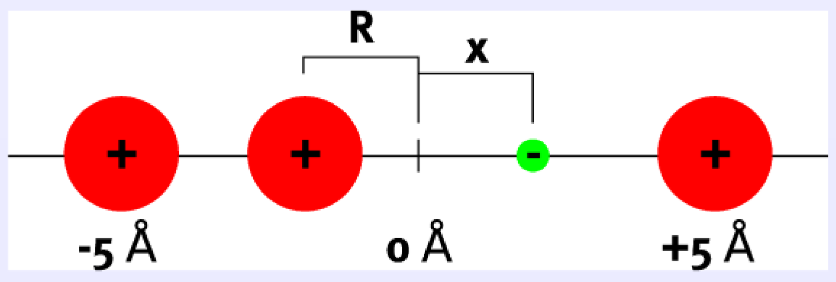
2D spectroscopy of coupled electronic-nuclear motion

J. Albert[1*], M. Falge[1], H. Hildenbrand[1], S. Gomez[2], I. R. Sola[2] and V. Engel[1]

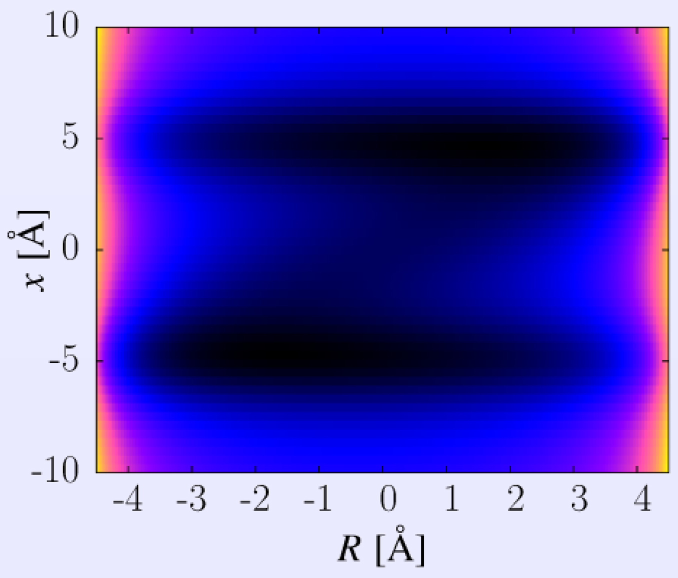
[1] ITPC, University Würzburg, D-97274 Würzburg, Germany / [2] Dep. de Quimica Fisica, Universidad Complutense, 28040 Madrid, Spain

We theoretically investigate the photon-echo spectroscopy for a model [1] which involves the coupled (c) quantum dynamics of an electron and a nucleus. This model serves to illustrate the limiting cases of an adiabatic and a diabatic motion [2]. In the first case, an interpretation of the two-dimensional (2D) spectra using the Born-Oppenheimer (BO) approximation is feasable. It is then possible to identify pure vibrational coherences in fixed electronic states. For the case of strong non-adiabatic coupling, i.e., a diabatic motion, the 2D-spectra reveal a complicated structure which is related to the breakdown of the BO-approximation. The spectra are then dominated by vibronic coherences.

Model



[1] Shin S., Metiu H. *J. Chem. Phys.* **102**, 9285 (1995)



Hamiltonian

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2M}\frac{\partial^2}{\partial R^2} + V(x,R) + W(x,R,t)\,,$$

$$W(x,R,t) = -(-x+R)\cdot E^{\pm}(t)$$

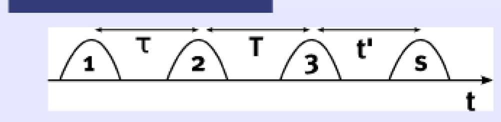
$$V(x,R) = \frac{1}{\left|\frac{L}{2}-R\right|} + \frac{1}{\left|\frac{L}{2}+R\right|} - \frac{\operatorname{erf}\left(\frac{|L/2-x|}{R_f}\right)}{\left|\frac{L}{2}-x\right|} - \frac{\operatorname{erf}\left(\frac{|L/2+x|}{R_f}\right)}{\left|\frac{L}{2}+x\right|} - \frac{\operatorname{erf}\left(\frac{|R-x|}{R_c}\right)}{|R-x|} + E_0\,.$$

$$E^{\pm}(t) = \frac{1}{2}\sum_{n=1}^{3} g_n(t-t_n)\,\mathrm{e}^{\mathrm{i}[\mp\omega_n(t-t_n)\pm k_n x]}$$

Born-Oppenheimer treatment

$$\hat{H} = \begin{pmatrix} T_1 + V_1(R) & \langle 1(x,R)\,|\,W(x,R,t)\,|\,2(x,R)\rangle_x \\ \langle 2(x,R)\,|\,W(x,R,t)\,|\,1(x,R)\rangle_x & T_2 + V_2(R) \end{pmatrix}$$

2D pulse setup



Calculation of 2D spectra

Third-order polarization ($-k_1 + k_2 + k_3$ - direction)

$$P_T^{(3)}(t',\tau) = \sum_{n=1}^{4}\langle\psi^{(n-1)}\,|\,\mu\,|\,\psi^{(4-n)}\rangle$$

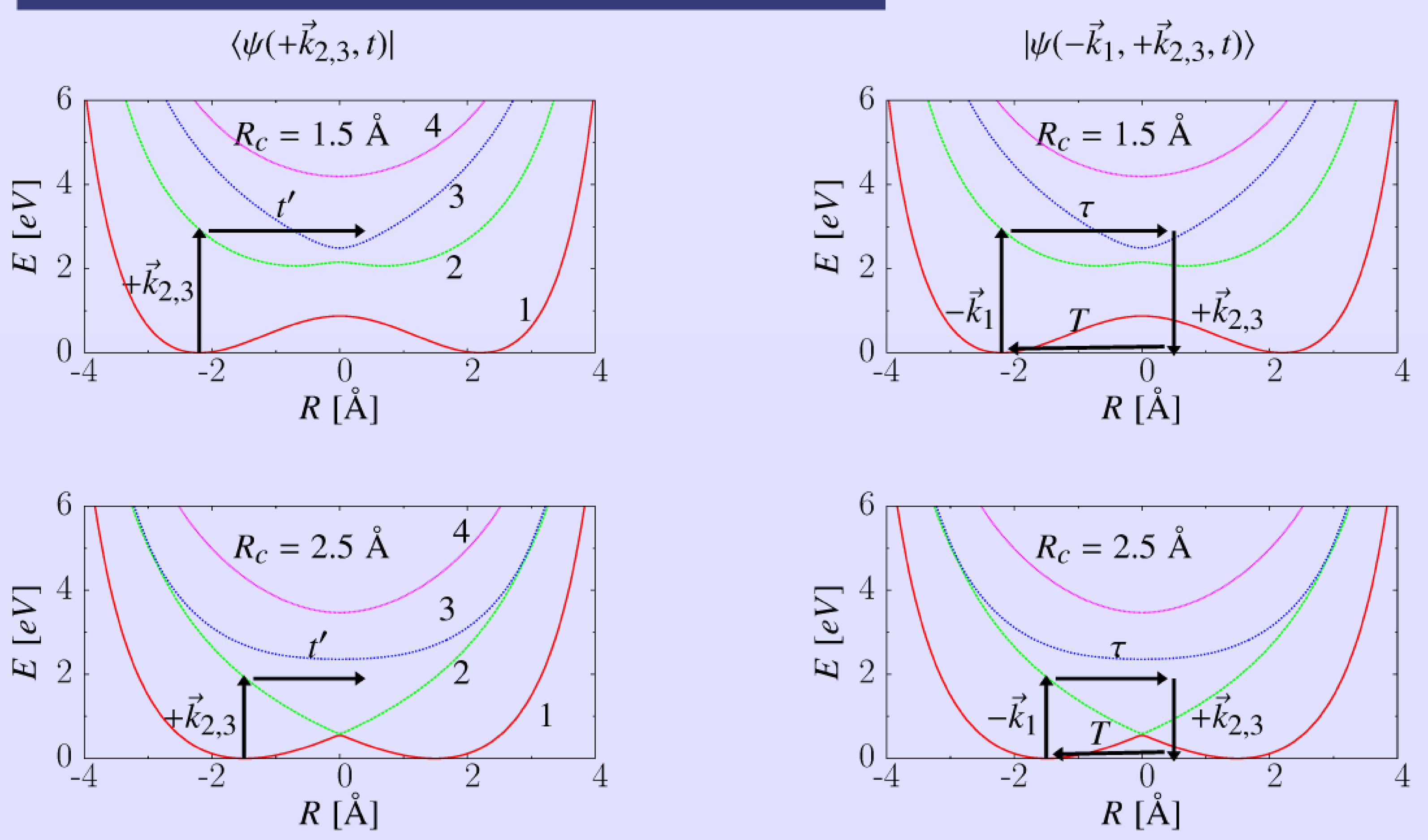
(→ no excited state absorption)

$$P_T^{(3)}(t',\tau) = \langle\psi(\vec{k}_3,t')\,|\,\mu\,|\,\psi(\vec{k}_2,-\vec{k}_1,t')\rangle + \langle\psi(\vec{k}_2,t')\,|\,\mu\,|\,\psi(\vec{k}_3,-\vec{k}_1,t')\rangle$$

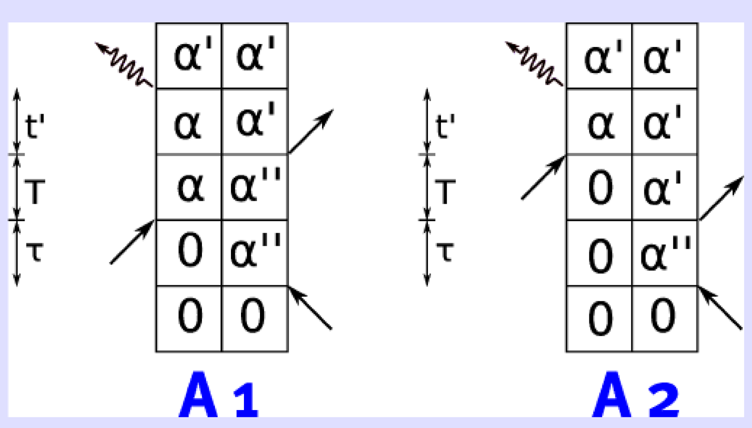
2D spectrum

$$S_T(E_{t'},E_\tau) = \mathrm{i}\int d\tau \int dt'\,\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(E_{t'}t'-E_\tau\tau)}\;P_T^{(3)}(t',\tau)$$

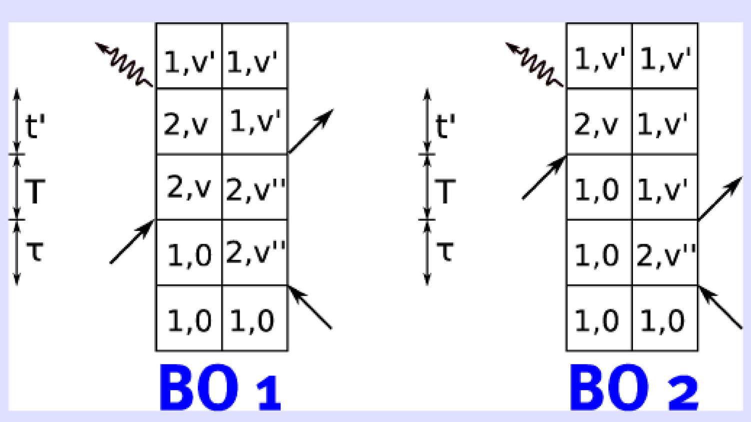
Born-Oppenheimer-Potentials for $R_c = 1.5$Å and $R_c = 2.5$Å



Contributions to 2D spectrum



coupled



Born-Oppenheimer

$$P^{(3,c)}(t',\tau,T) = \sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''} a_1(0;\alpha;\alpha',\alpha'')\,e^{i(E_{\alpha'}-E_\alpha)t'}\,e^{i(E_{\alpha''}-E_0)\tau}\,e^{i(E_{\alpha'}-E_0)T} + \sum_{\alpha}\sum_{\alpha'}\sum_{\alpha''} a_2(0;\alpha;\alpha',\alpha'')\,e^{i(E_{\alpha'}-E_\alpha)t'}\,e^{i(E_{\alpha''}-E_0)\tau}\,e^{i(E_{\alpha''}-E_\alpha)T}$$

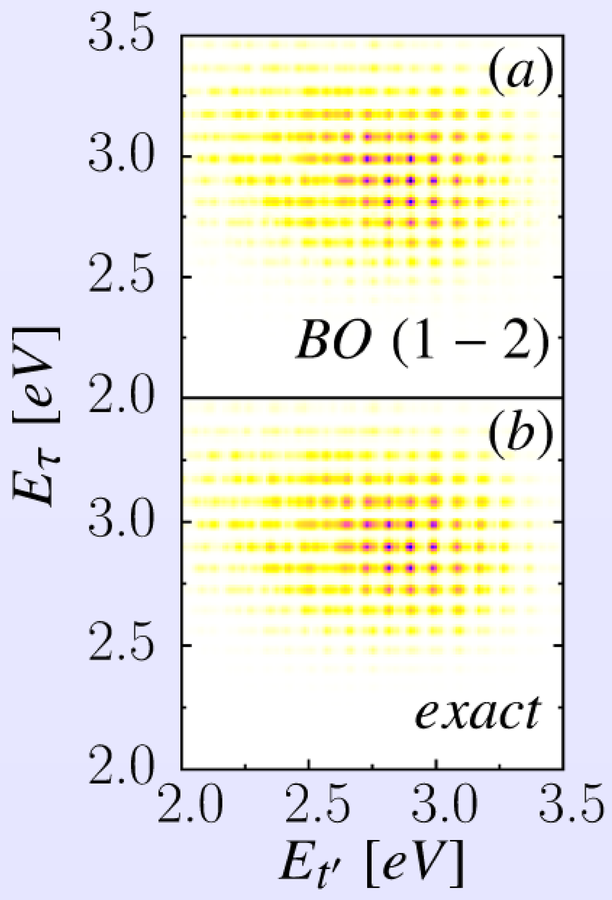
coupled

$$P^{(3,BO)}(t',\tau,T) = \sum_{v}\sum_{v'}\sum_{v''} b_1(0;v;v',v'')\,e^{i(E_{1,v'}-E_{2,v})t'}\,e^{i(E_{2,v''}-E_{1,0})\tau}\,e^{i(E_{1,v'}-E_{1,0})T} + \sum_{v}\sum_{v'}\sum_{v''} b_2(0;v;v',v'')\,e^{i(E_{1,v'}-E_{2,v})t'}\,e^{i(E_{2,v''}-E_{1,0})\tau}\,e^{i(E_{2,v''}-E_{2,v'})T}$$

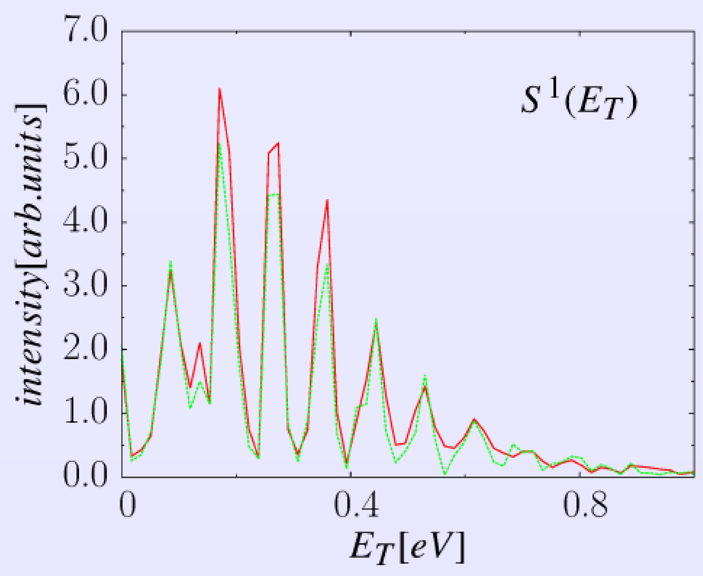
BO

Results

weak coupling case

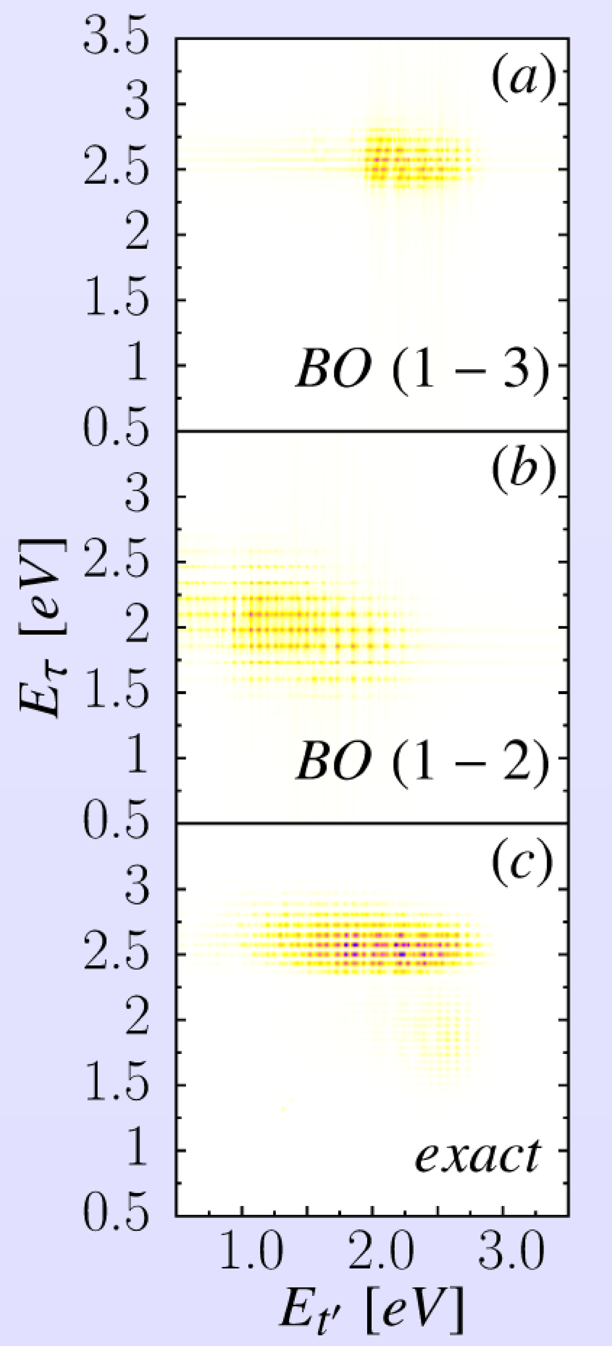


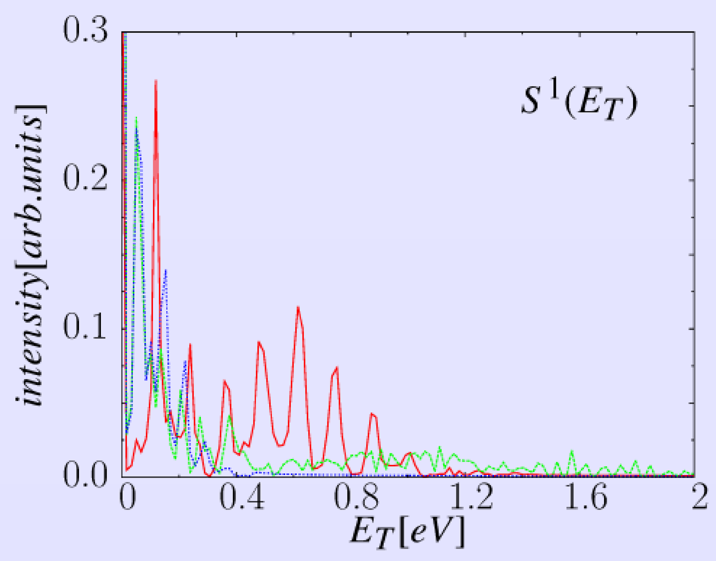
$$S^1(E_T) = \mathrm{i}\int dT\,\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}E_T T}\;P^{(3)}(T)$$



- Exact 2D spectrum can be reproduced within the BO-Approximation using ground and first excited state.
- Coherences can be associated with vibrational coherences in fixed electronic states.

strong coupling case





- Spectrum exhibits rich vibronic structure.
- The BO |1⟩-|2⟩ spectrum doesn't agree with the exact spectrum.
- The BO |1⟩-|3⟩ spectrum partially reproduces the exact spectrum.
- Breakdown of the Born-Oppenheimer Approximation.
- Coherences in T result from coupled/ vibronic dynamic.

Conclusion

Vibrational coherences in fixed electronic states can be identified if the Born-Oppenheimer approximation is valid. This is no longer possible in the case of strong non-adiabatic coupling.

References

[1] Shin S., Metiu H. *J. Chem. Phys.* **102**, 9285 (1995)
[2] Falge M., Engel V., Gräfe S. *J. Phys. Chem. Lett* **3**, 2617 (2012)
[3] Albert J., Falge M., Gomez S., Sola R. I., Hildenbrand H., Engel V. (2015) *J. Chem. Phys.* (submitted)

Acknowledgement

We thank the DFG for financial support within the FOR 1809.