Peer Review File

Manuscript Title: Magneto-optical trapping and sub-Doppler cooling of a polyatomic molecule

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

The manuscript by Vilas et al., presents the first 3D magneto-optical trap (MOT) for a polyatomic molecule and demonstrates sub-Doppler cooling to temperatures below the Doppler limit. MOTs are the workhorse technique in ultracold atomic physics and have enabled a vast amount of research in this field over the past 35 years. In my opinion, the extension of these laser cooling and trapping techniques to a polyatomic species is a landmark result that will be of significant interest to the broad readership of Nature. These results demonstrate that molecules with less favorable rovibrational branching can be laser cooled and trapped in a similar manner to the diatomic species CaF, SrF and YO, which all have more manageable rovibrational branching. This milestone result will facilitate the laser cooling and trapping of other challenging species, well-suited to specific applications such as quantum simulation and searches for BSM physics.

The authors probe the confining and cooling forces in their polyatomic MOT and blue-detuned molasses using a suite of measurements developed and used over the past 5-10 years to probe MOTs of diatomic molecules. These methods are entirely appropriate, and the data are of high quality and clearly presented to the reader. The conclusions drawn by the authors are valid and reliable.

I believe that this manuscript should be published in Nature provided that the authors address the following comments presented below:

1. Towards the end of the abstract the authors write "…quantum science applications, including the creation of optical tweezer arrays of CaOH molecules.", however, arrays of trapped CaOH molecules are not themselves an application. The authors should change this language to:

"…quantum science applications, including [example application] using optical tweezer arrays of CaOH molecules."

This change will avoid confusion for readers unfamiliar with this field.

2. On line 32, the authors should add “in the millikelvin regime or below.” since this statement is about MOTs in general and should also cover the properties of atomic type-I MOTs on weak transitions.

3. On line 33, the authors should highlight to the reader why the simultaneous cooling and compression provided by a MOT is highly desirable. A statement referring to phase-space density might be the best way to do this.

4. On lines 46-47, the authors should include this reference to YO molecules laser cooled to 1 μK:

https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.127.263201

when they write “…to lower temperatures [35, 36] and…”.

5. The references to white light slowing on line 67 should also include the first demonstration of this technique (using atoms):

https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.67.46

and the first demonstration on a molecule:

https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.108.103002

6. The authors should comment in the text on if the converging slowing laser beam (lines 89-91) provides a significant transverse force to the molecules. This looks to be the case based on the results in:

https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cphc.201600967

7. On lines 99-100 the authors comment that over half of the repump lasers require <100 mW. The authors should also stress that these stated repump powers are for spectrally broadened laser profiles. A key (and currently unclear) point is that if an alternate slowing method could be used, the CaOH MOT would require substantially less repump laser power.

8. Reference 12, presenting an RF MOT for YO, should be added to the collection of references currently on line 112.

9. On lines 113 and 114 the authors should highlight what diameter the MOT beams are clipped to by whatever the limiting aperture is (quarter-wave plate, viewport etc.).

10. Again, on line 132 the authors should stress that the repump lasers are frequency broadened throughout the entire experimental cycle. While this point is currently stated in the methods section, this might not be read by many readers and is a key detail when interpreting fig. 1(c).

11. On line 167 the authors should state the camera exposure time used for the oscillation measurements. Again, while this is stated in the methods section, a non-expert might not read this section and then wrongly assume that it is 10 ms, as stated on line 194. A 10 ms exposure would be problematic based on the measured trap frequencies of ~40-50 Hz.

12. Are the fluorescence images shown in fig. 3b on a common scale? If so, this should be stated in the caption. If not a common scale or stated scaling factor would be informative. At the moment the intensity axis of these images carries no information.

13. There is a typo in the trap frequency units in the fig. 3 caption.

14. In my opinion the word “desired” should be changed to “required” on line 247.

15. On line 252 the words “and practical” should potentially be reconsidered. A laser system with 12-13 lasers would potentially still be considered impractical by many. Perhaps this point would be

more appropriate if paired with a statement about “maturing solid-state laser technologies” but I will leave this point to the discretion of the authors.

16. On lines 450-452 the authors should re-emphasize that these repump lasers are frequency broadened.

17. The “CaOH production and buffer gas cooling” and “Radiative laser slowing” methods sections would be enormously improved with the inclusion of a figure showing the CaOH beam forward velocity profile before and (ideally) after slowing. While the realization of a 3D MOT of CaOH is the key result of this work, the laser slowing of a CaOH molecular beam to below the MOT capture velocity is a highly non-trivial result. I will leave this point to the discretion of the authors.

Referee #2 (Remarks to the Author):

The paper presents the results on magneto-optical trapping and sub-Doppler cooling of a triatomic molecule, CaOH. This is the first successful experiment on laser-cooling of a "larger" molecule (beyond diatomics) in a MOT, which has been long considered extremely challenging due to the lack of closed transitions required to scatter a large amount of photons. Here the authors achieve that by a clever use of repumping lasers on different bending and stretching modes unavoidable in polyatomic molecules. Moreover, they undertake another important step beyond MOT - Sub-Doppler cooling using blue-detuned optical molasses.

MOTs are the central ingredient of any ultracold atom lab, therefore enabling such a tool for complex molecules is a crucial and desirable step. Sub-Doppler cooling is, on the other hand, an unavoidable milestone on the way to a BEC of polyatomic molecules. The results are novel and interesting, this experiment is likely to open a new page in cold chemistry and many-body physics.

Since the results are important enough to appeal to the broad readership of Nature, I recommend to accept the paper for publication.

Author Rebuttals to Initial Comments:

Referee #1 (Remarks to the Author):

We thank the referee for their detailed comments and positive feedback on our work. We have included a point-by-point response to all comments below.

The manuscript by Vilas et al., presents the first 3D magneto-optical trap (MOT) for a polyatomic molecule and demonstrates sub-Doppler cooling to temperatures below the Doppler limit. MOTs are the workhorse technique in ultracold atomic physics and have enabled a vast amount of research in this field over the past 35 years. In my opinion, the extension of these laser cooling and trapping techniques to a polyatomic species is a landmark result that will be of significant interest to the broad readership of Nature. These results demonstrate that molecules with less favorable rovibrational branching can be laser cooled and trapped in a similar manner to the diatomic species CaF, SrF and YO, which all have more manageable rovibrational branching. This milestone result will facilitate the laser cooling and trapping of other challenging species, well-suited to specific applications such as quantum simulation and searches for BSM physics.

The authors probe the confining and cooling forces in their polyatomic MOT and blue-detuned molasses using a suite of measurements developed and used over the past 5-10 years to probe MOTs of diatomic molecules. These methods are entirely appropriate, and the data are of high quality and clearly presented to the reader. The conclusions drawn by the authors are valid and reliable.

I believe that this manuscript should be published in Nature provided that the authors address the following comments presented below:

1. Towards the end of the abstract the authors write “…quantum science applications, including the creation of optical tweezer arrays of CaOH molecules.”, however, arrays of trapped CaOH molecules are not themselves an application. The authors should change this language to:

“…quantum science applications, including [example application] using optical tweezer arrays of CaOH molecules.”

This change will avoid confusion for readers unfamiliar with this field.

We have reworded this sentence to read “...quantum science applications, including quantum simulation and computation using optical tweezer arrays.” We have additionally added two citations to papers proposing quantum simulation and computation applications with polyatomic molecules (these are also cited earlier in the abstract).

2. On line 32, the authors should add “in the millikelvin regime or below.” since this statement is about MOTs in general and should also cover the properties of atomic type-I MOTs on weak transitions.

We have incorporated this change per the referee’s suggestion.

3. On line 33, the authors should highlight to the reader why the simultaneous cooling and compression provided by a MOT is highly desirable. A statement referring to phase-space density might be the best way to do this.

We have modified the text on line 33 to read “...is highly desirable for increasing phase-space density of the trapped species…”

4. On lines 46-47, the authors should include this reference to YO molecules laser cooled to 1 μK:

https://journals.aps.org/prl/pdf/10.1103/PhysRevLett.127.263201

when they write “…to lower temperatures [35, 36] and…”.

We thank the referee for pointing out this omission, which we have now corrected. We additionally added a reference to Langin et al., PRL 2021 (previously Ref. 38), which describes Lambda-enhanced cooling of SrF to ~10 uK.

5. The references to white light slowing on line 67 should also include the first demonstration of this technique (using atoms):

https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.67.46

and the first demonstration on a molecule:

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We thank the referee for pointing us to these references, which have now been added as suggested.

6. The authors should comment in the text on if the converging slowing laser beam (lines 89-91) provides a significant transverse force to the molecules. This looks to be the case based on the results in:

https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/cphc.201600967

We have added the sentence, “The focusing provides transverse compression forces and has been shown to improve slowing efficiency in experiments with diatomic molecules.” Reference to the above paper, as well as to Truppe et al., NJP 2017 (previously Ref. 45), has been included.

7. On lines 99-100 the authors comment that over half of the repump lasers require <100 mW. The authors should also stress that these stated repump powers are for spectrally broadened laser profiles. A key (and currently unclear) point is that if an alternate slowing method could be used, the CaOH MOT would require substantially less repump laser power.

We also believe that this is an important point, and appreciate the suggestion to emphasize it. To that end, we have changed the text to read “Notably, over half of the *frequency-broadened* repumping lasers require less than 100 mW, a technically straightforward requirement. *These powers could be further reduced by using slowing techniques that do not rely on spectrally broadened lasers*.” (Italics denote new additions to the original text.)

8. Reference 12, presenting an RF MOT for YO, should be added to the collection of references currently on line 112.

We thank the referee for pointing out this oversight. We have added Ref. 12 to this list.

9. On lines 113 and 114 the authors should highlight what diameter the MOT beams are clipped to by whatever the limiting aperture is (quarter-wave plate, viewport etc.).

We have added a parenthetical phrase addressing this point. The text now reads “Each of the six MOT beams has a 1/e^2 Gaussian diameter of 10 mm (truncated at a diameter of 19 mm by in-vacuum baffles)...”

10. Again, on line 132 the authors should stress that the repump lasers are frequency broadened throughout the entire experimental cycle. While this point is currently stated in the methods section, this might not be read by many readers and is a key detail when interpreting fig. 1(c).

We have attempted to clarify this point by editing the text to read, “Thus, the same *frequency-broadened* repumping lasers are used for repumping molecules during all three tasks of the experiment…”

11. On line 167 the authors should state the camera exposure time used for the oscillation measurements. Again, while this is stated in the methods section, a non-expert might not read this section and then wrongly assume that it is 10 ms, as stated on line 194. A 10 ms exposure would be problematic based on the measured trap frequencies of ~40-50 Hz.

We have clarified this point by adding “...imaged for 1 ms…” on this line.

12. Are the fluorescence images shown in fig. 3b on a common scale? If so, this should be stated in the caption. If not a common scale or stated scaling factor would be informative. At the moment the intensity axis of these images carries no information.

The three images are not on a common scale due to the different MOT numbers and MOT scattering rates in each configuration. We have added two sentences to the caption clarifying the scale factor between images.

13. There is a typo in the trap frequency units in the fig. 3 caption.

We have corrected this typo in the revised manuscript by changing “ms” to “Hz.”

14. In my opinion the word “desired” should be changed to “required” on line 247.

We agree that high fidelity measurement and readout is essential for these quantum science applications, and have therefore changed this word per the suggestion of the referee. It should be noted, however, that there are alternative schemes (e.g. ion or Rydberg-based readout) that do not require high-fidelity photon cycling detection.

15. On line 252 the words “and practical” should potentially be reconsidered. A laser system with 12-13 lasers would potentially still be considered impractical by many. Perhaps this point would be more appropriate if paired with a statement about “maturing solid-state laser technologies” but I will leave this point to the discretion of the authors.

We believe that the low power required for many of the repumping lasers does make this work practical, though the referee’s point is well taken. In addition, the distinction between “feasible” and “practical” is not especially pronounced. With these two points in mind, we have removed the word “practical” from the text.

16. On lines 450-452 the authors should re-emphasize that these repump lasers are frequency broadened.

We have added the sentence “This is especially important given that frequency-broadened lasers are used to repump the MOT in the experiment,” after the lines in question.

17. The “CaOH production and buffer gas cooling” and “Radiative laser slowing” methods sections would be enormously improved with the inclusion of a figure showing the CaOH beam forward velocity profile before and (ideally) after slowing. While the realization of a 3D MOT of CaOH is the key result of this work, the laser slowing of a CaOH molecular beam to below the MOT capture velocity is a highly non-trivial result. I will leave this point to the discretion of the authors.

The slowing was optimized without the X(110), N’’=2 repumping laser, which was only added after the MOT had been realized. Therefore, we have no slowing data in the exact experimental configuration used to form the MOT and perform sub-Doppler cooling as described in this manuscript. We believe that including the older slowing data would only add confusion due to this detail, and we therefore choose to omit it.

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MOTs are the central ingredient of any ultracold atom lab, therefore enabling such a tool for complex molecules is a crucial and desirable step. Sub-Doppler cooling is, on the other hand, an unavoidable milestone on the way to a BEC of polyatomic molecules. The results are novel and interesting, this experiment is likely to open a new page in cold chemistry and many-body physics.

Since the results are important enough to appeal to the broad readership of Nature, I recommend to accept the paper for publication.

We thank the referee for their favorable comments and for their recommendation to accept the manuscript.