Electronic Transition Dipole Moment and Radiative Lifetime Calculations of Lithium Dimer Ion-Pair States

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Abstract

We present a computational study of lifetimes and transition dipole moment matrix elements for the Lithium dimer ion-pair states of $^1\Sigma_g^+$ symmetry. We report here the ab initio calculated electronic transition dipole moments between the $n^1\Sigma_g^+$ and the $A^1\Sigma_u^+$ states, that vary strongly as a function of internuclear distance. In addition, we have calculated the radiative lifetimes, τ, of these ion-pair states and compared them with the experimental results from literature when available.
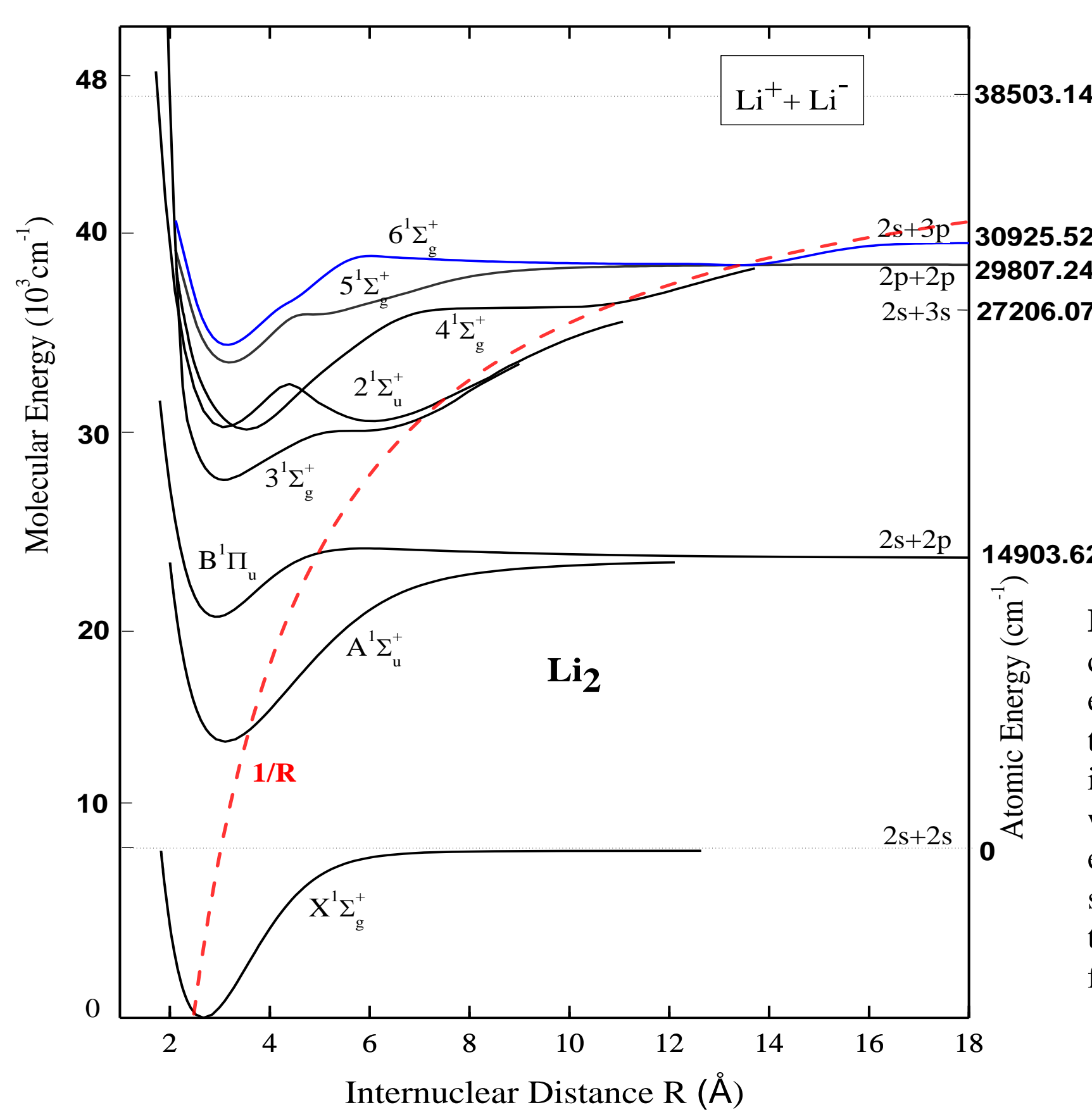
Fig. 1: Selected potential energy curves of the Li_2 molecule excited states. The dotted line is the ion pair $Li^+ + Li^-$ Coulomb interaction function $e^2/(4\pi\varepsilon R)$, which crosses the region of the electronic states and causes the secondary wells and shoulders to these potential energy functions [1-6].

Why are Electronic Transition Dipole Moment Matrix Elements important?

Obtaining absolute values for electronic transition dipole moment matrix elements allows us to determine line intensities and lifetimes accurately. Spectral line intensities are relative. One needs the absolute values of transition dipole moment matrix elements (TDM) to calibrate the relative line intensities and the relative transition dipole moment functions ($\mu_e(r)$).

$$I_{em.} \propto \nu_{ik}^4 \left|\langle i|\mu_e(R)|k\rangle\right|^2 \quad \text{Intensity of the emission line}$$

$$I_{abs.} \propto \nu_{ik} \left|\langle i|\mu_e(R)|k\rangle\right|^2 \quad \text{Intensity of the absorption line}$$

$$A_{ik} \propto \nu_{ik}^3 \left|\langle i|\mu_e(R)|k\rangle\right|^2 \quad \text{Einstein Coefficient}$$

$$\tau_i = \left(\sum_k A_{ik}\right)^{-1} \quad \text{Lifetime of an excited electronic state}$$

Electronic Transition Dipole Moment Matrix Elements (TDM) and Franck Condon Factors (FCF) Calculations

Solving The Radial Schrodinger Equation using LEVEL 8.0 ref.[7]

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_{v,J}(R)}{dR^2} + V_J(R)\psi_{v,J}(R) = E_{v,J}\psi_{v,J}(R)$$

The core of the program is concerned with determination of the discrete eigenvalues and eigenfunctions of the radial one dimensional Schrodinger equation

$$\mu_{v'J'v''J''} = \langle \Psi_{v'J'}(R) | \mu_e(R) | \Psi_{v''J''}(R) \rangle \quad \text{Transition Dipole Moment Matrix Element}$$

$$FCF = \left|\langle\Psi_{v',J'}|\Psi_{v'',J''}\rangle\right|^2 \quad \text{Franck Condon Factor}$$

Calculated Transition Dipole Moment Matrix Elements

$A^1\Sigma_u^+ - X^1\Sigma_g^+$ Transition

$E(3)^1\Sigma_g^+ - A^1\Sigma_u^+$ Transition

$F(4)^1\Sigma_g^+ - A^1\Sigma_u^+$ Transition

$5^1\Sigma_g^+ - A^1\Sigma_u^+$ Transition

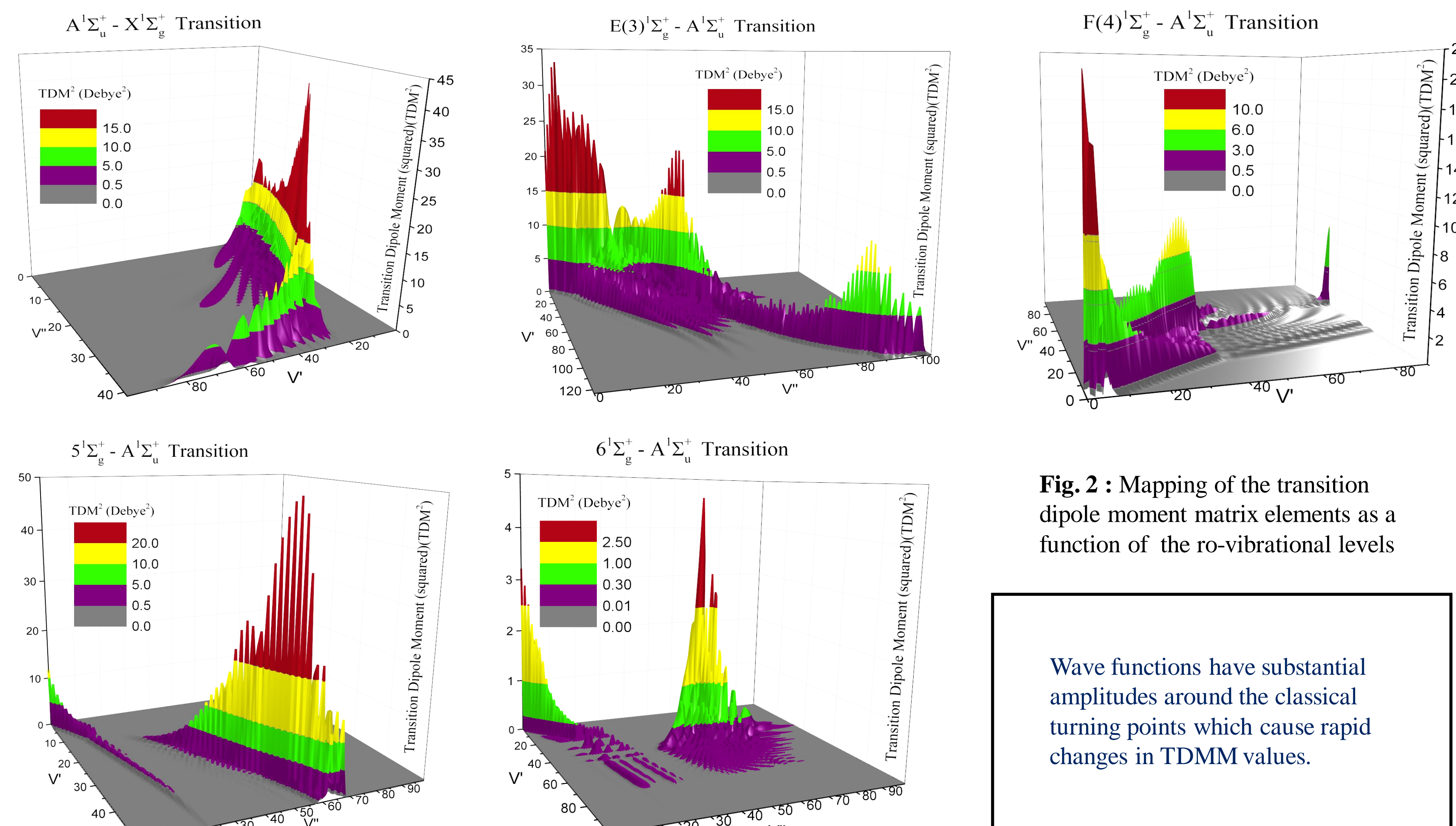$6^1\Sigma_g^+ - A^1\Sigma_u^+$ Transition

Fig. 2 : Mapping of the transition dipole moment matrix elements as a function of the ro-vibrational levels

Wave functions have substantial amplitudes around the classical turning points which cause rapid changes in TDMM values.
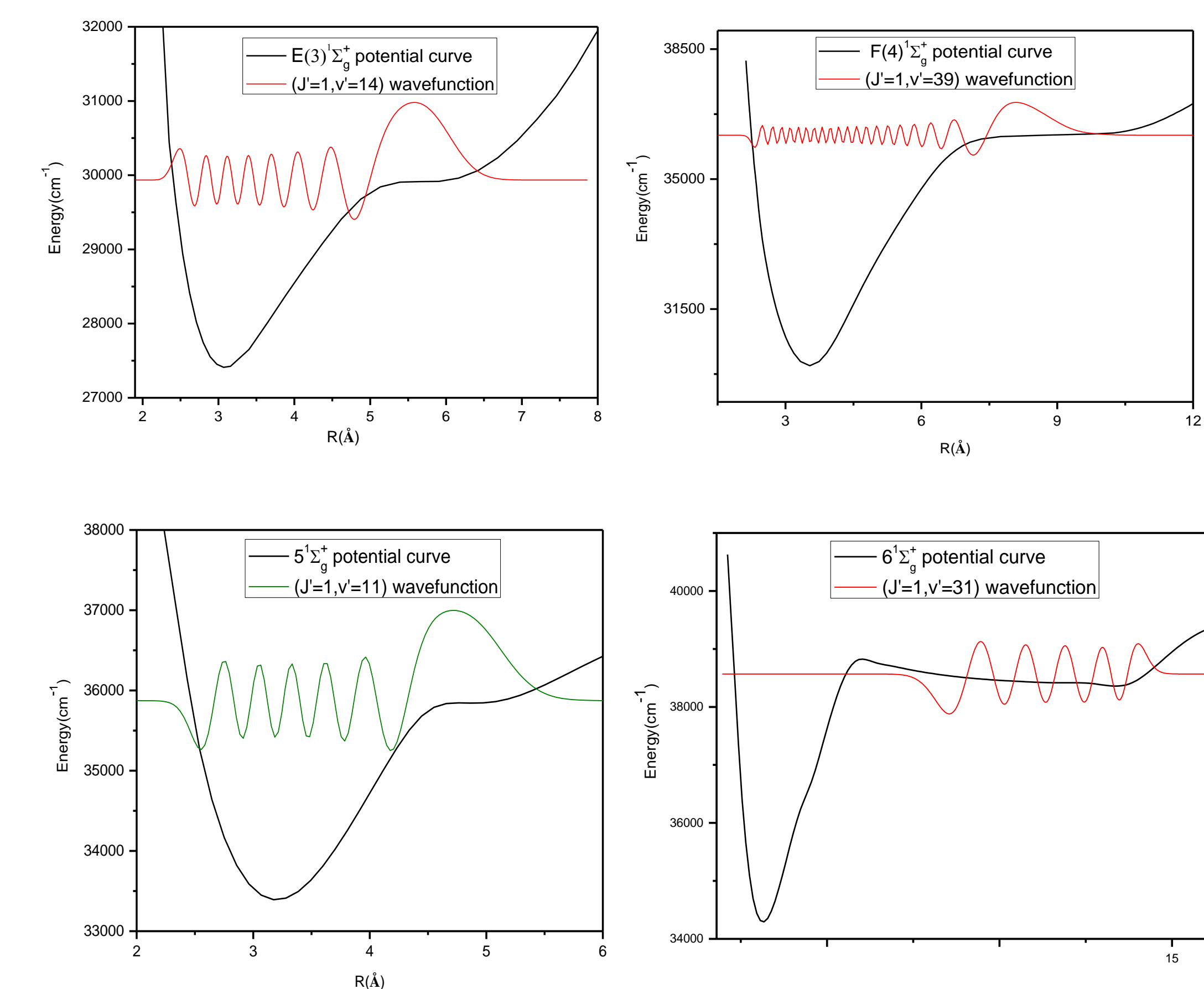
Calculated Lifetimes

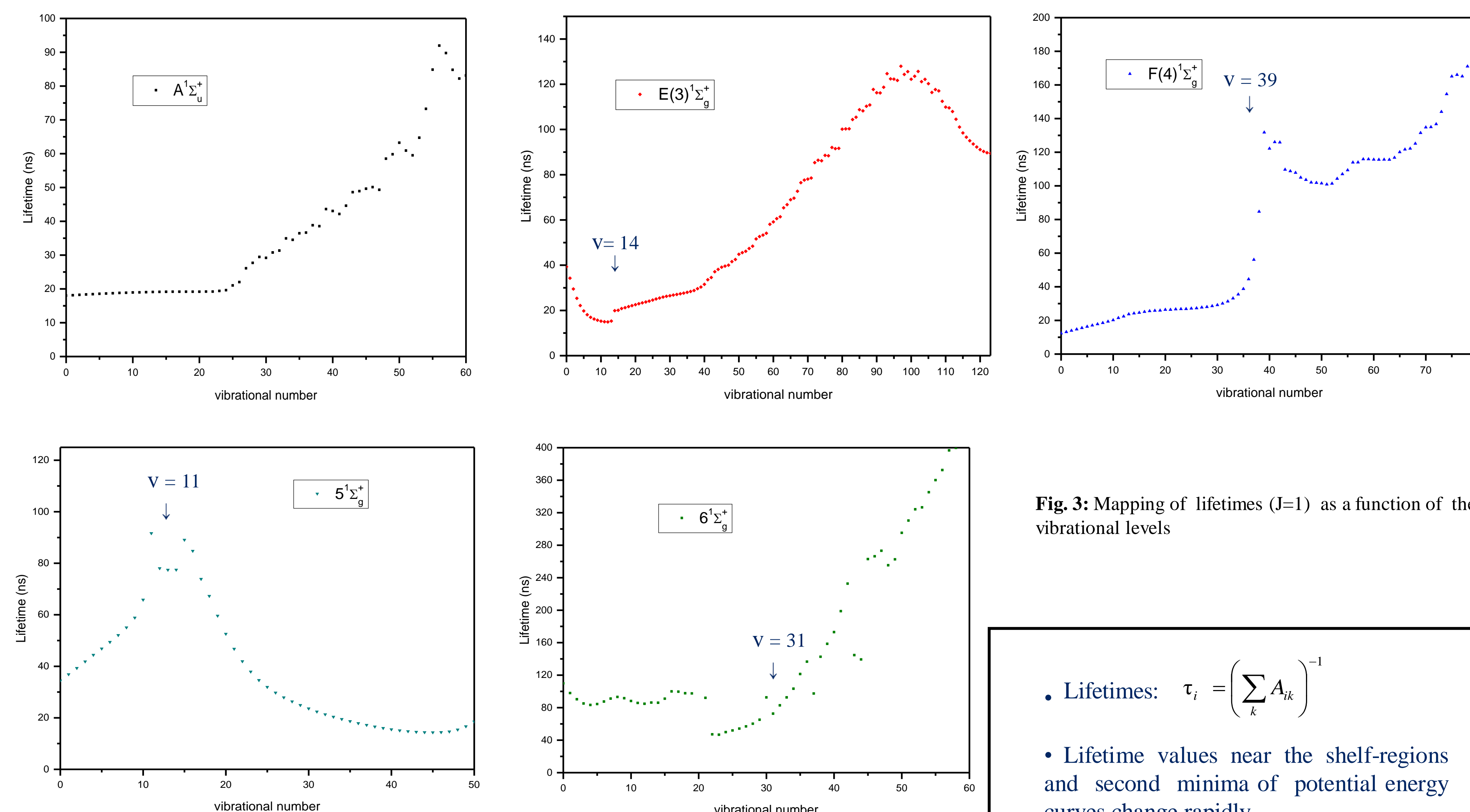**Fig. 3:** Mapping of lifetimes (J=1) as a function of the ro-vibrational levels

- Lifetimes: $\tau_i = \left(\sum_k A_{ik}\right)^{-1}$
- Lifetime values near the shelf-regions and second minima of potential energy curves change rapidly.
- $F(4)^1\Sigma_g^+$ state predissociates due to strong coupling to the $E(3)^1\Sigma_g^+$ state continuum (2s+3s atomic limit).
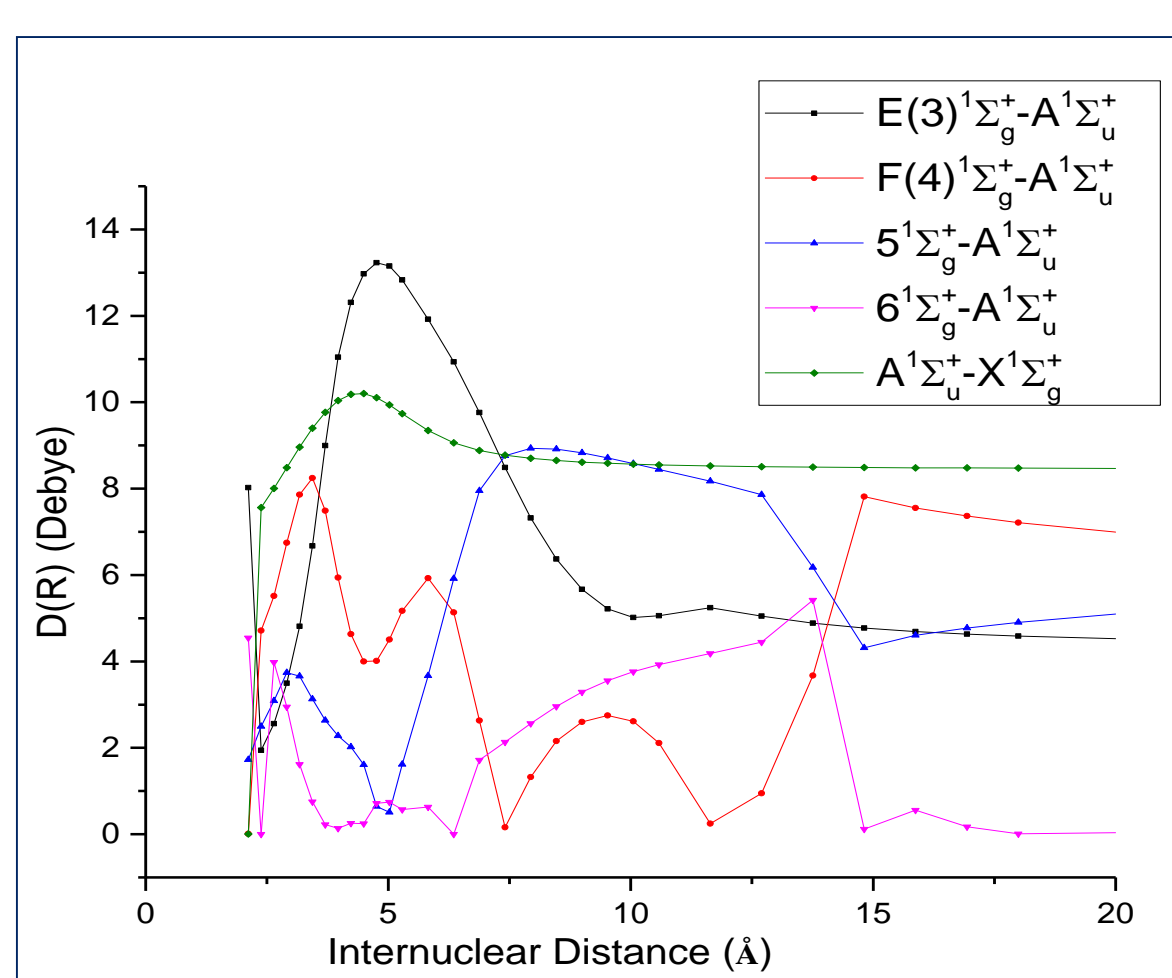- $6^1\Sigma_g^+$ state has a wide outer-well. The lifetimes belonging to each well are distinctively separate.

Fig. 4 : Ab initio transition dipole moment functions used in Level 8.0 program

Wavefunctions

Wave functions have substantial amplitudes around the classical turning points which cause rapid changes in TDMM values.

Fig. 5: Wave functions of $(3-6)^1\Sigma_g^+$ electronic states around the shelf-regions and second minima

Conclusion

We carried out a computational study of lifetimes and transition dipole moment matrix elements of ion-pair states of Lithium Dimer. Due to the ion-pair interaction, there are avoided crossings between the electronic states resulting in shoulders or additional wells in the potential energy curves. Around the shoulders and additional wells, the wave functions exhibit large amplitudes causing overlap integrals, lifetimes and TDMMs to change rapidly. We employed Le Roy's Level 8.0 program [7] to calculate the TDMMs and lifetime values. The program used the *ab initio* or experimentally constructed potential energy curves and transition dipole moment functions to solve the Schrodinger equation numerically.

References

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