­­­­Referee Comments:

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Report of Referee A -- LF16145/Reens  
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This paper presents a combined electric and magnetic trap for OH  
molecules designed to minimize losses due to non-adiabatic  
transitions. The design allows the loss rate to be tuned and to be  
suppressed to small values. Experimental data on trap loss is  
presented that seems consistent with the predictions of a model of  
loss due to non-adiabatic transitions.  
  
In addition to presenting the new trap, the authors suggest that the  
paper brings new insights into the loss mechanism. I do not find this  
convincing. The mechanism rests on two ideas, outlined in the first  
two pages of the paper. The first is that the molecule is insensitive  
to small magnetic fields that are perpendicular to a strong applied  
electric field. This has been known for about fifty years and is a  
general result, not specific to any Hund’s case or even specific to  
polar molecules. It applies to atoms [e.g. J. Phys. B 3, 1620 (1970)]  
and to molecules with no orbital angular momentum [e.g. Phys. Rev.  
Lett. 89, 023003 (2002)].

We thank the referee for introducing us to this important connection with the existing literature related to the influence of magnetic fields on eEDM measurements. We believe this connection enhances the relevance of our work. It is indeed the case that the very same suppression of Zeeman influence over atomic and molecular eEDM measurements is related to the effect we describe. Nonetheless, there are important differences. The loss mechanism for molecules in traps results from the suppression of Zeeman influence in a plane where E and B are truly perfectly perpendicular, a situation not realized in eEDM searches but often unavoidable in a magnetically confining geometry for a trapped species. Moreover, while the suppression is actually beneficial for moleculer beam eEDM searches, it has grave consequences for molecule trapping experiments, which is an especially important message for those who are or who might search for eEDM with trapped molecules. Finally, we point out that while the effect can certainly occur for all species, the strength of the electric field required is dramatically less for molecules than other atoms.

The second idea is that, in regions where  
the electric and magnetic fields are perpendicular, and the magnetic  
field is weak, this suppression of the Zeeman splitting will lead to  
an enhancement of spin-flip losses. Reference [29] of the paper  
already discusses exactly this point, and in a way that is  
considerably clearer than in the present manuscript. In reference [29]  
the non-adiabatic loss rate is calculated as a function of electric  
field. I do not see anything in the present paper that differs from  
that calculation.

We agree that the essential theoretical details of the loss enhancement that we describe appear in the appendix of Ref [29], but we strongly believe that a separate publication is nonetheless warranted. To give a bit of history, our primary motivation for performing the work that led to this manuscript was related to the calculations in the appendix of Ref [29]. These were originally performed to allow the deconvolution of single particle spin-flip loss from electric field induced collisions, but we discovered that they might have contained an error large enough to entirely account for the collisional effect presented in Ref [29]. Wanting to have true experimental verification of these calculations before reaching any premature conclusions, we set out to study the single particle loss in a manner that could not be confused with any collisional effects. We have obtained this, and they confirm the theoretical details of the loss enhancement including the corrections we discovered. These corrections lead to a dramatically different message to the community. Our message is no longer “the loss exists and can be deconvolved” but “the loss cannot be deconvolved and must be carefully addressed by anyone working in similar regimes”. The present manuscript is not an attempt to restate the appendix of ref 29 as its own paper. Rather, it is the culmination of a detailed investigation we performed to follow up on the possible corrections required in that work.

We greatly appreciate the reviewers opinion about the lack of clarity of the description of the effect in the present work verses the appendix of ref 29. In light of this, we have devoted more space and endeavored to more clearly exhibit the effect. Regarding the differences in calculation between the appendix of ref 29 and the present work, we chose not to elaborate on this in the main text, since our suspicion is that the breadth of readership of the appendix of ref 29 may be limited. However, we have added a supplementary section that gets into this. Essentially the correction relates to the partition functions of the integrals performed to evaluate the loss rate. Instead of integrating over the entire 3D spatial distribution as in ref 29, we integrate only over the 2D plane where loss occurs, directly computing the loss flux rather than having to assume something about the crossing frequency of the molecules.

In my view, the novelty in this paper is entirely the new trap design  
and the demonstration that it suppresses losses that were a problem in  
an earlier design. That is an incremental advance which, in my view,  
does not warrant publication in Physical Review Letters. The work will  
certainly be of interest to specialists in the field of cold  
molecules, especially to others who might be interested in trapping  
molecules using a combination of electric and magnetic fields. This  
paper would be suitable for a more specialized journal once the  
following points have been addressed:

We strongly disagree with this view of our trap as an incremental advance. We specifically designed this trap not necessarily as our next generation trap but as an important testbed for spin-flip losses. Nonetheless, we can see how this interpretation is supported by our previous manuscript, and we are very grateful for the reviewers feedback in this area. We have modified our discussion and presentation to address this.   
  
1. The paper seems to be correcting two earlier papers. Those  
corrections are important but they are described too briefly to  
understand their implications. The first is to reference [29]. The  
correction is mixed up with the introduction to the paper and appears  
as a single sentence “subsequent investigations have revealed it to be  
a threefold underestimate, enough to render deconvolution of any  
remaining collisional effect difficult.” The authors should give a  
fuller account here and give a clear statement about the implication  
of this correction. Does it mean that the effects previously  
attributed to collisions in [29] are now accounted for entirely by  
non-adiabatic losses leaving no remaining evidence for collisions?

We agree that a full account is needed, and as we have described a bit above, this desire for a full accounting motivated the investigations that have led to this manuscript. We agree with the reviewer’s observation of the brevity of the corrections, and we address this in several ways in this new manuscript. Regarding the implications, the effects previously attributed to collisions are *almost* entirely accounted for, enough so that any remaining influence of collisions will need to be explored in a separate experiment that more clearly separates the collisional and the spin-flip loss effects.

The second correction is to reference [22]. The authors write “This new  
understanding modifies our interpretation of evaporation data for OH  
[22], especially at 5 mK where the loss rate is significantly enhanced  
by the E-fields used for RF knife purposes. We do find enhancements in  
normalized density at low fields for shallow RF knife cuts from 55 -  
30 mK.” The observation of evaporative cooling of OH is a very  
important result. The community should know whether or not there  
remains strong evidence for evaporative cooling under this modified  
interpretation. The statement currently given is not clear on this.

Regarding the evidence for evaporative cooling, the information we provide is precisely all that we now know: “We do find enhancements in normalized density at low fields for shallow RF knife cuts from 55 – 30 mK.” This is what remains of our evaporative cooling result, and it is certainly not the strong evidence that we previously claimed. Nonetheless, it is suggestive enough of the beginnings of an evaporative effect, that we are actively seeking to amplify the signatures of a collisional effect in our apparatus, and hope to study this further in a separate publication. Because of the importance of this to the community, we have added a supplementary section describing these “normalized density” claims.  
  
2. H\_{E perp B} has not been defined. The context of the sentence  
implies that it refers to “the exact eigenenergies of OH”. But it  
seems from perturbation theory that the series expansion of the  
energies will have a non-zero second-order contribution, i.e. when a  
small magnetic field is applied perpendicular to the applied electric  
field, the energies scale as B2, not as B3. The energy splitting  
between the M=±3/2 states scales as B3. Is that what is meant by H\_{E  
perp B}?

Yes, this is exactly what is meant by H\_{E perp B}, we are grateful for the observation of this oversight. We address this by modifying the first sentence of the paragraph: We can quantify by diagonalizing the molecular Hamiltonian in mixed fields to find the energy splitting between the well trapped substate and its spin-flip partner (Fig. 1a-c). *We denote this splitting H\_{E perp B}.*  
  
3. The paragraph about molecules in Hund’s case (b) seems incorrect,  
at least when hyperfine structure is included, which is often  
necessary. There will be a tensor Stark splitting which suppresses the  
Zeeman splitting in a perpendicular magnetic field, and this  
suppression is stronger for larger electric fields.

Perhaps the referee is saying the following… tensor Stark splittings suppress the Zeeman splitting in perpendicular magnetic fields, so that Hund’s case (b) molecules with hyperfine induced tensor Stark splittings still experience loss enhancement. This statement is in agreement with our assertions about Hund’s case (b), where we already explain that the spin-rotational coupling results in the Stark splitting still suppressing the Zeeman. The spin-rotational coupling is in general quite large, and usually more significant than hyperfine effects.

4. The paragraph that begins “We can develop a scaling law…” is too  
densely written for readers to easily follow. It is not clear why the  
expression given for kappa is the correct one. The expression is given  
in the context of the Landau-Zener formula. That formula contains the  
matrix element of a term in the Hamiltonian that connects the two  
states. The two relevant states here are stated: “the spin-flips we  
have discussed connect |f, 3/2> to |f,-3/2>”. But I do not think there  
is a term in the Hamiltonian that connects directly these two states  
and so it is unclear how the Landau-Zener theory is being applied. It  
would be better to take some space to set out the theory clearly –  
what is the Hamiltonian, what are the adiabatic states being  
connected, what is the matrix element that goes into the Landau-Zener  
formula, and how does this then lead to the result given? The result  
given for eta is similarly obscure; again it would be better to  
explain more fully how to arrive at this result.

We agree that this description is written rather densely, and we endeavor to make it much more manifest in the text in a number of ways. While it is true that the states are not directly connected by the Hamiltonian, an effective 2-state Hamiltonian can be used in the vicinity of the level crossing, whose coupling term can be directly calculated from the 8-state Hamiltonian by finding the energy gap between the pair of states at their crossing.

5. It is unclear how the model results given in figure 4 are obtained.  
The paper gives a scaling law that can be used to estimate when the  
spin “will flip with probability at least 1/e”. A calculation of the  
actual loss rate does not seem to be given, yet it seems necessary to  
have it in order to obtain the results presented in figure 4 and to  
give corrections to previous work.

Indeed, the scaling law calculates the flux of molecules with probability at least 1/e, but for the full loss calculations presented here, the loss rate is computed by integrating the flux continuously across all velocity classes in the ensemble, with appropriate Maxwell-boltzmann weighting. The key idea is to focus on the flux of molecules through the 2D regions given by E perp B, where the energy splitting is necessarily at its minimum along the trajectories of the molecules in question. This is also a key distinction with ref [29], where molecules are assumed to follow unrealistic orbits. In this case, we don’t need to know the full orbit of the molecule, only the brief snippet during its closest approach to a loss region.

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Report of Referee B -- LF16145/Reens  
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In LF16145, the authors report a major advance on trapping OH  
molecules. They manage to increase the lifetime of the trapped  
molecules from 5 to 500 ms. The long lifetime should enable future  
evaporative cooling of the molecules.  
  
The key idea here is to employ the Ioffe configuration to remove the  
Majorana spin flip when the magnetic field is vanishing at the trap  
center. A careful analysis of the trap configuration shows that this  
is bad when the external electric field is applied perpendicular to  
the magnetic field. A new trap configuration is presented with a bias  
field to eliminate the field zero, and indeed greatly suppressed trap  
loss is observed.

Yes, but there is a key difference between our configuration and the Ioffe. In Ioffe the bias also needs to provide axial confinement, and in general must be rather large to do so. Even when the smallest bias necessary is employed, the trap is considerably weakened. In our configuration, the bias field does not need to provide any confinement, and so unusually small bias fields are possible- we achieve our two orders of spin-flip loss suppression with a bias field that is only 4% of the trap depth, 200 G out of 5 kG.  
  
If such suppression of loss indeed comes from the removal of spin  
flips, I would very strongly recommend the publication of the paper in  
Physical Review Letters. It would represent a significant advance in  
extending the lifetime of a cold dense OH molecules, where evaporation  
and collisions have been reported. The only issue is that it is  
unclear whether the extended lifetime comes from the suppression of  
spin-flips or the sample in the new trap is just prepared at a much  
lower density. The authors should provide an argument that the long  
lifetime is indeed due to the removal of spin flips.

We thank the reviewer for this positive recommendation of our work. We agree that the removal of this loss is a significant advance, and we can confidently claim that the lifetime increase comes only from spin-flip suppression and not from density effects. In fact, clear disambiguation was a key motivation of our design, and we have decided to make this a point of emphasis in our manuscript.  
  
Without more data taking, one possible check is to calculate the new  
trap potential similar to Figure 2 (b). I am sure the authors did or  
can do that. Combined with the 175mK measured in Fig. 5, one can  
estimate the density of the sample. As long as it is not too much  
lower than the previous work in Ref. [22], I will be satisfied.

We thank the reviewer again for raising this important point. Were we to plot the trap potential after application of the bias field as in figure 2 (b), the lines would not deviate noticeably from those without the bias field. The fact that the spin-flip loss can be alleviated without noticeable perturbation to the trapping geometry illustrates just how surprisingly magnified the spin-flip loss is relative to the familiar atomic case.

Other minor issues in the order of appearance in the manuscript  
  
1. page 1 intro: Molecules in the degeneracy regime have been reported  
before the KRb experiments, for example, by Deborah Jin on K2, Rudolf  
Grimm on Cs2 and Li2, Wolfgang Ketterle on Na2 and Li2 and so on.  
These works should be cited.

We will gladly incorporate citations to the important alkali dimer degeneracy experiments.  
  
2. Fig. 1: Please put E=0 in panel (e) and E>0 in panel (f). The  
arrangement of the figures confused me since it suggests (b) and (e)  
are based on E//B; (c) and (f) are based on E \_|\_ B.

We have inserted these titles as suggested, and agree that this was confusing before.  
  
3. page 2: The sentence that "...the molecules must switch from the  
vector sum quantization axis to the vector difference quantization  
axis..." is confusing, since vector difference can be B-E or E-B. The  
latter E-B will still have the problem if E and B are are in the same  
direction. Please clarify the meaning of "vector difference".

Either vector difference gives the same “quantization axis” with which states can align or anti-align, so that B-E and E-B, which differ only by a sign, are effectively the same. We have thoroughly re-worked this section at this point, and hope we have achieved greater clarity.   
  
4. Table I. "experiment length 100 ms" needs clarification. This table  
contains a lot of information not discussed in the text. "Polarizing"  
is not explained, for example. The table is only mentioned briefly  
regarding a less important point, so may possibly go.

Partly due to the important ramifications of our manuscript for our previous works, we have decided to keep this table. It’s contents now feature further discussion in the supplementary material describing the implications of this spin-flip loss on the interpretation of evaporation and e-field induced collision experiments.  
  
5. page 3: The sentence "Another possibility is to use one field only,  
but any experiment which aims to make use of the doubly dipolar nature  
of molecules cannot accept this compromise" is not understandable. The  
author should mention the advantage of having the E field trap.  
Otherwise, why can't the field be turned off if it only hurts the  
experiment?

We have revamped the discussion of how the spin-flip loss can be thought about in more general geometries, and have endeavored to increase the clarity of remarks like these. We agree that turning off the field may be the best decision in some cases, but point out that one of the key advantages to working with a dipolar species is the utilization of both fields during the experiment.  
  
6. page 4: "It is seen that increasing B\_coil increases population  
fist at low fields and then higher fields". I believe a word  
"decreases" is missing, right?

Thanks for your observation. This was a bit confusing. We have actually removed this section in order to accommodate greater clarity in our description of the details of molecule enhanced spin-flip loss, pursuant to the comments of our first reviewer.  
  
A final comment, high value of B\_coil is a bad idea for trapping since  
the confinement is greatly weakened than a quadrupole trap. Bare  
minimum Ioffe field just enough to remove spin flips is preferred to  
maintain a high molecular density at the center. In addition to weak  
confinement, strong B\_coil also gives a shallower trap, which is  
likely the origin of the fast initial loss seen in Fig. 4a. This  
picture is consistent with the observed absence of density-dependence.  
The initial loss in this case would be plain evaporation for hot  
molecules to escape.

We agree with these statements as far as the Ioffe-Pritchard trap lift is concerned, but this is not an issue in our geometry for the reasons discussed above. We reiterate our gratitude for the reviewer’s emphasis of this important distinction between density and single-particle effects. We believe these comments have enabled us to prepare an even stronger manuscript.

Possible Supplementary Material regarding Evaporation…

A. Regarding Corrections to Previous Work.

The present study on the role of mixed fields for spin-flip loss introduces important modifications to previously published work, especially reference 29 on electric field induced collisions and reference 22 on evaporation.

With regard to ref 29, an initial awareness existed of the possibility that spin-flip losses might interfere with a collisional effect when electric fields were applied. The problem was approached by considering spin-flips induced by variations in E-B angles along molecular trajectories. A particular class of possible molecule orbits was studied in an effort to perform some first order deconvolution of the effect. In the present work, we discover that it is specifically the plane where E-B are perpendicular that losses can occur, and calculate the loss probability based only on the flux of molecules through this plane. This enables calculations to be performed for all classes of possible molecules. The result ends up differing from that performed in ref 29 by only a factor of 3, but this is sufficient to eat away most of the remaining collisional effect. Unfortunately it is not yet possible to say exactly how much might remain, because it is not enough to resolve clearly without a new, dedicated experiment in a spin-flip free situation. This is an active area of investigation in our lab.

With regard to ref 22, the present study is only one of a number of important modifications to our understanding that have come up in the past few years. The first is related to the approximate Hamiltonian used for interpretation of microwave spectroscopies. As discussed in ref. “Hyperfine structure of the hydroxyl free radical (OH) in electric and magnetic fields” from L. Carr 2015, centrifugal perturbations result in a 15% correction to the inferred magnetic field at a particular microwave frequency. This would only shift the fitted temperatures a bit colder, except that it also changes the location of avoided crossings, and renders the assumption of a Boltzmann suppression factor related to these crossings untenable. The data show a sudden suppression below 480 G, but the crossing is actually located closer to 400 G. Without this, the fits used to calculate temperature when the population ought to be significantly built-up at lower magnetic fields are no longer trustworthy.

In fact, the unreliability of the deeper cutting spectra in ref 22 ( all but the shallowest, panel (c) of figure 3) is the same conclusion implied by the present study of spin-flip losses, which show that at low temperatures the spin-flip loss caused by the electric field used during evaporation are too large. It is still possible to ignore the fits, and use the normalized spectra to look for any enhancements in density at fields below the evaporation endpoint. Normalization does become harder to do properly without a fitting function, as integrated curve area necessarily conglomerates point uncertainty, but nonetheless our routines consistently demonstrate some enhancement.

We have also developed a few more sensitive tools to look for collisional or evaporative effects. One is to compare the populations under two related conditions- the first a normal evaporation sequence and the second an evaporation with time-reversed microwave frequency. In other words, the cut goes backwards from deep to shallow. This comparison subjects all molecules to the same integrated microwave power, and thus the two conditions would be equivalent in a situation with only single particle effects. With evaporative effects, the normal condition ought to perform better. This is indeed what we consistently observe, at the 5% level, see the attached.

Another tool we have pursued is the precise calibration of our LIF system, using a careful comparison to Raman scattering of H2, as described by William K. Bischel et al in “Absolute Calibration of a fluorescence collection system…”. Our results suggest that since 2014, our molecule number has been in the 1000 range, yielding a peak density of 10^7/cm3 assuming a thermal distribution, and a collision rate of not more than 0.1/s. This value would be far too low even for a slight evaporation during a 100 ms experiment, but it is possible that some decline in system performance could be involved, since we have a record of decreased voltage conditioning performance in our decelerator.

A final tool is the ability to reduce our density in a tunable manner via microwave depletion during deceleration, described and used in the present text. It is crucial for such a tool to reduce density without perturbing the distribution of the molecules, and for this reason we have not successfully developed such a tool before. For example, reducing the concentration of water at the very beginning of our experiment would change the discharge efficiency and change the efficiency of cooling during supersonic expansion. This tool enables searches for collisional effects by comparing experiments performed identically except for changes in the density of OH molecules. Unfortunately it can only do so by reducing the density, when obviously collisional effects would be most evident upon increasing it.

In conclusion, the evaporation results in ref [22] are significantly weakened by spin-flip loss and by modifications to the effective Hamiltonian. Efforts to calculate density suggest that it may simply have been too low, although back-application to the 2012 system is not possible. Nonetheless spectroscopic comparisons and evaporation subtractions still suggest an evaporative effect.