Vibrational Spectroscopy of Trapped and Sympathetically Cooled Molecular Ions

Internship presentation

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Vibrational Spectroscopy

Degrees of freedom

Molecular structures give rise to internal degrees of freedom, e.g For linear molecules there are total 3N degrees of freedom including 3 translational, 2 rotational and (3N-5) vibrational

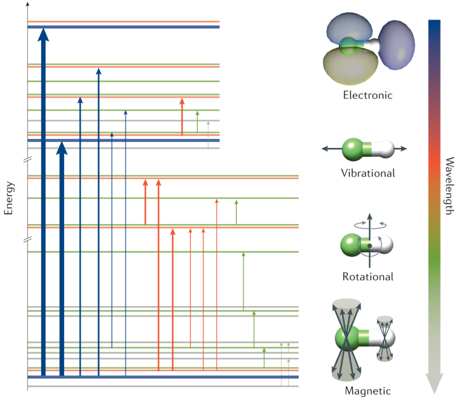


Figure 1: General scheme of the order of transitions for different classes of degrees of freedom

Sympathetic cooling and Laser-trapping

Quadrupole Ion Traps ("AC" Traps)

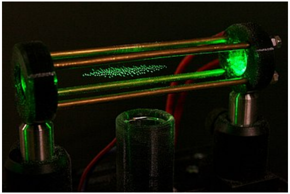


Figure 2: Paul Trap

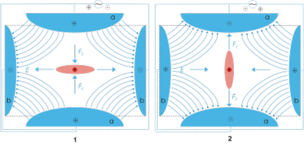


Figure 3: Quadrupole Ion Trap

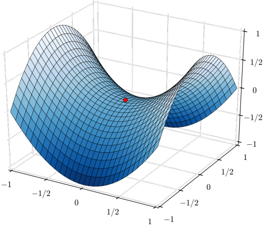


Figure 4: Saddle Point graph analogy

Sympathetic cooling

How?:

- Coulomb interaction between two species (Coolant ions and target ions)
- Laser cooling to reduce kinetic energy

Why?:

- Particles exchanging energy through Coulomb interactions (Maxwell-Boltzmann distribution $f(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{m v_s^2}{2 k_B T}\right)$) leading to **Reducion of Doppler broadening**, $\Delta\lambda_D = \lambda_0 \sqrt{\frac{8 k_B T \ln 2}{m c^2}}$.
- Reduce perturbations by the field on target ions
- High-resolution spectroscopy

How good?: reaching T $\sim \mu K$

Ion Coulomb Crystals

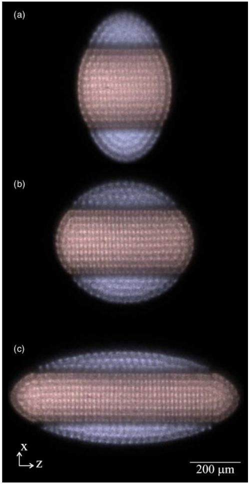


Figure 5: Projection images of two-species ion Coulomb crystals containing 1500 40 Ca + ions (red) and 2000 44 Ca + ions (blue) at different settings of the end-cap potential, U end . The camera exposure time is 100 ms and the trap potentials are U rf = 540 V and (a) U end = 46.1 V, (b) U end = 30.2 V and (c) U end = 13.8 V, respectively.

Post Hartree-Fock methods: CCSDT

Why CCSDT?

The Hartree-Fock mehtod:

- The foundational tool in qunatum and computational chemistry
- But does not account for electrons' correlation energy

Post HF methods:

- CI (Configuration interaction), (CIS, CISD, CISDT)
- CC (Coulpled Cluster)
- DFT (Density Functional Theory)...

Why CCSDT?

CCSDT and its advantages:

- Exponential Ansatz: $|\Psi\rangle = e^{T} |\Phi_0\rangle$
- Singles (T_1) :

$$T_1 = \sum_{i,a} t_i^a a_a^\dagger a_i$$

Here, i and j denote occupied orbitals, a and b denote virtual orbitals, $a_a^\dagger$ and a_i are creation and annihilation operators, and t_i^a are the single excitation amplitudes. Doubles (T_2) :

$$T_2 = \frac{1}{4} \sum_{i,j,a,b} t_{ij}^{ab} a_a^\dagger a_b^\dagger a_j a_i$$

- Fast convergence.
- Lower computatinal cost

Results for the PES (Potential Energy Surfaces) scans for the MgH+ molecule

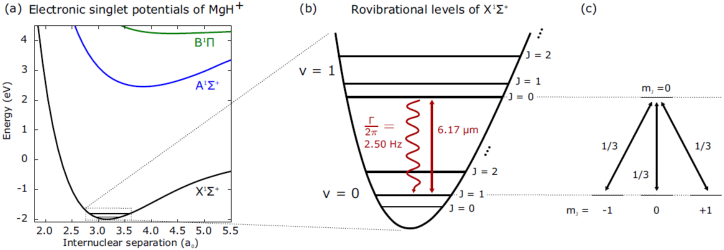


Figure 6: The electronic singlet potentials of MgH+. Only the electronic ground state X 1 + is considered in the simulation. (b) Rovibrational structure of the electronic ground state X 1 + showing the closed transition of interest |v = 0, J = 1 - |v = 1, J = 0. The decay rate of t = 2 Œ 2.50 Hz is the slowest timescale of our experiment and spontaneous emission is negligible. (c) Sublevels of the |v = 0, J = 1 and |v = 1, J = 0 states showing the norm squared of the Clebsch-Gordan coefficients.

Atom-light interactions and Einstein coefficients (for cooled atoms)

Toy model of 3 level system

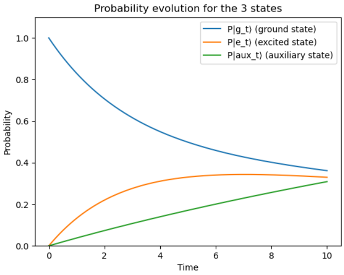


Figure 7: Probability evolution of a 3 state system

$$\frac{d}{dt}P_{|g_t\rangle} = -R_{\mathrm{abs},0}P_{|g_t\rangle} + \left(|\tilde{\xi}|^2 R_{\mathrm{stim},0} + \tilde{D}\Gamma_t\right)$$

$$\frac{d}{dt}P_{|e_t\rangle} = -\left(\Gamma_t + R_{\mathrm{stim},0}\right)P_{|e_t\rangle} + |\tilde{\xi}|^2 R_{\mathrm{abs},0}P_{|}$$

$$\frac{d}{dt}P_{|\mathrm{aux}\rangle} = \left[(1-\tilde{D})\Gamma_t + \left(1-|\tilde{\xi}|^2\right)R_{\mathrm{stim},0}\right]P_{|e_t}$$

$$+\left(1-|\tilde{\xi}|^2\right)R_{\mathrm{abs},0}P_{|g_t\rangle}.$$

Einstein A coeft1cients, A_{ij}, are found from the wavefunctions and the permanent dipole moment:

$$A_{ij} = \frac{\omega_{ij}^3 \, |D_{ij}|}{3 g_i c^3 \epsilon_0 \hbar \pi},$$

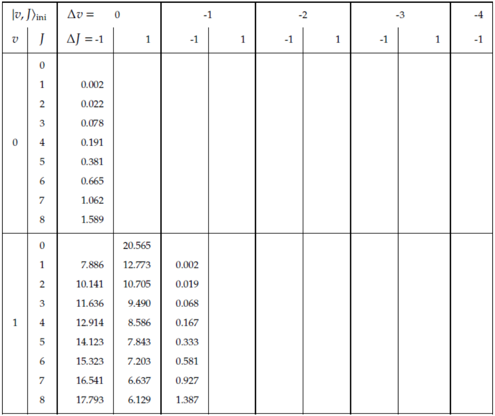
where $|D_{ij}|$ is the transition dipole moment between the states and g_i is the degeneracy of state i. The corresponding Einstein B coefficients are given by

$$B_{ij} = \frac{c^3}{4 h v_{ij}^3} A_{ij}$$
$$B_{ji} = \frac{g_i}{g_j} B_{ij},$$

where $v_{ij} = \omega_{ij}/2\pi$ is the frequency difference between state i and state j, and $g_i = 2J + 1$ is the degeneracy of the state i with rotational quantum number J.

Expectations

Our current findings for the coefficients agree to about 5% to 10% with the litterature



$\lvert v, J\rangle_{\text{ini}}$		$\Delta v =$ 0		-1		-2		-3		-4
v	J	$\Delta J =$ -1	1	-1	1	-1	1	-1	1	-1
0	0									
	1	0.002								
	2	0.022								
	3	0.078								
	4	0.191								
	5	0.381								
	6	0.665								
	7	1.062								
	8	1.589								
1	0		20.565							
	1	7.886	12.773	0.002						
	2	10.141	10.705	0.019						
	3	11.636	9.490	0.068						
	4	12.914	8.586	0.167						
	5	14.123	7.843	0.333						
	6	15.323	7.203	0.581						
	7	16.541	6.637	0.927						
	8	17.793	6.129	1.387						

Figure 8: Einstein A coefficient for transitions within the electronical ground state of MgH+

References I