Application of superlattice multipliers for high-resolution terahertz spectroscopy

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Frequency multipliers based on superlattice (SL) devices as nonlinear elements have been developed as radiation sources for a terahertz (THz) laboratory spectrometer. Input frequencies of 100 and 250 GHz from backward wave oscillators have been multiplied up to the 11th harmonic, producing usable frequencies up to 2.7 THz. Even at these high frequencies the output power is sufficient for laboratory spectroscopy. Comparisons to conventional high-resolution microwave spectroscopy methods reveal several superior features of this new device such as very high line frequency accuracies, broadband tunability, high output power levels at odd harmonics of the input frequency up to high orders, and a robust applicability. © 2007 American Institute of Physics. [DOI: 10.1063/1.2722401]

I. INTRODUCTION

The terahertz (THz) domain of the electromagnetic spectrum with frequencies between 0.5 and 5 THz is of great interest to astronomers and spectroscopists. Light hydrids possess their strongest absorption lines and larger molecules exhibit low-lying bending vibrations in this frequency regime. Today, several efficient technical approaches are well established for high-resolution spectroscopy in the THz region. Backward wave oscillators (i) are tunable and powerful monochromatic radiation sources, which have been phase locked for frequencies up to 1.26 THz.1 With sideband techniques even higher frequencies are attainable2,3 (ii), which are not easy to handle and laborious in most cases. Alternatively, tunable far-infrared (FIR) laser systems4,5 (iii) achieve excellent spectra. However, the paucity of laser lines prevents the complete coverage of larger spectral ranges. Besides the development of these high-resolution sources, Fourier transform spectrometers (iv) also are used to cover the complete THz spectral range, albeit with low resolution and limited sensitivity. Furthermore, the absolute accuracy of FIR lasers and Fourier transform spectrometers strongly depends on the accuracy and the availability of calibration lines.

The most compact THz radiation sources are THz-frequency multipliers, based on harmonics generation due to the nonlinearity of the current-voltage or capacitance-voltage characteristic of a fast electronic device. One well-known frequency multiplier is the Schottky barrier diode (v), which is successfully used in spectroscopy and astronomy by many groups. For references of our laboratory see, e.g., Refs. 6 and 7. In most cases the input frequency is supplied by a powerful cw Gunn oscillator or a solid-state field-effect transistor (FET) amplifier. Most often these devices are operated as frequency doublers and triplers. Higher order harmonics are available too, however, only with considerably lower power. As a consequence Schottky diodes require relatively high input frequencies with considerable input powers in the range of milliwatts to reach the THz range. Therefore, it is necessary to cascade several multipliers. Good examples of such devices are multiplier chains especially designed for the 1.5 THz regime8 and 1.9 THz regime9. However, their employment for spectroscopy is limited since they are optimized for a certain restricted frequency window.

With the advent of molecular beam epitaxy, the development of a new type of multiplier, the superlattice (SL) multiplier, became possible.10 A SL multiplier consists of a periodic arrangement of thin epitaxial layers. Due to the periodicity of the structure the electron energy is restricted to minibands with a specific miniband gap. The transport of miniband electrons leads to a negative differential resistance. Above a threshold value the current-voltage characteristic of SL devices is highly nonlinear and antisymmetric, making it suitable for high-frequency multiplication. This behavior was first proposed by Esaki and Tsu theoretically,11 and later on demonstrated by several groups.12,13 Enhanced characteristics due to intense theoretical and experimental studies14–18 make the SL an attractive alternative to Schottky diodes.

Here, first examples of high-resolution spectra in various spectrometer configurations are presented which use SLs as frequency multipliers. It is the purpose of this study to demonstrate that SLs serve as reasonably intense, widely tunable,
high-resolution THz sources which can be operated at moderate input frequencies and with high-frequency multiplication factors.

II. EXPERIMENTAL SETUP

The SL devices used in the current multiplier setups are made up of 18 monolayers GaAs and 4 monolayers AlAs with a total number of 18 periods (length 112 nm).\(^{19}\) For testing purposes the current-voltage characteristics of the device have been measured using a commercial curve tracer. The result of this $I/V$ curve is shown in Fig. 1. For small electric fields, corresponding to small voltages applied to the SL, the current, corresponding to the drift velocity of the electrons along the SL axis, shows a resistive behavior. Above a certain critical field strength, i.e., a critical voltage $U_{c}$, the SL device exhibits a negative differential conductance. This strong nonlinearity gives rise to the formation of higher order harmonics when instead of a dc field a high-frequency field of appropriate strength, i.e., exceeding the critical value, is applied. The $I/V$ curve is antisymmetric and therefore only odd-numbered harmonics shall be generated in such a device, if no bias is applied. The curve shown in Fig. 1 is in good agreement with the results of previous studies\(^{20}\) and with theoretical predictions.\(^{11,21}\) The hysteresis and jumps which occur above the critical voltage are assumed to originate from domain formation processes.

The design and understanding of SL devices is an active field of research.\(^{13,19–27}\) According to recent work by Scheurer et al., frequency multiplication by propagating dipole domains is feasible in a frequency range $\omega \tau < 1$, where $\tau (=10^{-13} \text{ s})$ is the intraminiband relaxation time, that is, at least up to frequencies of about $\omega \sim 1 \text{ THz}$.\(^{28}\) The application of SLs as frequency multipliers in high-resolution THz spectroscopy is therefore a very promising approach whose realization for the use as a source for molecular spectroscopy is the purpose of the present work. Another interesting aspect of the SL device is that it is considerably more robust to electrostatic discharge than a Schottky diode, since the induced current is limited above the critical voltage $U_{c}$, as can be seen from Fig. 1.
harmonics up to the 11th and in some favorable cases up to the 13th. The measurements show that harmonics up to the 11th order can be used for spectroscopic purposes. As sample gases CO, methanol, dimethyl ether, deuterated ammonia, and deuterated water were introduced. These molecules exhibit rich spectra of strong rotational lines in the THz frequency region. Due to intensive previous spectroscopic investigations of these species, our predictions were sufficiently good for line assignment. In some cases bandpass filters have been used to enhance spectral purity. The measurements shown in the following subsections shall demonstrate that (A) the SL-operated sources are indeed producing higher order odd harmonics in sufficient supply for laboratory spectroscopy; (B) very high line accuracies can be achieved; (C) broadband scans are feasible; and (D) overall very high frequencies up to 2.7 THz can be used for spectroscopy.

A. Output intensities at higher harmonics

To roughly estimate the fraction of power in each harmonic, measurements on the rotational spectra of CO in the vibrational ground state have been performed. As a diatomic molecule CO has rotational transitions which are spaced by 2B ≈ 115 GHz. These transitions are very suitable, since 115 GHz is in the operational range of the BWO, and for every harmonic generated by the SL a rotational transition of CO can be found. Consequently, the fundamental frequency has to be tuned only by a few megahertz in order to measure several CO transitions using higher harmonics generated by SL I. The frequency and the line strength of CO transitions are very precisely known.30 Line intensities have been determined as rectified voltage levels of a lock-in amplifier. To obtain a value for the SL output power at various harmonics, the line strength variations due to the Boltzmann distribution of the rotational levels as well as detector sensitivity have been accounted for. The intensity ratios of transitions recorded with different harmonics generated with the SL have been used to calculate the attenuation between the harmonics,

\[ a = 10 \log(U/U_0), \]

where \( U \) is the corrected voltage measured at the lock-in amplifier and \( U_0 \) is the corrected voltage measured for the third harmonic.

We have measured the rotational transitions \( J=3\rightarrow 2, J=5\rightarrow 4, J=7\rightarrow 6, J=9\rightarrow 8, \) and \( J=11\rightarrow 10 \) of CO in the vibrational ground state at room temperature using the third, fifth, seventh, ninth, and 11th harmonic, respectively. All spectra have been recorded with 17 kHz modulation frequency, 320 ms integration time, and with 20 kHz steps at the fundamental frequency. The modulation depth of the fundamental BWO carrier signal was 150 kHz. Each spectrum was recorded in a single scan, except the ones recorded with the ninth and the 11th harmonic. In the latter cases two and ten scans were added, respectively. The measured transitions are summarized in Table I together with their intensities, and the attenuation \( a \). Figure 3 illustrates the decrease of output power with increasing order of harmonics generation. The slope is in the order of 11.5 dB between two consecutive odd harmonics and 0.053±0.004 dB/GHz. This is even better compared to Schottky diodes, which reach typical values of 0.08 dB/GHz.31

Small deviations from the antisymmetry of the \( I/V \) curve also cause even harmonics to be generated. The second harmonic is suppressed by a factor of roughly 200 (see Fig. 4). We recorded the transition \( J=2\rightarrow 1 \) using the second harmonic generated by SL I. The measured intensity is at the order of the fifth harmonic. The fourth harmonic was below the detection limit. The total output power of the SL was \( P_{\text{tot}}=200\pm 50 \mu W \). This measurement was performed by using a calorimeter, which was directly connected to the output waveguide of the SL. The determination of the total output power allows calculation of the power of each harmonic using the attenuation \( a \) from Table I.

\[ P = P_0 \times 10^{-a/10}, \]

and \( P_0=P_{\text{tot}} \) assuming that the total power is strongly dominated by the power in the third harmonic. The calculated values are shown in Table I. At the 11th harmonic (≈1.27 THz) 2 nW is still available, which is sufficient for spectroscopic measurements of medium and strong transitions.

![Relative intensities of rotational transitions in CO in dependence of the harmonic associated with this measurement](image_url)

FIG. 3. Relative intensities of rotational transitions in CO in dependence of the harmonic associated with this measurement. All measurements were performed with the low-frequency BWO. For comparison, measurements performed by Maiwald et al.31 with a Schottky multiplier are also shown.
precise sub-Doppler measurements, are given in Table II for the verification of the frequency accuracy of the SL spectrometer. These reference data, based on a fit of Doppler and precise sub-Doppler measurements, are given in Table II together with the CO transition frequencies measured in this work for comparison. Transition frequencies measured up to the seventh harmonic (806 GHz) of the SL match better than 3 kHz. The uncertainties in these measurements are dominated by the signal-to-noise ratio and baseline effects, which become disadvantageous at higher frequencies.

B. Accuracy in frequency

Since rotational transition frequencies of CO are known within 500 Hz accuracy for frequencies below 800 GHz and 5 kHz for higher frequencies, CO is a very suitable probe for the verification of the frequency accuracy of the SL spectrometer. These reference data, based on a fit of Doppler and precise sub-Doppler measurements, are given in Table II together with the CO transition frequencies measured in this work for comparison. Transition frequencies measured up to the seventh harmonic (806 GHz) of the SL match better than 3 kHz. The uncertainties in these measurements are dominated by the signal-to-noise ratio and baseline effects, which become disadvantageous at higher frequencies.

C. Broadband scan of methanol

In order to study the broadband tunability of the SL device, a large number of methanol and dimethyl ether spectra were recorded in the frequency range from 170 to 1200 GHz by using harmonics from the third to 13th generated by SL I. In particular, scans over a broad frequency range of several gigahertz were of interest. These scans are feasible with the low-frequency BWO setup, because this spectrometer setup is fully controllable via a PC. Dichroic plates were used as bandpass filters. As an example, a 1.4 GHz broad scan with line precisions of several kilohertz is shown in Fig. 5. The scan was recorded with the seventh harmonic of SL I using 17 kHz as modulation frequency, 100 kHz modulation depth of the fundamental BWO carrier signal, 20 kHz frequency steps at the fundamental frequency, an integration time of 200 ms per data point, and a total integration time of 33 min. The pressure in the absorption cell was kept between 1 and 100 μbar for all measurements. The estimated frequency accuracy is 10 kHz for strong and 200 kHz for weaker transitions. These measurements verified that the SL multiplier covers the THz range. The coverage is only limited by the tuning width (78–118 GHz) of the fundamental frequency and the usable harmonic order.

Additional measurements of methanol spectra have been performed at 1 THz using the 11th harmonic of SL I in order to prove the frequency accuracy of the SL spectrometer. The transition frequencies were compared to measurements by Belov et al. using the fundamental frequency of a high-frequency BWO. Both measurements agree within error bars, which demonstrates that SL multiplication does not deteriorate the frequency accuracy (see Table III) and shows the high internal consistency of the two different methods.

D. Spectra above 1.5 THz

To test the high-frequency performance of SL devices, a large number of transitions of D₂O, HDO, NH₂D, and ND₃H in the range from 0.7–2.7 THz using multiplication factors up to the 11th have been performed. For spectroscopic details on ND₃H see Endres et al. For high-frequency measurements a BWO (180–260 GHz) has been used in combination with the CO transition frequencies measured by Winnewisser et al. for comparison.

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**TABLE II.** Center frequencies of the CO measurements recorded with the low-frequency BWO in combination with the SL I multiplier and the precise frequencies measured by Winnewisser et al. (Ref. 30) for comparison.

<table>
<thead>
<tr>
<th>n</th>
<th>J</th>
<th>Frequency [MHz]</th>
<th>Residual [kHz]</th>
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<tbody>
<tr>
<td></td>
<td></td>
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<td>Winnewisser et al. (Ref. 30)</td>
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<td>3</td>
<td>3</td>
<td>345795.987(10)</td>
<td>345795.989(5)</td>
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<td>5</td>
<td>576267.929(20)</td>
<td>576267.930(5)</td>
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<td>7</td>
<td>806651.805(20)</td>
<td>806651.806(5)</td>
</tr>
<tr>
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<td>9</td>
<td>1036912.393(50)</td>
<td>1036912.393(5)</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>1267014.486(50)</td>
<td>1267014.486(5)</td>
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**TABLE III.** Center frequencies of methanol at 1 THz measured with the SL I. For comparison, earlier measurements performed by Belov (Ref. 1) with the Cologne THz spectrometer are also given.

<table>
<thead>
<tr>
<th>Frequency [MHz]</th>
<th>Residual [kHz]</th>
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<tr>
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<td>1003529.866(20)</td>
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<td>1062312.246(50)</td>
<td>1062312.217(50)</td>
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</table>
nation with the SL II. Pressures in the absorption cell were typically in the range of 0.5–15 μbar, but in cases of weak lines pressures up to 150 μbar were used. To record frequencies above 2.3 THz the Ge:Ga detector was used. Mostly, uncertainties of 20–200 kHz for the transition frequencies were estimated. These estimations have been checked by the Russian Foundation of Basic Research (Grant No. 06-02-16598a). Detailed analysis of the data on D2O,33 ND2H32 has been published recently and will be made available via the Cologne Database for Molecular Spectroscopy.34–36 Spectra up to frequencies of 2.731 THz have been recorded (see Fig. 6), which demonstrate the suitability of the SL device for THz spectroscopy. To our knowledge, this is the highest frequency ever reached with frequency multipliers.

IV. DISCUSSION

In this work the new superlattice multiplier has been introduced to high-resolution microwave spectroscopy. It has been shown that superlattice multipliers are competitive sources for the terahertz range. The present results show advantages in the efficiency of harmonic generation when compared to the performance of Schottky diodes. This makes them very attractive to spectroscopy since only moderate input frequencies are necessary for the production of THz radiation. In the present study 2.7 THz has been generated at an input frequency of 250 GHz. In comparison, two triplers had to be used at an input frequency of 300 GHz to achieve comparable results. Very broad spectral ranges can be tuned by the SL as shown here for the first time. Setting up a chain of SLs will enable one to obtain almost 100% tuning range with only two elements operating as triplers and alternatively as a tripler and a quintupler. Moreover, the SL devices are less vulnerable to electrostatic discharge than Schottky diodes, which makes them even more attractive when only a single element has to be used as described above. In the near future a full solid-state THz spectrometer will be assembled where SL multiplication of 50 GHz radiation from a commercial synthesizer will be used to replace the BWO source used in the present investigation.

Technological progress and improved theoretical understanding in the new field of SL devices was immense during the last decade. Future aspects of further SL development concern the use of higher input frequencies like 350 GHz or even 600 GHz instead of 250 GHz in order to reach even higher output frequencies and higher output power. Much better performance of the SL is expected for cooled devices since ohmic losses will be reduced considerably. In the present setups only fixed waveguide configurations have been used. Enhanced performance will be attainable when online tuning elements are added to the waveguides.

The development of THz radiation sources is a very dynamic field of research, in which new devices such as the SLs outdate the widely used Schottky diode spectrometers. Considering the wide tuning range combined with the rather high frequencies reached, SL multipliers are presently the most interesting devices for THz spectroscopy. Further improvements will show whether these devices will also be used as active THz sources in spectroscopy and astronomy, or even as detectors.

ACKNOWLEDGMENTS

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The Cologne Database for Molecular Spectroscopy can be accessed free of charge at http://www.cdms.de/