Molecular-beam spectroscopy with an infinite interferometer: spectroscopic resolution and accuracy

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Abstract
An interferometer with effectively infinite maximum optical path difference removes the dominant resolution limit for interferometric spectroscopy. We present mass-correlated rotational Raman spectra that represent the world’s highest resolution scanned interferometric data and discuss the current and expected future limitations in achievable spectroscopic performance.

Keywords Rotational coherence spectroscopy · Fourier-transform spectroscopy

1 Introduction

The resolution of scanned interferometric spectroscopy is usually limited by the maximum optical path difference (MOPD) of the interferometer. As part of our development of mass-correlated rotational alignment spectroscopy (CRASY) [1], we constructed an interferometer with an effectively infinite MOPD [2], utilizing the discrete pulse train emitted from a femtosecond laser oscillator. Here we present the highest resolution data measured to-date and discuss the resolution-limiting factors in our molecular beam experiments. Discussed concepts are equally applicable to other types of interferometric or time-domain spectroscopy that rely on the scanning of a spatial path difference or a temporal delay range.

CRASY is a type of rotational coherence spectroscopy (RCS) [3] and measures rotational Raman spectra in the time-domain by scanning the path difference between two interferometer arms. The resulting data is useful for the structural characterization of non-dipolar molecules [1, 4–6] that are inaccessible to Fourier-transform microwave spectroscopy (FTMW) [7]. By extending the scanned interferometer length, our work obtained order-of-magnitude improved resolution [2, 8] as compared to preceding gas-phase Raman [9], RCS [3], and Fourier-transform infrared spectroscopy (FTIR) experiments [10].

The energy resolution (ΔE) of spectroscopic experiments is fundamentally limited by the observation time Δt, e.g., the time over which photons interact with the investigated molecules. The time-frequency formulation of Heisenberg’s uncertainty principle states this fundamental resolution limit as ΔE ⋅ Δt = h/2. Independent of the experiment, the effective observation time is always limited by the coherence time (or lifetime) of the observed quantum states. This leads to lifetime-broadening of observed spectral lines, either due to an intrinsically limited lifetime of the observed states or due to interactions with an environment, e.g., through molecular collisions. When lifetime broadening is small, the effective resolution will be limited by the constraints of the spectroscopic experiment.

In frequency domain spectroscopy, the coherence length of the interacting photons limits the effective observation time. The situation is fundamentally different in interferometric Fourier-transform spectroscopy, where the observation time is limited by the MOPD of the interferometer. The non-apodized full-width at half maximum (FWHM) resolution limit in FTIR is given as ΔE_{FWHM} = 0.61 ⋅ d_{MOPD}⁻¹ [10]. The highest-resolution interferometer described in the literature features a MOPD of 11.7 m [11], which corresponds to a delay range of t_{max} = 39 ns and a non-apodized resolution limit of 15.6 MHz FWHM.

RCS is based on the impulsive excitation and probing of rotational coherence with ultrfast (femtosecond or picosecond) laser pulses. In our CRASY variant of RCS, the rotationally excited molecules are probed by resonant
multi-photon photoionization and rotational coherence is observed as interferometric signal modulation in resulting ion signals. CRASY therefore correlates rotational spectra with ion masses and thereby facilitates the assignment of signals in heterogeneous samples. As in FTIR, or other scanned interferometric spectroscopies, RCS experiments scan the optical path difference in an interferometer and show a resolution limited by the MOPD.

2 Infinite interferometer design for CRASY

To obtain mass-CRASY data, ion signals were detected in a time-of-flight mass spectrometer as function of the scanned delay between alignment and ionization laser pulses. The experimental details for CRASY measurements were described previously [2, 4, 8, 12, 13] and here we focus on the interferometer design used to scan extended optical path differences. Focussed alignment pulses with 800 nm wavelength, ≤ 2 ps pulse duration and 100 μJ-level pulse power created a coherent rotational wavepacket by impulsive Raman excitation. Alignment, in this context, denotes the transient molecular alignment that is commonly observed upon excitation of a coherent wavepacket [14]. Ionization pulses with 200 nm or 266 nm wavelength, 45 fs pulse duration and few-μJ pulse power photoionized molecules by two-photon resonant photoionization. Ion signals showed temporal signal modulations due to the interference of the coherent rotational states in the probe step, as depicted in Fig. 1A, B. Fourier-transformation of these signal modulations reveal the spectrum of the coherent wavepacket, as shown in Fig. 1C.

An interferometer for high-resolution spectroscopy should have the longest possible MOPD, combined with a small step size and high positioning accuracy. As described above, the achievable spectroscopic resolution is directly proportional to the MOPD and, as described by the Shannon–Nyquist theorem [15], the spectroscopic range \(v_{\text{max}}\) is inversely proportional to the sampling step size (\(v_{\text{max}} = 1/(2 \cdot \text{t}_{\text{step size}})\)). CRASY is performed on cold molecular beams with beam temperatures below 10 K and a 0.5–5 ps steps size (maximum spectroscopic range of \(v_{\text{max}} = 0.1–1\) THz) is sufficient to resolve the complete thermally occupied set of rotational states. The positioning accuracy should remain well-below the scanned step size to avoid a degradation of the spectroscopic signals.

Interferometers used for FTIR, RCS, and other types of scanned interferometer spectroscopy are based on opto-mechanical delay stages, i.e., moving mirrors in one interferometer arm to change the optical path length. The largest interferometers can be found at national synchrotron facilities but are not practical within the restricted space and budget of University-based laboratory research. Instead, our interferometer combined electronic and opto-mechanical delays to achieve an infinite effective optical path length within a compact interferometer design.

A schematic representation the infinite interferometer is shown in Fig. 2. The mechanical delay was based on a Physik Instrumente MD-531 motorized stage with 30 cm stage length. The optical beam path across the stage was 16-times folded to obtain a MOPD of 4.8 m (16 ns). Longer delays were achieved by electronic pulse selection of oscillator pulses that were amplified in two separate regenerative Ti:Sa amplifiers, forming the two arms of the interferometer. The repetition rate of the laser oscillator (Coherent Vitara) was 80 MHz and selection of subsequent pulses added discrete 12.5 ns delays in the second interferometer arm. Note that the timing accuracy of the electronic delays is governed by the stability of the oscillator repetition rate and not the accuracy of the electronic delay generator.

The pulse selection delay was controlled via an electronic delay generator (SRS-DG535) and allowed to extend the
delay range to quasi-arbitrary values. The amplifiers were operating at 1-kHz repetition rate and probe pulses delayed by more than 1 ms therefore arrive after a subsequent pump pulse. The molecular beam velocity in our experiments was close to 1100 m/s and molecules travel meter distances within milliseconds. Experiments with > 1 ms delays can therefore rely on spatial discrimination of the excited molecules. Therefore, for all practical purposes, our set-up represents an interferometer with infinite MOPD and the achievable spectroscopic resolution is no longer limited by the size of the interferometer, but by other experimental limitations, such as the ability to track the molecular beam.

3 High-resolution CRASY data

Figure 3 shows rotational Raman spectra for CS₂ and illustrates the progress achieved by combining electronic and opto-mechanical delays. The maximal opto-mechanical delay range of 16 ns was sufficient to obtain an effective resolution of 60 MHz FWHM, as shown in Fig. 3 (Top). The effective resolution remained below the non-apodized resolution limit of 38 MHz because the mechanical delay stage was not perfectly flat, leading to a loss of signal when the stage approached either end of the delay range. A combined opto-mechanical and electronic delay range of 15 m (50 ns) gave a greatly enhanced effective resolution of 17.5 MHz FWHM, near the resolution limit of 12.2 MHz, as shown in Fig. 3 (Bottom). The sample used for the latter measurement contained only trace amounts of CS₂ and the spectrum therefore had a lower signal-to-noise ratio (SNR).

The measurement time required to scan large delays scales linearly with the scan range and the collection of mass spectra for a large number of alignment-ionization delays was time-consuming and created exceedingly large data-sets. The data shown in Fig. 3 (Bottom) was obtained with 50 ns MOPD and a 2 ps step-size and therefore required the accumulation of 25,000 mass spectra. Data was acquired with 500 Hz repetition rate and ion signals for 1000 laser shots were accumulated for each mass spectrum, leading to a 2 s acquisition time for each mass spectrum. The resulting scan time was almost 14 h. Each time-of-flight mass spectrum contained 400,000 points and the acquired raw data quantity corresponds to 10 Gb. It is readily apparent that the brute-force extension of the scanned delay range will lead to impractical requirements in terms of measurement time and data storage.
We reduced the data quantity by lossless compression and the use of sparse data formats. Because mass spectroscopic data is highly discrete, we routinely achieved > 100-fold in-memory compression with zlib compression algorithms. Fourier transform analysis is only possible on decompressed data, but down-sampling of the mass axis and the conversion into sparse data formats facilitates the signal analysis and allows real-time exploration of experimental data.

Random sparse sampling was used to accelerate long delay scans. i.e., data was only measured for a randomly selected sub-set of delays along the extended time axis. Different sparse sampling strategies were explored in the field of multi-dimensional NMR [16, 17], and are discussed in more detail below. Figure 4 compares spectra from a fully-sampled and a sparsely-sampled measurement, with the latter collecting mass spectra for 5.5% of delays along an extended delay axis. The sparsely sampled data was acquired 2.5-times faster than the fully sampled data and improved the spectroscopic resolution by a factor 20. Sparse sampling added noise to the spectra, as readily apparent in the logarithmic representation depicted in Fig. 4.

The highest resolution spectrum measured to-date with the CRASY technique was based on a 10 μs scan of a benzene sample, containing residual CS₂ in small concentration. Due to the limited size of our spectrometer window, tracking of the molecular beam was only achieved for a delay range \( \leq 3 \mu s \) (equivalent to \( \leq 900 \text{MOPD} \)), reducing the achieved signal contrast and resolution. Figure 5 shows signal for the CS₂ mass channel, with an effective resolution of 330 kHz FWHM. This data represents the highest-resolution Fourier-transform interferometric spectrum in the world, representing a 50-fold improvement over the highest-resolution FTIR data in the literature [10, 11, 18]. To comprehend the scale of this improvement, we invite the reader to visualize the 11.7 m MOPD interferometer used for the FTIR experiments (see Ref. [19] for a photographic image) versus the km-scale MOPD achieved with our compact laboratory experiment.

Table 1 compares the resolution limit of spectroscopic techniques that are used to characterize rotational spectra at high resolution. CRASY currently represents the highest-resolution method for rotational Raman spectroscopy and, more generally, among all methods used for the rotational characterization of non-dipolar molecules. Modern FTMW experiments reach a significantly higher resolution [20], but can only be performed for dipolar species and only cover a spectral range of tens of GHz, more than one order-of-magnitude below the spectral coverage obtained with CRASY.

| Spectroscopic method | Resolution limit |
|----------------------|------------------|
| Raman, single-mode laser\(^a\) | 1500 MHz [9] |
| Raman, FTIR\(^a\) | 300 MHz [9] |
| Raman, RCS\(^b\) | 150 MHz [3, 9] |
| Raman, low resolution CRASY\(^a\) | 39 MHz [8] |
| Coherent anti-Stokes Raman\(^a\) | 30 MHz [9] |
| FTIR\(^b\) | 16 MHz [10] |
| Raman, high resolution CRASY\(^a\) | 330 kHz \(^c\) |
| FTMW\(^a\) | few kHz [7, 20] |

\(^a\)Achieved effective resolution. \(^b\)Theoretical resolution limit. \(^c\)This work
In terms of resolving power \( \frac{\text{spectral range}}{\text{resolution}} > 10^6 \), CRASY is at parity with state-of-the-art FTMW experiments.

Table 1 omitted frequency comb measurements [21, 22] and related techniques. Highest-resolution frequency comb measurement covered only very small spectral ranges and a direct comparison is therefore not meaningful. Dual-comb or direct comb spectroscopy (DCS) [23–25] allow the rapid, broad-band, and high-resolution characterization of molecular spectra. We omit DCS from Table 1 because it requires extended interaction times with significant molecular sample densities (i.e., condensed phase samples) and, to our knowledge, the effective resolution of all broad-band DCS spectra is far lower than the calculated resolution limit. A comparison with estimated DCS resolution limits is therefore not meaningful.

4 Limits to spectroscopic resolution and accuracy

The use of an infinite interferometer removes resolution limits due to the MOPD. We must therefore consider other factors that limit the resolution or accuracy of interferometric measurements. Three distinct types of uncertainties must be considered: (i) Uncertainties in delay positions accrued over the length of the opto-mechanical delay line. (ii) Uncertainties in the laser oscillator repetition rate, which affect the accuracy of the discrete 12.5 ns pulse-selection delays. (iii) Uncertainties due to Doppler shifts and Doppler broadening. In the following, we discuss each error source separately.

4.1 Uncertainties in opto-mechanical delays

The MD-531 motorized stage in our interferometer contains a 100 nm internal encoder. This encoder is mounted on an aluminum rod with correspondingly large thermal instabilities [26, 27] and the calibration of known spectra revealed relative positioning errors up to \( \Delta r/r = 10^{-4} \).

We addressed the internal encoder errors by mounting an external optical encoder (Sony Laserscale BL57-RE) with a low thermal expansion coefficient of \( 0.7 \times 10^{-6} \) m/(m K). Comparison of internal versus external encoder positions revealed a very linear error for the internal encoder and we recalibrated the internal encoder against the oscillator repetition rate, by measuring laser cross-correlation signals displaced by one oscillator pulse jump. With a typical ±0.2°C temperature stability on our laser table, we found that the internal encoder was sufficient to confine positioning uncertainties to \( \Delta r/r < 3 \times 10^{-6} \) (equivalent to a 40 fs delay uncertainty across the stage). Higher accuracy could be achieved by continuous monitoring of the external encoder, with resulting positioning uncertainties below \( \Delta r/r < 2 \times 10^{-7} \) (3 fs delay uncertainty across the stage).

Additional uncertainties arose due to the variation of the air refractive index \( n \) with air pressure, temperature, and composition. For 800 nm light, the air refractive index changes by \( \Delta n/n \approx 10^{-7} \) for a 40 Pa change in air pressure, a 0.1 °C change in temperature, or a 10% change in air humidity [28, 29]. These uncertainties were readily suppressed by the continuous measurement of, and correction for, changes in air temperature, pressure, and humidity. The NIST shop-floor equation [28, 30] was sufficient to approximate \( n \) with a relative uncertainty of \( \Delta n/n < 10^{-7} \).

Uncertainties accrued over the range of the opto-mechanical delay line are reset with each electronic pulse selection delay jump, when the mechanical delay line is re-set to its initial position. The impact of opto-mechanical delay uncertainties therefore scaled inversely to the number \( N \) of electronic delay jumps and became small for large \( N \). It is therefore sufficient to suppress relative stage positioning errors into a regime where the accrued phase shift for the highest measured frequencies becomes negligible. Stage errors in the \( \Delta r/r = 10^{-6} \) regime correspond to a 12.5 fs phase shift across the mechanically scanned 12.5 ns delay range and were negligible for any feasible experiment with our minimal 50 fs laser pulse duration (impulsive Raman excitation possible for < 10 THz transition frequencies). We should note that significant calibration errors between the mechanical stage and the pulse-selection delays led to the formation of pronounced 80 MHz sidebands that were readily identified in the experimental spectra.

4.2 Uncertainties in the oscillator repetition rate

Extended delays were achieved by electronic pulse-selection of subsequent oscillator pulses from a Coherent Vitara laser oscillator. This adds delays in multiples of 12.5 ns to one arm of the interferometer. Any undetected drift of the laser oscillator repetition rate from the nominal value of 80 MHz will introduce a corresponding calibration error. We used a frequency counter (Aim-TTI TF930) to monitor the stability of the oscillator against a GPS-stabilized clock (Leo Bodnar GPSDO) with an expected frequency accuracy of \( \Delta f/f \leq 10^{-10} \).

The Allan deviation allows to diagnose the relative frequency stability of independent oscillators, based on an simple comparison of clock frequencies over an extended period of time [31]. Figure 6 shows the Allan deviation and the modified Allan deviation for the oscillator versus GPS clock frequency, measured over a 1-day period. For periods < 100 s, the observed slope of –1 (–1.5) in the Allan (modified Allan) deviation is characteristic for random white noise [31]. This noise is due to the frequency counter digitization noise (±1 count over the measurement period) and does not
reflect any drift of the clock or oscillator. For periods $> 100$ s, the Allan deviation remained below $10^{-10}$, giving an upper limit for the frequency stability of the oscillator. It is quite possible that the GPS clock stability was limiting in this regime and that the oscillator frequency was more stable than our measurement indicates.

Slow frequency drifts of the oscillator are readily corrected by a corresponding adjustment of the opto-mechanical delay position. A continuous monitoring of the oscillator frequency therefore allows a feed-forward correction of delays, which fulfills the same purpose as the feed-back oscillator stabilization in frequency comb spectroscopy [21], albeit with much smaller technical efforts. With our inexpensive monitoring system and a typical frequency counter period of 1 or 10 s, we readily achieved a single-sigma uncertainty (Allan deviation) $\Delta \nu / \nu \ll 10^{-7}$ and a longer frequency counter integration period could reduce this uncertainty towards the $\Delta \nu / \nu \approx 10^{-10}$ noise floor of the frequency measurement. We expect that the uncertainty can be further reduced with the use of a high-fidelity reference clock:

### 4.3 Uncertainties arising from Doppler effects

Textbooks commonly label skimmed molecular beam spectroscopy as “Doppler-free”. But as illustrated in Figs. 7 and 8, a non-zero collimation angle and an imperfect alignment of a molecular beam versus laser beams contributes some Doppler effects. We separately assessed Doppler broadening and Doppler shifts by geometric consideration of the molecular beam velocity components $v \parallel$ in the direction of the alignment and ionization laser beams.

In our experiments, a 1 mm skimmer at 280 mm distance from the pulsed valve led to a molecular beam collimation angle of $\epsilon = 0.10^\circ$. We measured the molecular beam velocity for a helium-seeded beam of CS$_2$ to be $v_{\text{beam}} \approx 1100$ m/s and calculated a velocity spread $v_{\parallel} = \pm 1.96$ m/s and a maximal Doppler broadening of $\Delta \nu / \nu = v_{\parallel} / c = 6.6 \times 10^{-9}$. This estimated Doppler broadening was significantly larger than a value obtained based on the textbook treatment (see Chapter 4 in Demtröder [32]) because we accounted for the similar velocity profiles of the heavier CS$_2$ molecules and the lighter helium atoms in the seeded molecular beam.

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**Fig. 6** Allan deviation (top) and modified Allan deviation (bottom) for the 80 MHz Coherent Vitara-T laser oscillator, measured against a GPS-disciplined clock.

**Fig. 7** Illustration of Doppler broadening. The non-zero molecular beam collimation angle $\epsilon$ leads to a distribution of beam velocity components $v_{\parallel}$ that are parallel to the laser beam propagation axis: $v_{\parallel} = v_{\text{beam}} \cdot \tan(\epsilon)$

**Fig. 8** Illustration of the Doppler shift: To correct for molecular beam propagation within the delay $\Delta t$ between alignment and ionization pulses, the ionization laser is tracking the molecular beam for a distance of $d = \Delta t \cdot v_{\text{beam}}$. When the angle between molecular beam and laser beams deviates from 90°, this leads to an additional path $\delta x$ for the ionization beam and an additional delay $\delta t = \delta x / c$.
Doppler broadening becomes relevant when it approaches or exceeds the spectroscopic resolution. In our best CRASY data, we observed sub-MHz line-width for 100 GHz line frequencies ($\Delta v_{\text{FWHM}}/v$ in the $10^{-6}$ regime). The Doppler broadening estimated above is several orders-of-magnitude smaller than our best achieved resolution and will not affect spectroscopic results until we reach sub-kHz level resolution. The use of slower molecular beams and better molecular beam collimation can further reduce Doppler broadening and we expect to observe sub-100 Hz line widths for 100 GHz lines before Doppler broadening becomes a limiting factor.

A Doppler shift occurs if the angle between laser and molecular beam deviates from $\alpha = 90^\circ$. As illustrated in Fig. 8, tracking of the molecular beam then changes the effective path length of the alignment versus the ionization arm of the interferometer and introduces an additional delay of $\delta t = \frac{\Delta v}{c} = \Delta t \left(1 + \frac{\hbar \omega}{c \sin(\alpha)}\right)$, proportional to the scan delay $\Delta t$. Resulting Fourier transformed spectra show a frequency shift proportional to the delay time errors $\delta t/\Delta t$. The line positions for well-resolved lines can be determined with an accuracy that is orders-of-magnitude better than the spectroscopic resolution and our experiment is therefore highly sensitive to Doppler shifts.

To measure the angle $\alpha$ between laser and molecular beam, we propagated a laser pointer through the skimmer onto the pulsed valve orifice and measured the relative angle of laser pointer beam and alignment / ionization laser beams against a reference frame. For our experiments, we determined an angle of $\alpha = 91.6 \pm 0.4^\circ$ and calculated a Doppler correction factor of $\delta t/\Delta t = (1.0 \pm 0.26) \times 10^{-7}$. The Doppler shift was not negligible for our most-accurate measurements and reduced measured rotational frequencies by one part in $10^7$ (some 320 Hz for a 3.2 GHz rotational constant fitted for CS$_2$) [2]. The Doppler shift uncertainty of $2.6 \times 10^{-8}$ can be reduced by a careful measurement of the relative angles between the molecular beam and the laser beams. The Doppler shift can be measured, and thereby completely eliminated, by performing complementary experiments with laser beams propagating in opposite directions: Measurements from opposing directions show opposite signs for the Doppler shift.

### 4.4 Signal degradation by sparse sampling

Sparse sampling is an essential tool to extend the MOPD and to increase the spectroscopic resolution without excessive requirements in terms of measurement time and data storage. A number of sparse sampling approaches were discussed in the context of multi-dimensional NMR spectroscopy [16, 17, 33, 34]. Sparse sampling methods other than random sampling affect the line shape and are therefore problematic, unless the natural line shape in the investigated spectra is known or negligible. Randomly sparse sampled data merely showed an elevated noise level and correspondingly reduced SNR, without introducing any significant artifacts [35]. The combination of random sparse sampling with an infinite interferometer therefore offers a unique spectroscopic tool, where resolution and SNR can be freely traded against one-another.

Figure 9 shows the effect of random sparse sampling in a simulated delay trace for CS$_2$. The Fourier transform of a fully sampled trace showed negligible noise due to the synthetic nature of the data. To simulate 3% random sparse sampling, 97% randomly selected points in the delay trace were set to zero. The random selection was based on the Mersenne-Twister pseudo-random number generator, as implemented in the numpy library of the Python programming language. The Fourier transform of the sparsely sampled data showed significant noise but only a modest degradation of the resolution. An estimate of the noise distribution, using the modified Z-score [36], gave a noise level of $\sigma = 0.2\%$ relative to the largest signal peak. Experimentally observed SNRs in sparsely sampled data showed similar signal degradation. Note that longer scans can be performed with lower sparse sampling rates.
5 Expected resolution limits for CRASY experiments

For all practical purposes, we can consider the coherence lifetime of cold rotational states as limited only by collisional dephasing. In collision-free molecular beams, rotational decoherence occurs when the molecules hit the spectrometer wall. The resolution limit of CRASY is therefore purely a function of the MOPD. With the infinite interferometer design presented above, we removed all practical limitations to the MOPD and two other experimental factors become limiting: (i) The molecular beam travels with supersonic velocities and must be accurately tracked. (ii) Sparse sampling is necessary to achieve large MOPDs within reasonable measurement times, but may degrade the SNR to a point where spectra can no longer be resolved.

The resolution of current CRASY measurements is limited by factor (i): due to a limited size of the laser windows, we can track the molecular beam only over distances of a few mm. The beam velocity for our dilute, helium-seeded molecular beams was measured to be \( v_b \approx 1100 \text{ m/s} \) and the 330 kHz resolution data shown in Fig. 5 therefore required tracking of the molecular beam over a distance of approx. 2 mm. The molecular beam velocity can be significantly reduced by using a heavier seed gas with lower speed-of-sound. With a suitably larger laser window, the tracking distance can be extended, e.g., an extension to 10 cm tracking, would offer a 50-fold increase of the accessible MOPD. We expect that the combination of longer tracking and slower molecular beams will push the resolution limit into the single-kHz regime. Further extensions would require the construction of a spectrometer with a dedicated chamber for decimeter- or meter-scale tracking of the molecular beam, e.g., as depicted in Fig. 10. Signal collection might be accelerated with the correlation to other spectroscopic observables. E.g., probing of rotational coherence via fluorescence excitation would remove the nonlinearity of our two-photon photoionization probe step and might allow a multiplexed detection of large signals along the molecular beam axis.

The sampling of a delay axis containing \( 10^8 \) points could allow to collect spectroscopic data with single-kHz resolution and 100 GHz spectral range. Clearly, this is only possible with severe sparse sampling and a corresponding degradation of the SNR. Figure 11 shows that such measurements are feasible: a simulated spectrum based on the sampling of 100,000 points along a 2 ms delay range combines excellent SNR with sub-kHz resolution.

6 Conclusions

In conclusion, we demonstrated that pulse-selection from a stable laser oscillator allows to perform interferometric spectroscopy with an effectively infinite interferometer. This approach removed previous limits to the available interferometric MOPD and we presented rotational spectra with sub-MHz effective resolution over a 500 GHz spectral range. The achieved resolution was several orders-of-magnitude better than that from any preceding RCS or FTIR measurements and corresponds to the scanning of km-scale optical path differences. Further order-of-magnitude improvements are expected and progress is only limited by experimental challenges such as the requirement to track skimmed molecular beams over extended distances.
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