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Vibrational State Resolved Lifetimes of the Na2 21Σ+u Double Well State

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Lifetime Measurements of the $2^1\Sigma_u^+$ state of Na_2

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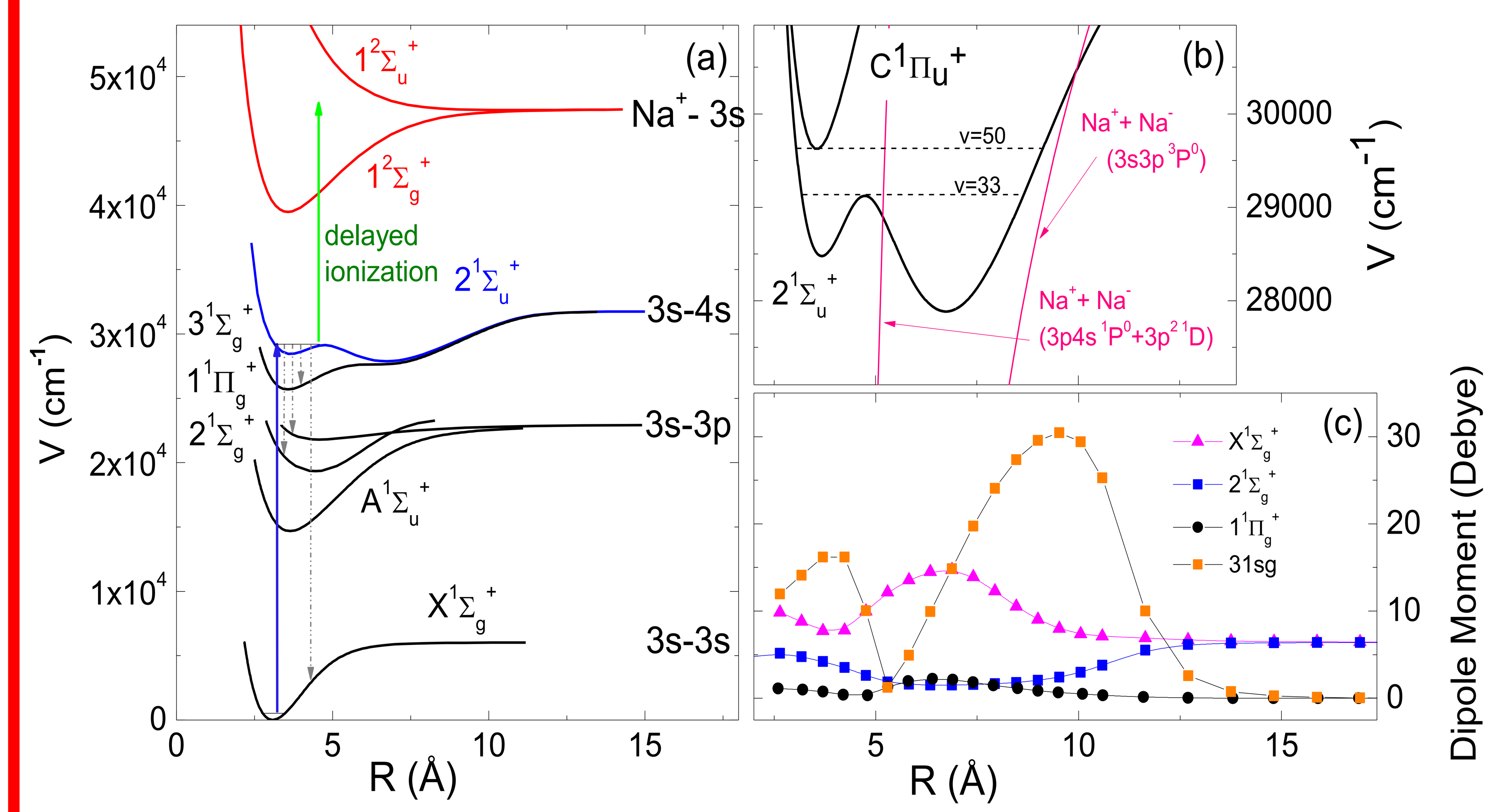
Abstract

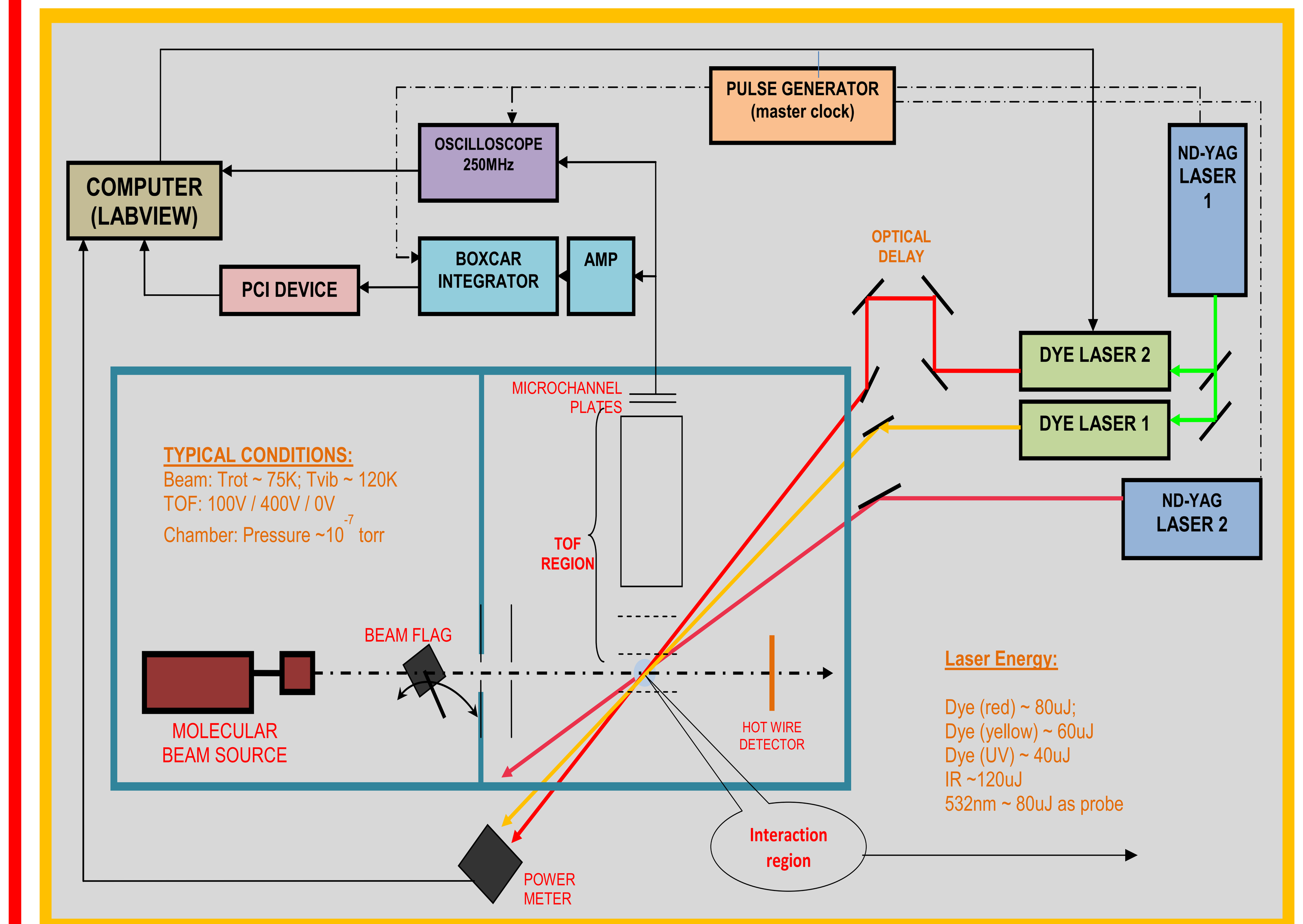
Lifetimes of individual Na_2 ro-vibrational levels of the $2^1\Sigma^+_u$ double well-state have been measured using a delayed photoionization technique. Ground state Na_2 molecules, produced in a molecular beam, are resonantly excited by the frequency doubled output of a pulsed dye laser (333–357 nm). They are subsequently ionized by one 532 nm photon from a time-delayed Nd:YAG laser. By appropriate tuning of the excitation laser and systematic variation of the probe laser delay, (partially) ro-vibrational level resolved lifetimes are obtained for v'=22-49.

We have also performed calculations of corresponding lifetimes using the LEVEL8.2 and BCONT programs by LeRoy[1], the latter in a version modified by Brett McGeehan[2]. Using only bound-bound transitions, we find theoretical lifetimes to be larger by a factor of up to 2 compared to the experimental values. Inclusion of pertinent bound-free transitions improves the agreement noticeably.

Excitation Scheme & Transition Dipole Moments

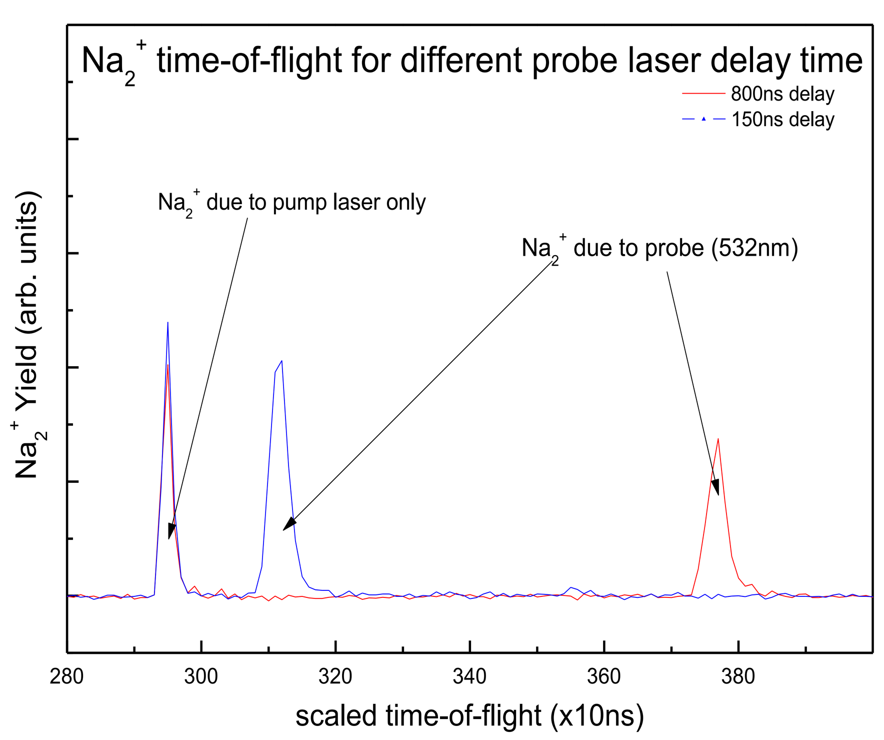


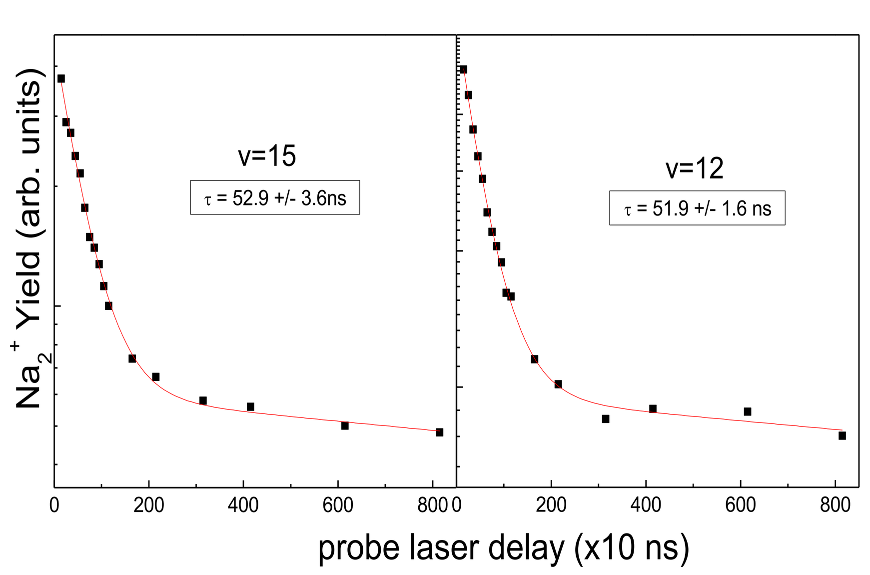
Experimental Set-up



Methodology

- Ground state Na_2 is resonantly excited to the $2^1\Sigma_u^+$ state by a frequency-doubled dye laser (28,000 to 30,000 cm^{-1})
- Nd:YAG laser (532 nm) with variable delay is used for ionization
- Signal is corrected for any contribution from non-resonant channels



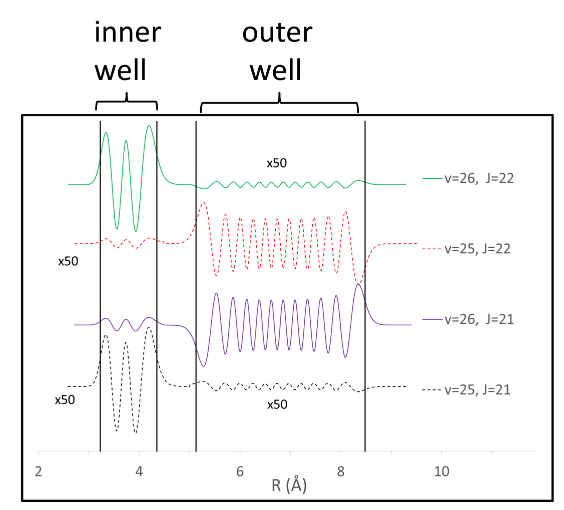


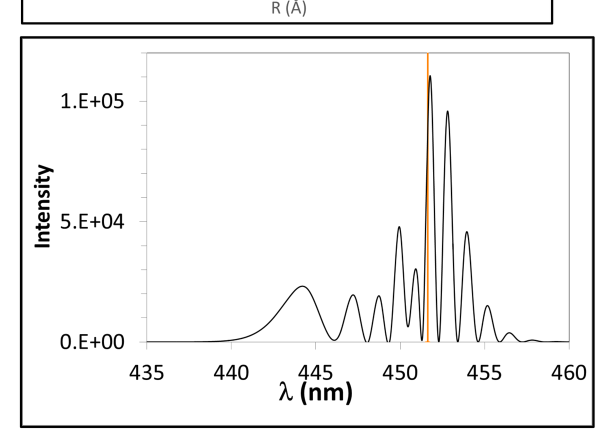
Calculation

- Schrödinger Equation is solved for bound and continuum states using the program[1] Level 8.2 and a modified version of the BCONT program[2], respectively
- Einstein Coefficient

$$A=\frac{16\pi^3}{3}\frac{\nu^3}{\varepsilon_0 hc^3}\frac{S(J',J'')}{2J'+1}\left|\left\langle\Psi_{v',J'}\right|M(r)\left|\Psi_{v'',J''}\right\rangle\right|^2$$

- Potential data:
  - $X^1\Sigma_g^+$ and $B^1\Pi_u^+$ from Camacho[3]
  - $A^1\Sigma_u^+$ from Kaminsky[4]
  - $2^1\Sigma_u^+$ from Kowalczyk[5]
  - $1^1\Pi_g^+$; $2^1\Sigma_g^+$ from Barrow[6]
- Dipole moment functions, M(R) private communications by S. Magnier.
- Assignment of absolute vibrational quantum number associated with given inner well level depends on rotational quantum number
- Bound-continuum contributions to Einstein coefficients are matched to discrete bound-bound values with help of modified BCONT program





References

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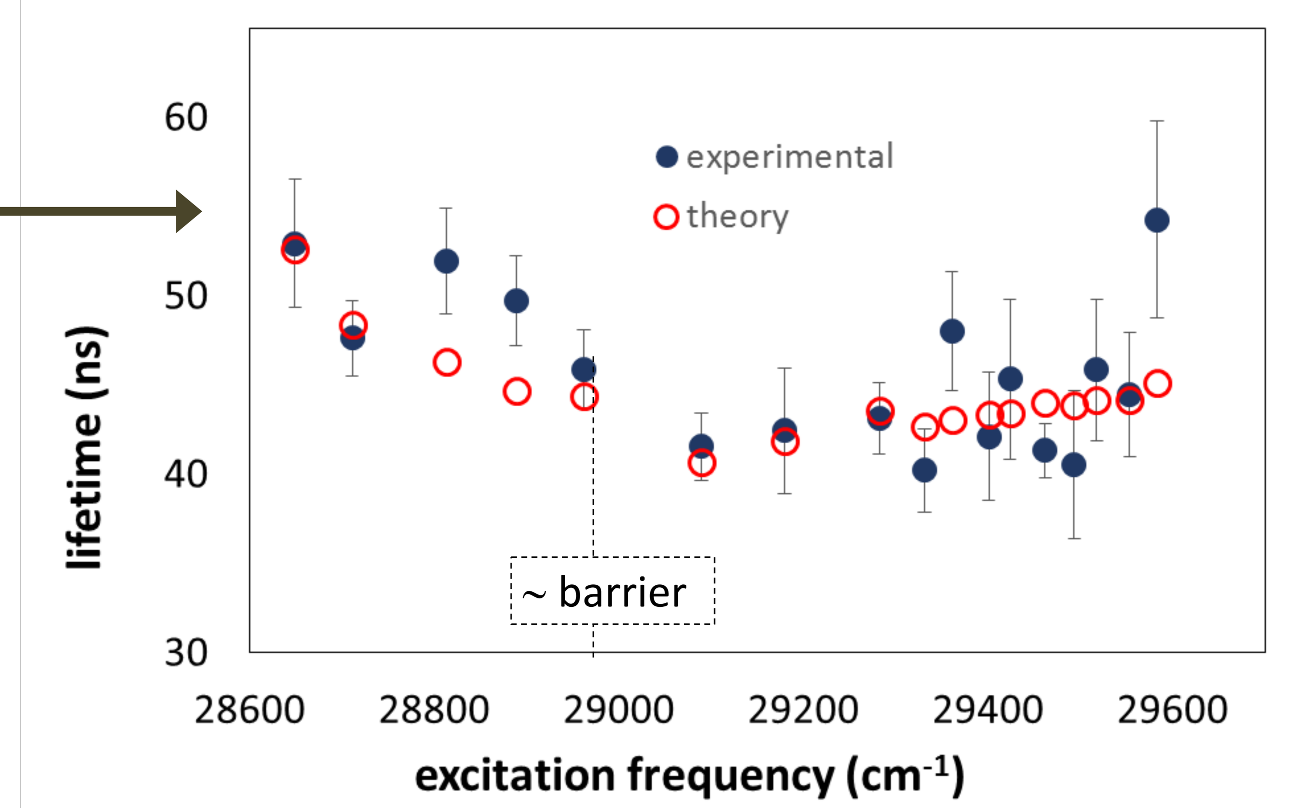
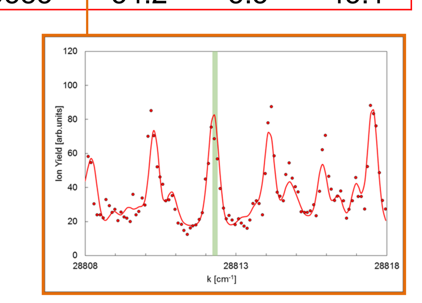
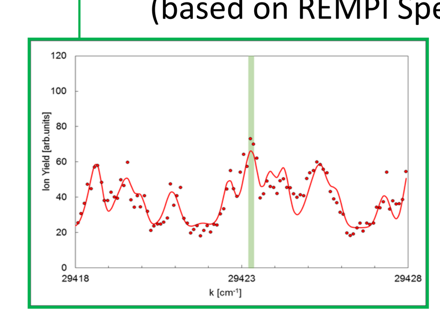
Results

run #	line	lifetimes in ns exp τ	Δτ	calc τ
1	28649	52.9	3.6	52.6
2	28711	47.6	2.1	48.3
3	28812	51.9	2.9	46.3
4	28888	49.7	2.5	44.7
5	28962	45.9	2.2	44.4
6	29089	41.5	1.9	40.7
7	29179	42.4	3.5	41.8
8	29282	43.1	2.0	43.5
9	29331	40.2	2.3	42.6
10	29361	48.0	3.3	43.0
11	29401	42.1	3.6	43.4
12	29423	45.3	4.5	43.4
13	29461	41.3	1.5	44.0
14	29493	40.5	4.2	43.8
15	29517	45.8	4.0	44.2
16	29553	44.4	3.5	44.2
17	29583	54.2	5.5	45.1

Experimental vs. Calculated Lifetimes of the $2^1S_u^+$ State of Na_2

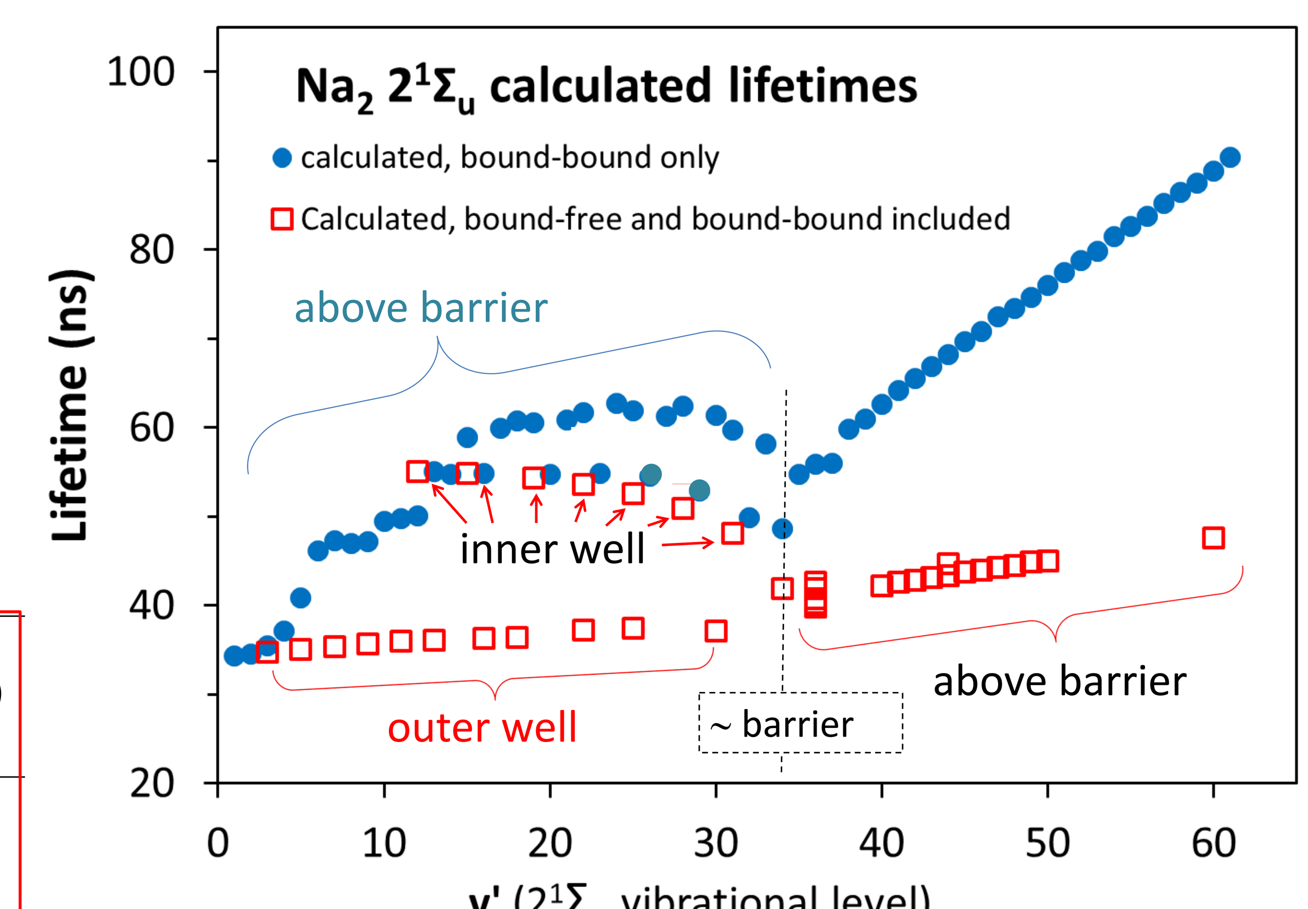






Sample Line Assignments (based on REMPI Spectrum)

solid lines = spectral simulation
symbols = experimental data



Other Lifetimes (ns)
(first two used to validate methodology)

	Our Results	Literature
$3p^2P$	16.45 ± 0.2	16.299 [7]
$4p^2P$	107 ± 3	108.2 [8]
$2^1\Sigma_u^+$	40.2 – 54.2	52.5 [9]