance window for NIR radiation, B: screw for lateral displacement of the DAST crystal, C and D: Screws for adjusting the orientation of the DAST crystal, E and F: Screws to adjust the tilt angles of the off-axis parabolic mirror (see text for details). TOF: time-of flight.

frequency range and are used to align and focus the THz radiation.

The two collinear pulse-amplified NIR beams enter the vacuum chamber via a side window (A in Fig. 3) and are incident on the DAST crystal, the position (B) and orientation (C,D) of which can be adjusted from outside the vacuum chamber. The generated THz radiation propagates toward the first OAPM, the tilt angle of which can also be adjusted (E,F). The

OAPM focuses the THz radiation near the point of intersection with the VUV and supersonic beams. The THz radiation then propagates toward a second OAPM that focuses it behind a polyethylene window inside a bolometer which is used solely for alignment purposes. This design allows for a straightforward adjustment of the frequency between 0.1 – 14.3 THz. In moving from the low-frequency to the high-frequency end of this region, only a slight modification of the tilt angles (E,F) is necessary, as well as a rotation of the polarization of the incident NIR beams by $\sim 30^\circ$.

The relative timings of the VUV, NIR and gas pulses can be adjusted using a digital delay generator. The Rydberg-Rydberg transitions were detected by selective field ionization of the $33f$ final states of the transitions by applying a pulsed electric field about $1\mu\text{s}$ after the THz-radiation pulse. When recording the ion signal in mass-selective measurements, an electric field of 530 V/cm was applied. For transitions recorded by monitoring the electron signal, an electric-field ramp was used that enabled us to distinguish electrons produced by the field ionization of Rydberg states of different n^* by their different detection times. The electric field also served the purpose of extracting the ions or electrons toward a micro-channel plate (MCP) detector.

The photo-excitation region and ion/electron time-of-flight (TOF) tube are surrounded by two concentric magnetic shields. The stray electric fields along the TOF axis can be minimized by applying weak compensation fields. The spectra are recorded by monitoring the ion or electron signal arriving in a selected time window as a function of the frequency of the THz radiation. The length of the NIR and THz pulses can be adjusted in the range of 10 ns–400 ns by adjusting the length of the pulses applied to the AOM, as will be explained in more detail in section III A.

C. Frequency Calibration

The frequency of the terahertz radiation (ν_{THz}) was determined from the frequencies of the tunable (ν_{NIR1}) and fixed-frequency (ν_{NIR2}) ring lasers by calculating their difference $\nu_{\text{THz}} = \nu_{\text{NIR1}} - \nu_{\text{NIR2}}$. The frequency ν_{NIR1} was calibrated by simultaneously recording Doppler-free saturated absorption spectra of molecular iodine for the determination of the absolute frequency, and transmission spectra through a confocal Fabry-Perot (FP) etalon (FSR = 149.963(3) MHz, finesse = 30) for the relative frequency calibration. The length

FIG. 4. Spectrum of the $33f[5/2]_2 \leftarrow 17d[3/2]_1$ transition of Xe plotted as a function of the wave number $\tilde{\nu}_{\text{NIR1}}$ of the tunable NIR laser (a) and as a function of the difference $\tilde{\nu}_{\text{NIR1}} - \tilde{\nu}_{\text{NIR2}}$ of the wave numbers of the tunable and fixed-frequency NIR lasers (b). The top and middle traces in panel (a) represent the Doppler-free absorption spectrum of I_2 and the transmission spectrum through an etalon, respectively. The asterisks designate transitions of ^{129}Xe and ^{131}Xe .

of this etalon was stabilized by locking to a polarization-stabilized HeNe laser as described in Ref. 16. The fixed-frequency NIR ring laser was locked to a transmission maximum of the FP etalon. The absolute frequency of this laser was determined in a similar manner to that of the tunable laser by scanning to the closest-lying I_2 transition while simultaneously recording an etalon transmission spectrum.

The frequency calibration procedure is illustrated in Fig. 4 with the example of the $33f[5/2]_2 \leftarrow 17d[3/2]_1$ transition of Xe. Panel a) depicts the spectrum as a function of the wave number of the tunable laser (bottom trace), the transmission spectrum through the FP etalon (middle trace) and the Doppler-free I_2 absorption spectrum (top trace). The etalon spectrum was used for wave-number linearization by cubic spline interpolation and the absolute wave number was calibrated using the a_{10} hyperfine component of the P70, $B - X$ (0-13) rovibrational transition of I_2 and comparing to reference data²⁶. In an analogous manner, the a_4 hyperfine component of the P79, $B - X$ (0-15) transition of I_2 was used for

determining the absolute frequency of the fixed-frequency laser. Panel b) of Fig. 4 shows the same spectrum after taking the difference of the wave numbers of the two NIR lasers. Because the frequency chirps and shifts²⁷ of the two NIR beams occurring in the Ti:Sapphire bow-tie amplifiers are equal (see above), they cancel out when determining the difference $\nu_{\text{NIR2}} - \nu_{\text{NIR1}}$.

Systematic and statistical errors could be evaluated and minimized by making separate measurements of the frequency of the $33f[3/2]_2 \leftarrow 21d[3/2]_1$ transition on different days, after realignment of the optical setup and separate locking of the fixed-frequency ring laser. This procedure resulted in a value of 6.284 561 9(28) THz, the standard deviation of 2.8 MHz representing the absolute frequency accuracy of the method, which is currently limited by the accuracy of the frequency calibration procedure. This uncertainty could be reduced by locking the frequency of the fixed laser using a phase-locked frequency comb or by recording spectra by scanning ν_{NIR1} on both sides of ν_{NIR2} , i.e., $\nu_{\text{NIR1}} - \nu_{\text{NIR2}}$ and $\nu_{\text{NIR2}} - \nu_{\text{NIR1}}$.

III. RESULTS

A. Pulse Length and Resolution

Figure 5 illustrates, with the example of the $33f[3/2]_{J=1,2} \leftarrow 31d[3/2]_1$ transitions of Xe, how the spectral resolution can be adjusted in the range between ~ 2.8 MHz and ~ 85 MHz by changing the duration of the NIR laser pulses. The spectra were recorded for NIR pulse lengths of 400 ns, 200 ns, 60 ns, 20 ns and 10 ns, as displayed in panels a)-e), respectively. The assignments of the transitions labeled 1 – 8 are presented in Table I. The transitions labeled 2 and 3 in Fig. 5 could only be resolved in the spectra recorded with the longest pulses (400 ns).

The signal-to-noise ratio (SNR) of the spectra depicted in Fig. 5 first increases with increasing pulse length and then decreases. This observation can be understood by considering the effect of the NIR pulse length on the power and the bandwidth of the THz radiation. For the process of difference-frequency generation, the i -th component of the second-order nonlinear polarizability tensor $\mathbf{P}^{(2)}$ is given by²⁸:

$$P_i^{(2)}(\omega_{\text{NIR1}} - \omega_{\text{NIR2}}) = 2\epsilon_0 d_{ijk}^{(2)}(\omega_{\text{NIR1}} - \omega_{\text{NIR2}}) E_j(\omega_{\text{NIR1}}) E_k^*(\omega_{\text{NIR2}}), \quad (1)$$

where ω_{NIR1} and ω_{NIR2} correspond to the frequency output of the tunable and fixed ring

FIG. 5. Spectra of the $33f \leftarrow 31d$ transition of Xe recorded using pulse lengths of a) 400 ns, b) 200 ns, c) 60 ns, d) 20 ns, e) 10 ns. The assignments of the lines labeled 1-8 are given in Table I. The spectra have been shifted along the vertical axis for clarity.

TABLE I. Assignments and relative positions (in cm^{-1}) of the fine and hyperfine-structure components of the $33f \leftarrow 31d$ transitions observed in Fig. 5.

peak	wave number cm^{-1}	isotope	assignment
1 ^a	-0.020516(54)	^{129}Xe	$33f[3/2]_2(3/2) \leftarrow 31d[3/2]_1(1/2)$
2 ^a	-0.018002(51)	^{129}Xe	$33f[3/2]_1(3/2) \leftarrow 31d[3/2]_1(3/2)$
3 ^a	-0.017776(57)	^{132}Xe	$33f[3/2]_1 \leftarrow 31d[3/2]_1$
4 ^a	-0.015175(51)	^{131}Xe	$33f[3/2]_2(7/2) \leftarrow 31d[3/2]_1(5/2)$
5 ^a	-0.011319(51)	^{129}Xe	$33f[3/2]_2(5/2) \leftarrow 31d[3/2]_1(3/2)$
6 ^a	-0.008801(51)	^{131}Xe	$33f[3/2]_2(5/2) \leftarrow 31d[3/2]_1(3/2)$
7	31.31303(22)	^{132}Xe	$33f[3/2]_2 \leftarrow 31d[3/2]_1$
8 ^a	0.00258(12)	^{131}Xe	$33f[3/2]_2(3/2) \leftarrow 31d[3/2]_1(1/2)$

^a The spectral positions are given relative to the $33f[3/2]_2 \leftarrow 31d[3/2]_1$ transition of ^{132}Xe . Note that the uncertainties of the relative positions (transitions 1 – 6, 8) are smaller than the uncertainty of the absolute position (transition 7).

lasers, respectively, $d_{ijk}^{(2)}$ is the relevant second-order nonlinear optical coefficient, and $E_{j,k}$ are components of the electric field vector. Because the THz-generation process is nonlinear (see Eq. (1)), the power of the THz radiation P_{THz} is proportional to the product of the incident NIR powers ($P_{\text{THz}} \propto P_{\text{NIR1}}P_{\text{NIR2}}$), and the maximal incident power is determined by the damage threshold of the DAST crystal ($\sim 6 \text{ W/cm}^2$, or a peak power of 4 MW/cm^2 for a pulse of 60 ns duration), shorter NIR pulse lengths with correspondingly higher peak powers lead to quadratically higher THz peak powers. One therefore expects the SNR to be best for the shortest pulses and to decrease with increasing pulse length. However, because the bandwidth of the THz radiation is larger than the Doppler width $\Delta\nu_{\text{D}}$ of the transitions ($\Delta\nu_{\text{D}} \approx 5 \cdot 10^{-8} \nu$ in the present case), the photon density at the transition frequency and the SNR of the spectra are reduced for the shortest pulses, even though the overall photon number is higher. Moreover, the efficiency of the pulse generation in the AOM decreases for pulses shorter than 40 ns. The best SNR is obtained for pulse lengths of about 60 ns.

FIG. 6. Effect of the NIR pulse length on the spectral resolution with the example of the $33f[3/2]_1 \leftarrow 31d[3/2]_1$ transition of the $I = 0$ isotopes of Xe. a) and b) display two measured NIR pulse shapes and c) and d) the corresponding spectral lineshapes.

In Fig. 6, the pulses with the longest (~ 400 ns, panel a)) and shortest (~ 10 ns, panel b)) lengths are shown next to the corresponding spectra of the $33f[3/2]_2 \leftarrow 31d[3/2]_1$ transition of ^{132}Xe , which exhibit full widths at half-maximum (FWHMs) of 3.1 MHz and 75 MHz, respectively. Table II summarizes an analysis of the FWHM in dependence on the pulse length. The experimental results (second column) agree closely with the FWHMs determined by convolution of two Gaussian NIR pulses that are perfectly overlapped in time and subsequently Fourier-transformed (third column). For intermediate pulse lengths, the experimental and calculated FWHMs agree to within the error margins. We attribute the larger observed widths for the measurements with the longest and shortest pulses to the deviations from a pure Gaussian pulse shape under these conditions.

TABLE II. Comparison of the NIR laser pulses with the measured (exp) full widths at half-maximum (FWHM) of the Rydberg-Rydberg transitions. The calculated (calc) widths were determined by convolution and Fourier-transformation assuming a Gaussian temporal profile of the NIR pulses.

pulse length	FWHM exp	FWHM calc
ns	MHz	MHz
400	2.78(0.62)	1.56
200	5.06(0.54)	3.12
60	9.9(1.3)	10.4
20	29.7(4.2)	31.2
10	85(12)	62.4

B. Tunability

Figure 7 depicts spectra of transitions between $nd[3/2]_1$ and $33f[K]_J$ Rydberg states in ^{132}Xe , ^{131}Xe and ^{129}Xe for selected values of the initial-state principal quantum number between $n = 16$ and 31 . The figure illustrates that the frequency of our THz radiation source can be adjusted between 0.9 and 14.3 THz. Spectra were also recorded at ~ 1.2 THz and ~ 1.5 THz but are not shown here (see supplementary material²⁹ for a list of all measured transition frequencies). The strongest line in these spectra corresponds to the transitions of the $I = 0$ isotopes (^{128}Xe , ^{130}Xe , ^{132}Xe , ^{134}Xe , ^{136}Xe) which are not resolved. The weaker lines correspond to transitions between the hyperfine components of the nd and $33f$ levels of the isotopes ^{129}Xe ($I = 1/2$) and ^{131}Xe ($I = 3/2$).

The hyperfine structure of the spectra changes only slightly with n because all transitions have the same final states and the hyperfine intervals in the initial state result primarily from the hyperfine structure of the ions²⁰. Consequently, the assignment of the lines labeled 1-8 in Figure 7 is the same as presented for the $33f \leftarrow 31d$ transitions in Table I, and the lines 9 and 10 correspond to the $33f[3/2]_2(5/2) \leftarrow 21d[3/2]_1(5/2)$ transition of ^{131}Xe and the $33f[3/2]_1(3/2) \leftarrow 21d[3/2]_1(1/2)$ transition of ^{129}Xe , respectively. The SNR of the spectra displayed in Fig. 7 decreases rapidly beyond 350 cm^{-1} (~ 11 THz) primarily because

FIG. 7. Fine and hyperfine structure of the $33f \leftarrow nd$ transitions of Xe for $n = 31$ (a), 21 (b), 18 (c), 17 (d) and 16 (e). The assignments of the lines labeled 1 to 8 are given in Table I. Lines 9 and 10 correspond to the $33f[3/2]_2(5/2) \leftarrow 21d[3/2]_1(5/2)$ transitions of ^{131}Xe and $33f[3/2]_1(3/2) \leftarrow 21d[3/2]_1(1/2)$ of ^{129}Xe , respectively.

the intensity of the VUV radiation used to prepare initial states with n below 20 rapidly decreased. The intensities of Rydberg-Rydberg transitions decrease with increasing Δn value³⁰. This decrease is almost entirely compensated by the fact that the power of the THz radiation increases with increasing frequency¹⁶. The spectra were recorded for several pulse lengths between 10 ns and 400 ns, the latter pulse length resulting in an optimal resolution of ~ 3 MHz over the entire THz frequency range. Indeed, the Doppler width in our supersonic Xe beam is smaller than the laser bandwidth even at the highest frequencies (14.3 THz). For the spectra presented in Fig. 7, a pulse length between 40 – 60 ns was chosen because it led to an optimal SNR (see section III A).

C. Mass-Selectivity

Panel a) of Figure 8 shows that the main naturally occurring isotopes of Xe can be resolved by time-of-flight (TOF) mass spectrometry followed by pulsed field ionization of the Rydberg states and demonstrates the possibility of simultaneously recording mass-selective spectra of these isotopes, as presented in panels b)-d) of Fig. 8. Spectra of ^{128}Xe , ^{130}Xe , ^{134}Xe and ^{136}Xe (all of them isotopes with $I = 0$) are not depicted here because the transition frequencies are the same as for ^{132}Xe within our experimental resolution. Spectra of ^{129}Xe ($I = 1/2$) and ^{131}Xe ($I = 3/2$) have more transitions because of the hyperfine structure. The ability to obtain separate spectra of the different isotopes greatly facilitates the spectral assignments.

D. Comparison to Calculated Transition Frequencies

The results of the measurements of the $33f[3/2]_2 \leftarrow nd[3/2]_1$ and $33f[5/2]_2 \leftarrow nd[3/2]_1$ transitions of ^{132}Xe are presented in Table III, where they are compared with the results of MQDT calculations based on the MQDT parameter set reported in Ref. 20. A complete list of all observed transitions, including those of ^{129}Xe and ^{131}Xe , is provided in the supplementary material²⁹. Whereas the deviations between measured and calculated frequencies are of the same order of magnitude as the experimental uncertainty of our new measurement at n values between 29 and 33, they become significantly larger at lower n values. The good agreement at high n values is expected because the MQDT parameters used for the compar-

FIG. 8. a) Time-of-flight (TOF) spectrum of Xe^+ ions formed following photoionization above the $^1\text{S}_0 \rightarrow ^2\text{P}_{3/2}$ ionization threshold. b) Spectra of the $33f \leftarrow 31d$ transitions of ^{132}Xe (b), ^{131}Xe (c), and ^{129}Xe (d) recorded following selective field ionization of the $33f$ level and measuring the ion signal at the relevant TOF position.

ison were derived from very-high-resolution millimeter-wave spectroscopic measurements at n values beyond 40. The increasing disagreement at lower n values (and therefore at lower energies) suggests that the energy dependence of the MQDT eigenquantum defects might be improved using the present data set. A global analysis of the present data and data obtained in the range $n = 80 - 100$ which contains information on s/d interactions will be published separately³¹.

IV. CONCLUSIONS

The THz radiation source and VUV-THz double-resonance spectrometer presented in this article are well-suited for high-resolution atomic and molecular spectroscopy. Its narrow bandwidth (~ 3 MHz) and broad tunability ($0.1 - 14.3$ THz) make this radiation source ideal for investigations of rotational transitions in light molecules, low-frequency vibrational transitions in large molecules and clusters, and Rydberg-Rydberg transitions in a range of

TABLE III. Observed and calculated frequencies of the $33f[3/2]_2 \leftarrow nd[3/2]_1$ and $33f[5/2]_2 \leftarrow nd[3/2]_1$ transitions for $n=16,17,18,21,29,30$ and 31. The calculated frequencies were obtained using the set of MQDT parameters reported in Ref. 20.

n	$33f[3/2]_2 \leftarrow nd[3/2]_1$		$33f[5/2]_2 \leftarrow nd[3/2]_1$	
	$\nu_{\text{exp}} / \text{THz}$	$(\nu_{\text{exp}} - \nu_{\text{calc}}) / \text{MHz}$	$\nu_{\text{exp}} / \text{THz}$	$(\nu_{\text{exp}} - \nu_{\text{calc}}) / \text{MHz}$
31	0.938 741 2(67) ^a	21.7	0.943 292 7(97) ^a	-3.0
30	1.229 493(26) ^b	-11.2	1.234 074(20) ^a	-6.1
29	1.553 439(11)	4.2	1.557 995(14) ^a	-15.7
21	6.284 561 9(28)	49.8	-	-
18	10.154 203 9(72) ^b	99.9	10.158 762 0(73) ^b	81.8
17	11.993 391 3(45)	133.9	11.997 950 4(49)	116.9
16	14.245 138 7(49) ^b	182.1	-	-

^a Values obtained from several measurements of the transition frequency, however, without separate locking of the fixed-frequency laser.

^b Only one measurement of transition frequency was performed.

principal quantum numbers where high-resolution spectroscopic data are still rare. Moreover, the 25 Hz repetition rate of the pulsed supersonic beam in combination with detection of terahertz transitions by photoionization opens up the possibility of mass-selective spectroscopy.

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