

### Stimulated raman scattering metrology of molecular hydrogen



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Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In this paper, Lamperti et al use frequency combs to assist in stimulated Raman scattering metrology. Essentially, the authors create a comb-calibrated Raman spectrometer. This enables high-precision measurements. The authors combine their frequency comb assisted approach with a multi-spectra fitting procedure and use this to study the stretching mode of H<sub>2</sub>. Their results agree extremely well with theory. The manuscript appears technically correct and to the best of knowledge this is the first time this has been done. Therefore, I can recommend it for publication in Communications Physics pending the following minor revisions.

1. The manuscript figures appear totally in black and white for me. This makes it hard to distinguish between various traces.
2. Methods should be described in enough detail that someone can repeat the work. Please provide all manufacturer details and part numbers for the setup.
3. A photograph of the system should be provided in addition to the experimental schematic in Figure 1.
4. How many experiments were included for the experimental measurements in Figure 4.
5. Please justify the number of significant figures used in Table 1.

Reviewer #2 (Remarks to the Author):

The paper presents an investigation in which a frequency comb assisted SRS technique has been developed and used to measure the transition frequency of the Q(1) fundamental line of H<sub>2</sub> with almost shot-noise limited accuracy. The paper is well written and well presented and I recommend publication. However, I have a few minor concerns that should be addressed.

(1) I have some problem with the scope of the paper. Do the authors present a new measurement technique (comb-assisted SRS) or do they present results from an investigation of H<sub>2</sub> at different pressures? It remains unclear. The title and abstract imply the former while the paper as a whole would suggest the latter. Please be clear.

(2) The title is too broad. I do understand the intention that the frequency comb may turn SRS into an absolute metrology tool, but I would anyway recommend to add frequency comb assisted (SRS metrology). There are other ways to calibrate SRS signals.

(3) To reflect the measurements at different pressures, the authors are recommended to extend or comment the equation in the Results section to include molecule concentration and Raman cross-section. That would add a possibility to discuss absolute responses in Figure 2.

(4) Would it be possible to add details on the CW pump and Stokes lasers (power, linewidth)? Does the quality of these lasers influence the results?

(5) The big difference between the ab initio calculations and the fitted parameters presented in Supplementary table 1 is a bit problematic and I see no approach to evaluate the susceptibility of the fits or to estimate the random uncertainties in the fitted parameters. What sort of fitting routine was used? Did they use robust kernels or normal L2 fitting.

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1. The manuscript figures appear totally in black and white for me. This makes it hard to distinguish between various traces.

We are sorry for this inconvenience, and we agree that it is difficult to understand the figures in black and white. In the submitted pdf we see the figures in colour, as they were originally made. We hope the editorial office can help the referee to fix this issue.

2. Methods should be described in enough detail that someone can repeat the work. Please provide all manufacturer details and part numbers for the setup.

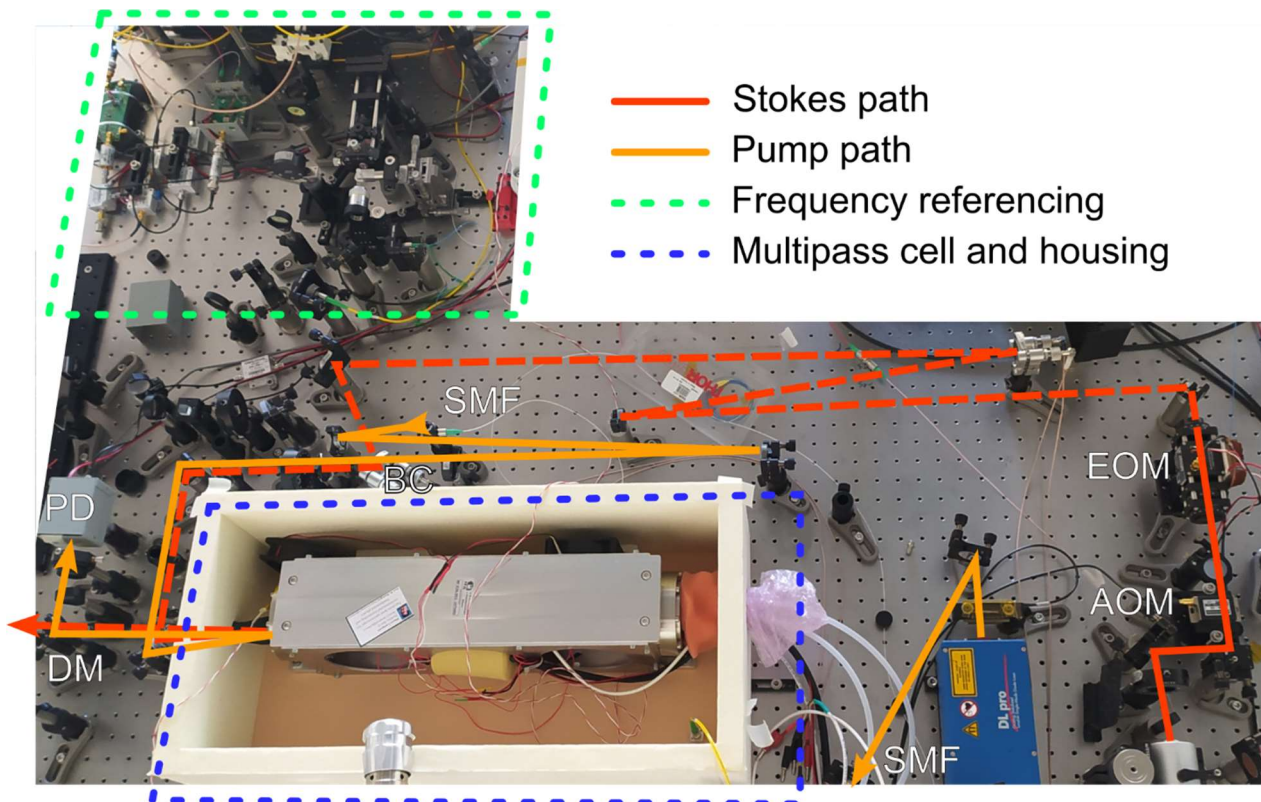
We thank the referee for the suggestion. We have added all the information for the laser sources and key components of the setup, including specification of the key laser emission characteristics for the former (as suggested also by Reviewer #2). We haven't provided additional details for generic parts (e.g. photodetectors) for which we use a variety of standard commercial products or home-made versions without the need for specific parts.

3. A photograph of the system should be provided in addition to the experimental schematic in Figure 1.

We thank the reviewer for the suggestion. We have added an annotated photograph of the system in the Supplementary Material, in a new Section titled "Implementation of the spectrometer":

## 6. Implementation of the spectrometer

The implementation of the spectrometer is shown in Supplementary Figure 6, where a photograph of the system is provided, together with annotations to identify the paths of laser beams. Stokes and pump laser paths are shown in red and orange, respectively. The Stokes beam passes through an acousto-optical modulator (AOM) for active power stabilization and a resonant electro-optical amplitude modulator (EOM), then through a reflective telescope for mode matching to the multipass cell. It is overlapped to the pump beam at a dichroic beam combiner (BC), sent to the multipass cell, and separated from the pump beam at a dichroic mirror (DM) after exiting the cell. The pump beam is first sent through a single mode fibre (SMF) for mode cleaning, then through a reflective telescope for mode matching, and combined with the Stokes beam before entering the cell. After exiting the cell, it is reflected by the dichroic mirror and sent to the detection photodiode (PD). Frequency referencing of the two lasers is performed in the region identified by the dashed green box, where the layout shown in Supplementary Figure 1 is implemented. The multipass cell is housed in a thermally insulated box, identified by the blue dashed box. White tubes exiting the cell housing connect the multipass cell with the pressure sensor and two flow controllers used to maintain a constant gas flow and to actively stabilize pressure.



**Supplementary Figure 6.** Optical setup of the spectrometer. AOM: acousto-optical modulator; EOM: electro-optical amplitude modulator; BC: beam combiner; DM: dichroic mirror; SMF: single mode optical fibre; PD: photodiode.

4. How many experiments were included for the experimental measurements in Figure 4.

The data presented in Figure 4 comes from a total of 10 experiments performed by 8 different groups. The data point corresponding to our result summarizes the results from 10 measurement series acquired over a period of 5 months. We have added this last information to the caption of Figure 4, which now reads:

Data points represent the discrepancy on the transition frequency (experiment – theory), with error bars given by the experimental uncertainty ( $1\sigma$ ) and the height of the red shaded area at the bottom representing the theoretical uncertainty. Line names are reported next to data points, while the rovibrational band is identified through the point colour (see legend). **The data point corresponding to this work summarizes 10 measurement series acquired over 5 months.**

5. Please justify the number of significant figures used in Table 1.

We thank the referee for indicating the lack of an explicit description of the uncertainties in the data reported in Table 1. We have updated the caption to describe explicitly the reported uncertainties:

**The uncertainties expressed in parentheses represent one standard deviation, obtained as the quadrature sum of the statistical and systematic uncertainties (for experimental values), or the estimated systematic uncertainty (for theoretical values).**

Reviewer #2 (Remarks to the Author):

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and used to measure the transition frequency of the Q(1) fundamental line of H<sub>2</sub> with almost shot-noise limited accuracy. The paper is well written and well presented and I recommend publication. However, I have a few minor concerns that should be addressed.

(1) I have some problem with the scope of the paper. Do the authors present a new measurement technique (comb-assisted SRS) or do they present results from an investigation of H<sub>2</sub> at different pressures? It remains unclear. The title and abstract imply the former while the paper as a whole would suggest the latter. Please be clear.

We thank the reviewer for this remark. We agree that the combination of a broad title and an abstract that equally weights the technique and the spectroscopic target is misleading. As the reviewer notices, the main point of the article is the study of molecular hydrogen, and the spectrometer has been developed for this purpose, although it has the potential to be exploited for the study of many different molecular systems.

We have changed slightly both the title and the abstract in a way that, we think, makes it clear that the paper aims primarily to show the innovative result on molecular hydrogen.

The title now reads:

Stimulated-Raman-Scattering Metrology: **application to molecular hydrogen**

while the abstract has been modified as follows:

Frequency combs have revolutionized optical frequency metrology, allowing one to determine highly accurate transition frequencies of a wealth of molecular species. ~~Despite a recognized scientific interest,~~ These progresses have only marginally benefited infrared-inactive transitions, due to their inherently weak cross-sections. Here we overcome this limitation by introducing stimulated-Raman-scattering metrology, where a frequency comb is exploited to calibrate the frequency detuning between the pump and Stokes excitation lasers. ~~We apply this approach to molecular hydrogen to test quantum electrodynamics. We apply this approach to the investigation of molecular hydrogen, which is a recognized benchmark for tests of quantum electrodynamics and of theories that describe physics beyond the standard model.~~ Specifically, we measure the transition frequency of the Q(1) fundamental line of H<sub>2</sub> around 4155 cm<sup>-1</sup> with few parts-per-billion uncertainty, which is comparable to the theoretical benchmark of *ab initio* calculations and more than a decade better than the experimental state of the art. Our comb-calibrated stimulated Raman scattering spectrometer extends the toolkit of optical frequency metrology as it can be applied, with simple technical changes, to many other infrared-inactive transitions, over a 50-5000 cm<sup>-1</sup> range that covers also purely rotational bands.

(2) The title is too broad. I do understand the intention that the frequency comb may turn SRS into an absolute metrology tool, but I would anyway recommend to add frequency comb assisted (SRS metrology). There are other ways to calibrate SRS signals.

We agree with the reviewer that the title in its original form was too broad. Following reviewer suggestion (1), we modified it to make it clear that the main result of the paper is the result obtained through SRS on molecular hydrogen. We think that the present form is clearer and there is no more the need to specify the technical approach used to obtain metrology-grade frequency calibration.

(3) To reflect the measurements at different pressures, the authors are recommended to extend or comment the equation in the Results section to include molecule concentration and Raman cross-section. That would add a possibility to discuss absolute responses in Figure 2.

Unfortunately, our setup is very accurate on the frequency axis (horizontal axis) yet rather inaccurate on the absolute response axis (vertical axis). This is mainly due to the unprecise knowledge of the sizes of pump and Stokes beams throughout the multipass cell: there are needed to compute their overlap integral and eventually quantify an absolute value for SRL. We estimate the SRL given in the paper to be accurate within a factor of 2, this being the reason why we avoid discussing absolute responses.

(4) Would it be possible to add details on the CW pump and Stokes lasers (power, linewidth)? Does the quality of these lasers influence the results?

We thank the reviewer for noticing the lack of reported linewidths for the pump/Stokes lasers. They have been added along with the corresponding powers under section “**Comb-calibrated coherent Raman spectrometer**”. Our cw lasers have linewidth narrower than 300 kHz, but this is not a crucial requirement given the broad hydrogen lines (FWHM > 200 MHz for all pressures).

“The spectrometer (depicted in Figure 1) employs a pair of single-frequency lasers for the pump (2 mW at 740 nm, <300 kHz linewidth) and Stokes (5 W at 1064 nm, <100 kHz linewidth) fields”

(5) The big difference between the ab initio calculations and the fitted parameters presented in Supplementary table 1 is a bit problematic and I see no approach to evaluate the susceptibility of the fits or to estimate the random uncertainties in the fitted parameters. What sort of fitting routine was used? Did they use robust kernels or normal L2 fitting.

We haven’t originally reported the uncertainties on the ab initio and fitted parameters, but we understand that this lack of information makes it difficult for the reader to evaluate some of our sentences preceding the table. We have now updated the table to include the estimated uncertainties on the *ab initio* collisional parameters and on the fitted parameters. The table now reads:

**Supplementary Table 1.** Comparison between *ab initio* calculated collisional parameters (**Ab initio** column) and fitted collisional parameters. Column **Fit 1** corresponds to a fit with only  $\gamma_2$  and  $\delta_2$  fixed to reference (*ab initio*) values, while **Fit 2** corresponds to a fit with all collisional parameters except  $\delta_0$  fixed to reference values. Units are  $10^{-4} \text{ cm}^{-1}/\text{bar}$  for  $\gamma_0$  and  $\gamma_2$ ,  $10^{-3} \text{ cm}^{-1}/\text{bar}$  for  $\delta_0$  and  $\delta_2$ ,  $10^{-2} \text{ cm}^{-1}/\text{bar}$  for  $\nu_{VC}$ ,  $10^{-3} \text{ cm}^{-1}/\text{bar}$  for  $\text{Im}\{\nu_{VC}\}$  and MHz for  $\nu_0 - \nu_{ref}$ . **Uncertainties reported between parentheses are standard errors obtained from the covariance matrix for fitted parameters, and from estimated contributions from the uncertainty of potential energy surfaces and computational parameters (basis set size, range of propagation) for ab initio values.**

| Parameter               | <i>Ab initio</i> | Fit 1            | Fit 2            |
|-------------------------|------------------|------------------|------------------|
| $\gamma_0$              | 6.29(63)         | 6.461(7)         | <i>ab initio</i> |
| $\delta_0$              | -1.15(12)        | -2.6892(6)       | -2.6963(6)       |
| $\gamma_2$              | 1.05(10)         | <i>ab initio</i> | <i>ab initio</i> |
| $\delta_2$              | 2.27(22)         | <i>ab initio</i> | <i>ab initio</i> |
| $\nu_{VC}$              | 4.25(21)         | 4.214(2)         | <i>ab initio</i> |
| $\text{Im}\{\nu_{VC}\}$ | -1.46(146)       | -3.05(3)         | <i>ab initio</i> |
| $\nu_0 - \nu_{ref}$     | 0                | 1.77(7)          | 4.17(4)          |
| $\chi_r^2$              | /                | 1.2              | 1.3              |

We used weighted least-squares (L2) fitting, with equal weights for all points of the same spectrum, calculated as the square of the SNR, which is equivalent to the usual  $1/\sigma^2$  weighting. Uncertainties on the fit parameters are obtained from the covariance matrix of the least squares fit function at the best fit point, while those on the *ab initio* values are estimated from the uncertainty of the PES and computational parameters (basis set size, range of propagation) for ab initio values.

Additionally, we noticed a typo in the table: decimal figures of  $\nu_{VC}$  in Fit 1 were exchanged (4.12 instead of 4.21), they are now fixed.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors have addressed my comments and I recommend this manuscript for publication. g

Reviewer #2 (Remarks to the Author):

The authors have responded satisfactory to previous comments and concerns and have updated the manuscript accordingly. I have no further comments and recommend publication.