QSS44 - Dietrich Leibfried - Questions & Answers

Dietrich Leibfried

Bill Philipps: You mention molecules with good Franck-Condon factors, which are "special". Is quantum logic a possible route to doing laser cooling on more general molecules? Not by sympathetic cooling, via collisions, but in this more sophisticated way? Does this make any sense?

DIDI: For molecules it is not sufficient to address just the translational motion, which can be done relatively easily for molecular ions by sympathetic cooling with the co-trapped "logical" ion. For molecules with a dipole moment, the vibration often takes care of itself; excited states are coupled to the electromagnetic vacuum, so the molecular vibration decays to its ground state by spontaneous emission of photons, just like electronic excited states decay. The rotation reaches equilibrium with the blackbody radiation from the environment of the molecule, and in equilibrium at 300 K a lot of states are populated. It is possible to laser cool the rotation to some extent, this has been demonstrated by Michael Drewsen's group in Aarhus for MgH+ [Staanum et al., "Rotational laser cooling of vibrationally and translationally cold molecular ions", Nature Phys 6, 271 (2010)] and by Brian Odom's group for SiO+ [Lien et al., "Broadband optical cooling of molecular rotors from room temperature to the ground state", Nat Commun 5, 4783 (2014)]. These demonstrations required special lasers that were tailored to the molecules under study. With quantum logic and Raman transitions, a single near infrared continuous wave laser that is in no way specific to the molecule under study is enough. We like to think that this simplicity and generality makes this method quite sophisticated. Time will tell whether the idea is a general as we suspect it is right now.

What are the conditions on the molecule / molecular transition for the logic spectroscopy to work? Does this work for any ion?

DIDI: The molecule must have a decent shared normal mode of translational motion with the logic ion. This requires "impedance matching", the charge-to-mass ratio of the molecule and the logic ion should not be too different. A rule of the thumb from sympathetic cooling and quantum logic with atomic ions states that the ratio of charge-to-mass ratios of the logic ion and the molecule can be at least as large as three. Quantum logic at approximately such a mass ratio was successful in the first quantum logic clock with 9Be+ and 27Al+. The lightest good logic ion is 9Be+, which may well work down to the lightest molecular ion H2+, which would be very interesting to study. The heaviest good logic ion in 173Yb+ that should allow for singly charged molecular ions up to a mass of 519 amu, which includes small proteins. If one allows for multiply charged molecules, the mass range may be extendable accordingly. The highly charged atomic ion Ar14+ has been successfully interrogated by quantum logic spectroscopy [Micke et al., "Coherent laser spectroscopy of highly charged ions using quantum logic", Nature 578, 60 (2020)]. For the last question "Does this work for any ion?", the direct answer is "No, but it should work for a lot of ions. The specifics are in the answer to Philipp Schindler further below.

Bill Philipps: How does the CaH+ equilibrate its vibrational motion? Long-range collisions with the other Ca+ would seem (and I guess I am wrong) ineffective in damping vibrational motion. How is it different for rotational motion?

DIDI: As long as the molecule has an average dipole moment, the vibrational motion will decay by spontaneous emission of photons. Like in laser cooling of atoms, the electromagnetic vacuum is a near perfect "T=0" environment for the photons emitted when vibrational states decay. For CaH+

the vibrational states only need a few 10 ms to decay to their ground state. Decay times are longer than for electronic excited states, mostly due to the fact that the transitions are at longer wavelength. The dipole matrix elements of "typical" molecules are order elementary charge times the Bohr radius, similar to "typical" atoms. The rotational spectrum has much lower transition energies that overlap with the blackbody radiation at room temperature, so photons from this bath are not only emitted but also absorbed by the molecule, leading to a thermal equilibrium with finite population in excited states.

Does the idea of quantum logic spectroscopy transfer over from the ion case to the general system of two two-level systems or spins coupled to the same harmonic oscillator? How about two atoms in a cavity for example or motional excitations in a large molecule?

DIDI: In principle any system in which different two-level systems can be coupled with "sidebands" to a shared harmonic oscillator degree of freedom should be suitable for quantum logic spectroscopy. It is necessary to be able to prepare the harmonic oscillator in its ground state and to bring the two systems into resonance with the harmonic oscillator. For two identical atoms, there is no natural distinction between "spectroscopy atom" and "logic atom", so it seems like one needs to find two distinct atoms that share a resonant transition that can be coupled to the same cavity. I can imagine that Raman transitions could be the way to go again, because one can relatively freely choose one of the photons as long as the other photon provides the proper energy difference, and if the Ramancoupling is sufficient to drive the spectroscopy and logic sideband transitions well within the decay time of the cavity. Motional excitations of molecules encompass rotation, translational and vibrational motion (how to classify vibrations is a bit of a matter of taste), so we are already working on all three of these (controlling vibrational excitations still has to be demonstrated). Large molecules are harder to control. Please read the answer to Philipp Schindler for more details.

Mackenzie Suben: For the Raman transition, is the main scattering rate due to the upper electronic state, do you see influence from the higher vibrational states or are the FCF too weak?

DIDI: The main scattering rate is through the excited electronic states. This is mostly due to the larger Raman-detuning to vibrational transitions. Their frequencies are so low that in essence the detuning is almost equal to the full energy of the Raman photons. As far as matrix elements to the excited electronic state are concerned, it turns out that one gets to sum over the FCFs of the vibrational states in the excited electronic states and at least for CaH+ these factors sum up to order one. In other words, the Raman-Rabi frequency is not diluted by the fact that there are several vibrational states within the excited electronic manifold, but almost looks like one would expect for a single excited state with no vibrational sub-structure.

Bill Philipps: Would you say a little more about where the entropy goes when you "cool" something by observing what state it is in?

DIDI: That is a great question, and I am afraid that I did not answer it very well during the talk and also the talk itself did not really explain this aspect. A molecule in rotational equilibrium at room temperature typically has many rotational states populated. In CaH+ the lowest 11 rotational states have populations of 1% or more. We "find" the rotational state by sifting through transitions one by one until we "catch" or "project" or "collapse" the rotational state by finding that we have driven the corresponding signature transition. Before getting there, every time we don't drive a signature transition, we know the molecule is not in that state and can cross that state off the list. In this way we reduce our ignorance or equivalently remove entropy from the molecule. This process of searching involves a lot of energy to prepare the logic ion and to cool the joint motion to the ground state, so we are not defying any laws of thermodynamics. I still think that one could still loosely call the logic ion our "Maxwell's demon" that sifts through the states for us and alerts us when the state of the molecule has been found. Even more food for thought: Instead of reading out the molecule with the logic ion, we can also use it to cool the motion back down to the ground state after exciting

a certain transition in the molecule on a blue sideband that excited the motion. This makes the sideband transition a one-way process, because the molecule can't Rabi-flop back to where it came from once the motional quantum that is essential for reversing the transition is removed. So, rather than learning about the state, we just make the transition irreversible by using the logic ion and its coupling to the electromagnetic vacuum as a "zero-temperature environment". Now, rather than learning about the molecule, it looks a lot more like traditional laser cooling/optical pumping where the information (entropy) is just dumped into the environment. This shows that the two approaches are intimately related. In one case, we learn information to remove the entropy. In the other, we leave traces in the environment (the photons we scatter to cool the logic ion back to the ground state in case a transition on the molecule has added a quantum of motion) that requires the quantum state to change irreversibly. The moral of the story to me is that humans can be (via a few detours through the logic ion) the witness to "collapse" the state, but it also works if no human ever looks at the record, so it appears like Wheeler's friend is a sufficient but not a necessary condition for state "collapse".

Bill Philipps: The upper trace for J = 1 Ramsey doesn't look like a good fit. What is the explanation for this?

DIDI: Experimental imperfections. Collecting this data is a slow process and we are infrequently recalibrating the experiment in between data points. Most likely the experiment was drifting off and starting to fail in the few points that went astray and then a subsequent calibration put us back on track. However, the number of data points off the fit is consistent with the single standard deviation the uncertainty bars show. Therefore, we believe our fit is a fair representation of the coherence in the experiment. We hope to continue to improve the experiment until statistical uncertainties (projection noise) dominates over such driftrelated issues.

Bill Philipps: There is a lot of talk about dipole moments, but nothing has a dipole moment if it is in a state of good parity, e.g., in a rotational eigenstate. How does this perspective fit with all of this?

DIDI: A non-symmetric molecule is a great system to think about this. In the frame of reference of such a molecule the states have no definite parity, in other words the wavefunction is not symmetric or anti-symmetric under reversal of a coordinate. Good parity would mean that one can mirror the wavefunction around a chosen origin and either have the same wavefunction ("even") or one that only needs a global sign change ("odd"). For CaH+ (and any other non-symmetric molecule) this is not the case. You can definitely say that the Ca-nucleus is left or right of the center of mass and no sign change can make that unseen. Of course, we are not observing the molecule in its rest frame but rather in the laboratory. Unless one does this extremely fast, observations are averaged over many rotational periods so to a very good approximation, the Ca-nucleus spends as much time on one side of any plane containing the rotation axis as on the other. For the rotational ground state, quantum mechanics prescribes a completely isotropic distribution, corresponding to a classical system that is not stabilized against torques by its rotation. In ground and excited rotational states, the description in the lab-frame averaged over many rotational periods effectively has good parity. For excited rotational states, we can find the axis of rotation in the lab more and more precisely (this is essentially what the growth of m-states associated with larger J allows for) and if we prescribe an axis of quantization, for example by imposing a static magnetic field that can torque the rotational magnetic moment of the molecule, we can know how rotation is oriented relative to this lab-axis within the bounds of the uncertainty principle. Finally, dipole moments make themselves clearly noticeable by the fact that there are radiative rotational and vibrational transitions in non-symmetric molecules while these transitions are absent for symmetric molecules where the parity symmetry holds even in the frame of reference of the molecule. One way of thinking about this is that the radiation that the molecule emits or absorbs when making (say) a rotational transition is changing on the timescale of the rotation, so in the "rotating frame" of this

radiation, the dipole moment of the molecule is not averaged out but has a well-defined orientation. This makes the dipole moment of the molecule an important and observable factor in its physical behavior, no matter which frame of reference on uses for observations.

Philipp Schindler: Hi Didi, great talk. If you have a more complex molecule, you need to include more rotational states that might be populated initially. Can you estimate how many levels can be populated before imperfections in the readout become a problem?

DIDI: Thanks Philipp, I am glad that you liked it. Larger molecular ions will have more nuclear spins, a more complicated rotational structure and open shell electrons that lead to spinorbit coupling and hyperfine structure. There will be a lot more Hilbert space to search through to finally project the molecule to a pure state. One can hope to overcome this in two ways: One is to just make the environment colder. In equilibrium with a 4 K blackbody a lot less states are substantially populated compared to 300 K. In addition, the equilibration processes slow down a lot at cold temperatures, so compared to 300 K, the rotational states change in "slow motion". Therefore, we have started to set up a cryogenic system that also has a more versatile molecular beam attached to the trap to allow for quick changes of the molecular ions we load next to the logic ion. The second possibility is to allow some time for the tedious initial search, but then to keep a tight record of what the molecular state is doing. Fortunately, rotational transitions due to blackbody radiation have very strict selection rules, so if one has found the rotational state once and then loses it, there are only the few "neighboring" states allowed by the selection rules that the molecule may have "escaped" to and one would hope to quickly locate the new state (much faster than the average time to the next transition) and then either work from the newly located state or bring the molecule back to where the "escape" started. This neat picture breaks down for collisions with background gas. Unless the gas is very cold, many partial waves are populated and even a single collision can have the molecule end up in a wildly different rotational state. This is another good reason to go to cryogenic environments where the background gas density can be very low. How well these strategies will work needs to be determined, but we hope to be able to interrogate more complicated molecules in this way. Another direction is to look at symmetric molecules such as $H2+$ or $N2+$, etc. They will not equilibrate with the surrounding radiation, but one can still drive Raman-transitions, because these involve induced dipole moments of the electrons and are even possible in the rare case where there is no stable excited state, which holds for $H2+$. Background gas collisions can still be a factor, because the charge of the symmetric molecular ion can induce a dipole moment in the approaching neutral atom or molecule (Langevin collision). For $H2+$ these collisions would even be resonant, so a very good cryogenic vacuum seems a like a necessity to have any hope to keep track of the states in that molecule.

Brandon Iritani: Perhaps a somewhat naive question, how do you control the Raman light shifts with the comb spectroscopy?

DIDI: Not a naïve question at all. Such shifts are important and need to be controlled. Fortunately, there are a few tricks that work especially well for very large Raman-detuning to eliminate the lowest order light shifts. The basic idea is to have the polarization of the Raman beams look equivalent to unpolarized light. We do this by using twice the intensity for s-polarized light compared to the p-polarized beam. By definition, unpolarized light cannot act differently on states based on their orientation in space, therefore all it can do is shift all m-states by the same amount, irrespective of m-state. The shifts can be different for different J-states, but their spacing is small compared to the detuning we use, leading to small differential shifts between J-states as well. We try to account for the remaining differential shifts by measuring transition frequencies at different intensities and extrapolating to zero intensity. Finally, when doing comb-spectroscopy, one has to be wary of so called "four-photon shifts". These can be largely avoided by choosing the repetition rate of the comb suitably. More details on light shifts can be found in our publications.