Strong Quantum Level Dependence of Na_2 ($4^1\Sigma_g^+$) Lifetimes

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Abstract

Radiative lifetimes of Na_2 ro-vibrational levels of the $4^1\Sigma_g^+$ state have been calculated in a continuation of our previous work[1] to investigate the importance of including the bound-free transitions into radiative lifetimes. The lifetime calculations are performed for selected vibrational levels from 0 to 75 and rotational levels, J=1, 20, 40, 60, and 80 and for rotational levels from 0 to 90 in vibrational levels v = 49, 50 and 51. We find that radiative lifetimes vary significantly with vibrational level, particularly around the shelf state. In addition, we observe a strong, unusual oscillatory radiative lifetime dependence on rotational quantum number. Another aspect we want to emphasize is the significance of including the bound-free transitions into the calculation which reduces the lifetime noticeably compared to the results of recent work that did not include this channel[2]. The lifetimes of individual ro-vibrational levels of the $4^1\Sigma_g^+$ shelf state were calculated using the LEVEL 8.2 and BCONT programs by Robert Le Roy, the latter in a version modified by Brett McGeehan.

Lifetimes of excited states of molecules

Lifetime τ_i of a initial level i = (α', v', J'),

$$\frac{1}{\tau_i} = \sum_{\alpha''}\left(\sum_{v'',J''} A^{\alpha'\alpha''}_{v'J',v''J''} + \sum_{J''}\int_0^{E_{i\alpha''}} \Gamma^{\alpha'\alpha''}_{v'J',E''J''}dE''\right) \qquad ; f = (\alpha'', v'', J'')$$

$$A_{if} \equiv A^{\alpha'\alpha''}_{v'J',v''J''} = \frac{16\pi^3}{3}\frac{k_{if}^{\ 3}}{\varepsilon_0 h}\frac{S_{J'J''}}{2J'+1}\left|\left\langle \psi^{\alpha''}_{v''J''}(R)\middle|M_{\alpha'\alpha''}(R)\middle|\psi^{\alpha''}_{v''J''}(R)\right\rangle\right|^2 \leftarrow \text{Bound-Bound}$$

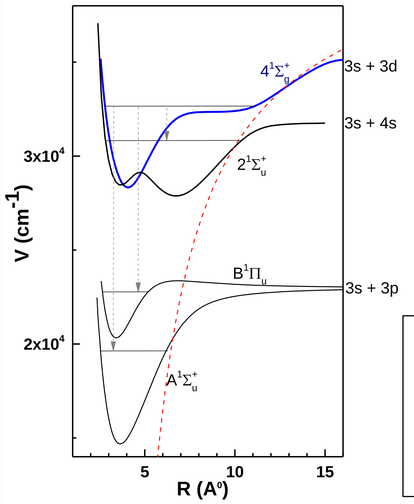
$$\Gamma^{\alpha'\alpha''}_{v'J',E''J''} = \frac{16\pi^3}{3}\frac{k_{if}^{\ 3}}{\varepsilon_0 h}\frac{S_{J'J''}}{2J'+1}\left|\left\langle \psi^{\alpha''}_{E''J''}(R)\middle|M_{\alpha'\alpha''}(R)\middle|\psi_i(R)\right\rangle\right|^2 \leftarrow \text{Bound-Free}$$

Where,

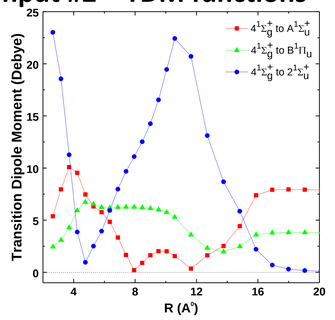
- k_{if} - Emission wavenumber
- $S_{J'J''}$ - Hönl-London rotational intensity factor
- $\psi^{\alpha'}_{v'J'}$ - Normalized nuclear wavefunctions of upper state
- $M_{\alpha'\alpha''}(R)$ – Transition dipole moment function

Inputs for lifetime calculations

Input #1 – Potential functions



Input #2 – TDM functions



- Potential data:
  - $4^1\Sigma_u^+$ -Tsai et *al.*[3]
  - $2^1\Sigma_u^+$ - Kowalczyk et *al.*[4]
  - $B^1\Pi_u^+$ - Camacho et *al.*[5] and E. Tiemann[6]
  - $A^1\Sigma_u^+$ - Tiemann et *al.*[7]
- TDM function: Work by Sylvie Magnier[2,8]

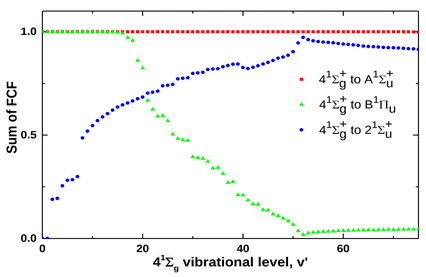
Calculations

Schrödinger Equation is solved for bound and continuum states using the Level 8.2 program[9] and a modified version of the BCONT program[10], respectively

Completeness relation of the energy eigen function[11]

$$\sum_{v''}\left|\left\langle \psi^{\alpha''}_{v''J''}(R)\middle|\psi_i(R)\right\rangle\right|^2 + \int_0^{\infty}\left|\left\langle \psi^{\alpha''}_{E''J''}(R)\middle|\psi_i(R)\right\rangle\right|^2 dE'' = 1$$

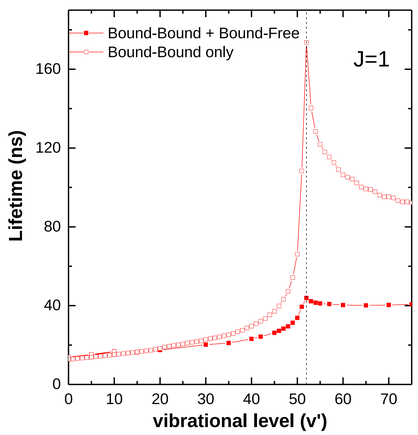
bound-bound transitions — bound-free transitions

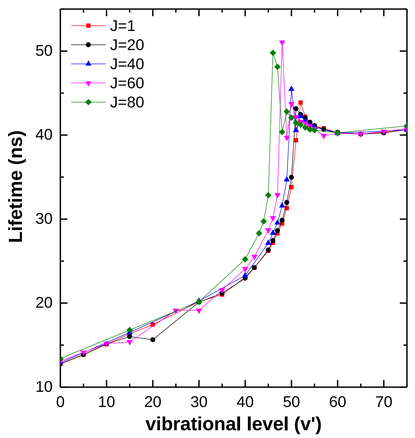


If the FCF sum falls short of reaching 1, this is an indication that bound- free transitions should be considered

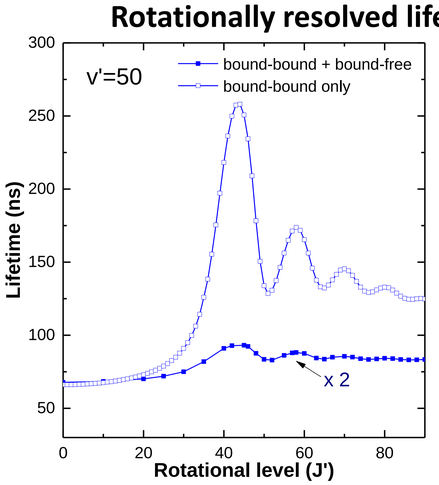
Results

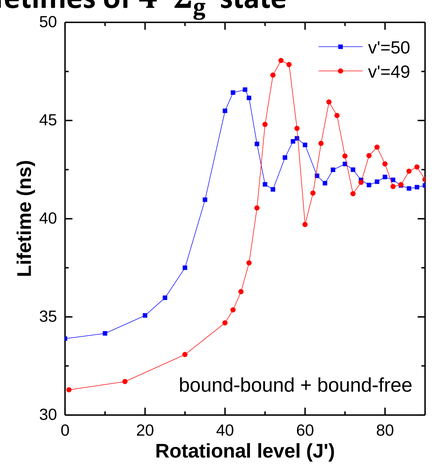
Vibrationally resolved lifetimes of $4^1\Sigma_g^+$ state





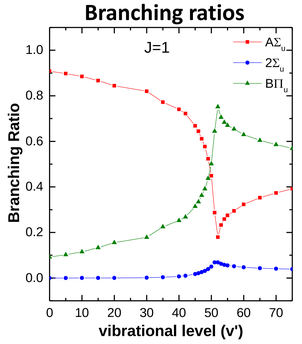
Rotationally resolved lifetimes of $4^1\Sigma_g^+$ state



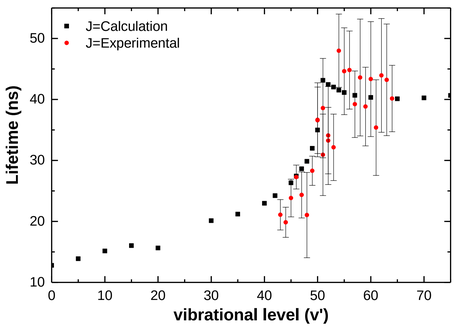


Discussion

Branching ratios

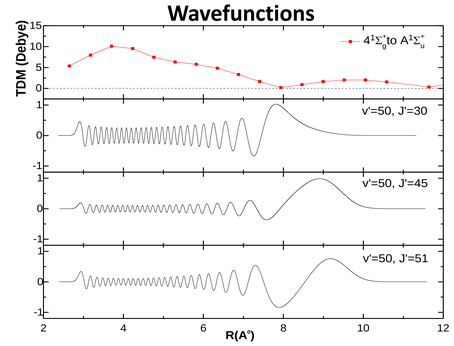


Comparison with preliminary experimental data



Experimental values are for J'≈ 20 from time delayed pump—probe molecular beam experiments. For details see reference 1

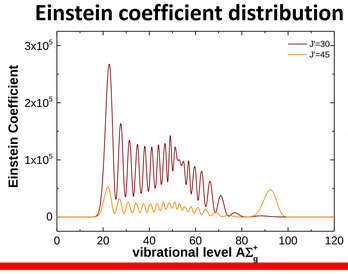
Wavefunctions

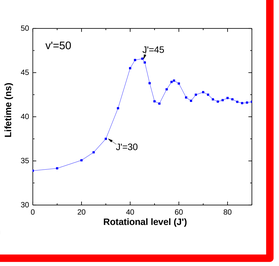


Depending on the which part of the TDM we sample, changes the Einstein coefficient distribution considerably

Einstein coefficient distribution

The sum of the Einstein coefficient over all the $A^1\Sigma_u^+$ state vibrational levels for J'=30 is greater than that of J'=45, which results in higher lifetime for J'=45 than J'=30.





References

1. Anunciado et *al.*, J. Chem. Phys. **145**, 174306 (2016)
2. Sanli et *al.*, J. Chem. Phys. **143**, 104304 (2015)
3. Tsai et *al.* ,JCP **101**, 25 (1994)
4. Kowalczyk et *al.* JMS **203**, 264–267(2000)
5. Camacho et *al.* JPB **38**, 1935 (2005)
6. E. Tiemann, Z.Phys. D **5**, 77-82 (1987)
7. Tiemann et al, ZPD **37**, 323 (96)
8. S. Magnier, private communication
9. R. J. LeRoy, http://scienide2.uwaterloo.ca/~rleroy/level/
10. McGeehan et *al.*, J. Mol. Spectrosc. **265**, 74 (2011)
11. M. Selg , J. Mol. Spectrosc. **220,** 187–200 (2003)