Non-adiabatic effects in the optical spectra of H_2^+

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nano-bio spectroscopy group

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Outline

- Motivations:
  - Ions are usually treated classically (BOA)
  - Effects of a full quantum treatment ?
- Model system: H_2^+ in 1D
- Optical spectra: BOA vs full quantum
- BOA theoretical analysis
- Conclusions

Motivations

- Full quantum treatment

$$H_{eI}(R,r)\psi_{eI}(R,r)=E_{eI}(R,r)\psi_{eI}(R,r)$$

$$H_{eI}(R,r)=T_I(R)+T_e(r)+V_{eI}(R,r)+V_{ee}(r)+V_{II}(R)$$

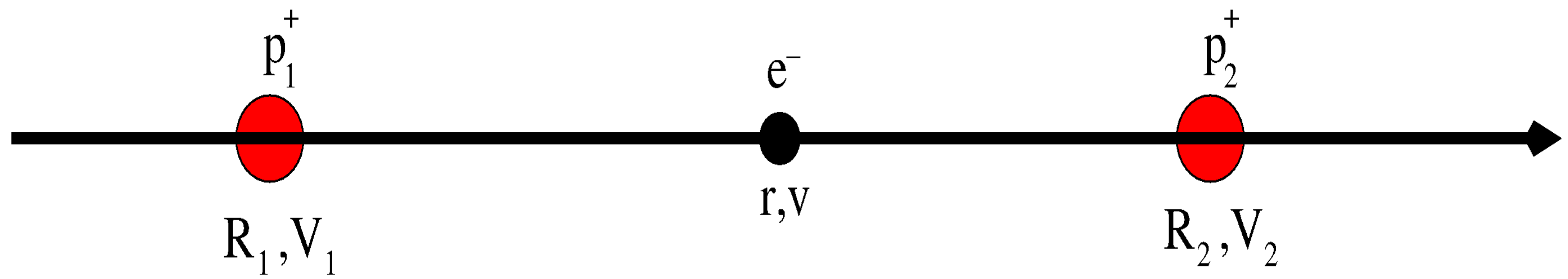
- Adiabatic approximations $\frac{m_e}{m_I}\ll 1$ → decouple electron-ion
  - Born Oppenheimer Approximation (BOA)

$$\psi_{eI}(R,r)\approx\psi_{BOA}(R,r)=\chi_I(R)\varphi_e^R(r)$$

  - Electron: $\varphi_e^R(r)H_e=\varepsilon(R)\varphi_e^R(r);H_e=T_e+V_{eI}+V_{ee}+V_{II}$
  - Ion: $H_I^i\chi_I(R,t)=E_I^i(R)\chi_I(R,t);H_I^i=T_I+\varepsilon_i(R)$

See effects of BOA vs full quantum treatment

Model system: H_2^+ in 1D



- Hamiltonian in 1D (centre of mass)

$$H_{internal}(R,\xi) = -\frac{1}{2\mu_I}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e}\frac{\partial^2}{\partial \xi^2} - \frac{1}{\sqrt{\left(\frac{R}{2}+\xi\right)^2+1}} - \frac{1}{\sqrt{\left(\frac{R}{2}-\xi\right)^2+1}} + \frac{1}{\sqrt{R^2+1}}$$

Negligible if $\mu_I >> \mu_e$

$$R = R_2 - R_1 \qquad \xi = r - \frac{R_1+R_2}{2} \qquad \mu_I = \frac{m_I}{2} \qquad \mu_e = \frac{2m_I}{2m_I + m_e}$$

- Exact numerical diagonalisation feasible
- Octopus code

Change only m_I → H_2^+ .. D_2^+ .. Li_2^+ .. K_2^+ → assess electron-ion coupling

Optical spectra → theory

- Kicked initial state in the dipole approximation

$$\psi_{eI}(R,r)=\psi_0(R,r)e^{ikr}\approx(1+ikr)\psi_0(R,r)$$

$$\psi_{eI}(R,r,t)\approx\psi_0(R,r)e^{\frac{H_0 t}{i\hbar}}+ik\sum_{i>0}\psi_i^*(R,r)\,r\,\psi_0(R,r)\psi_i(R,r)e^{\frac{H_i t}{i\hbar}}$$

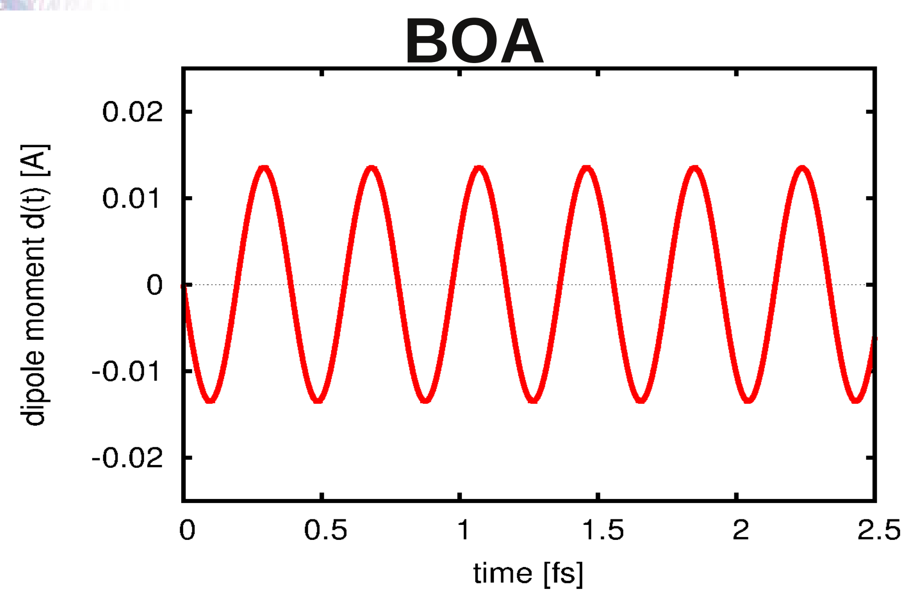
- Dipole moment

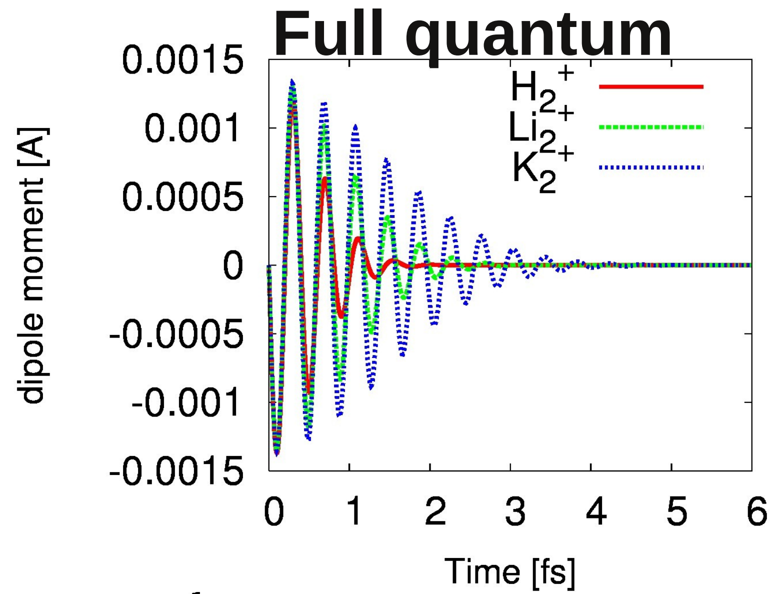
$$d(t)=\int\psi_{eI}^*(R,r,t)\,r\,\psi_{eI}(R,r,t)$$

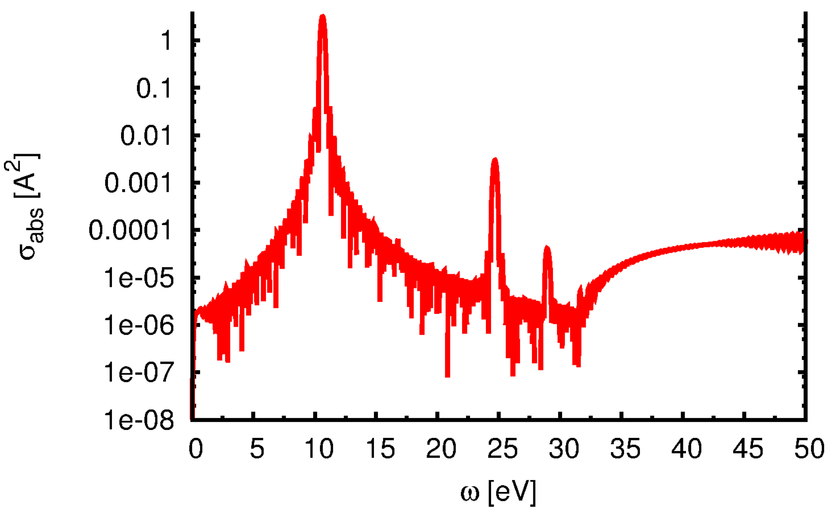
- Optical spectra

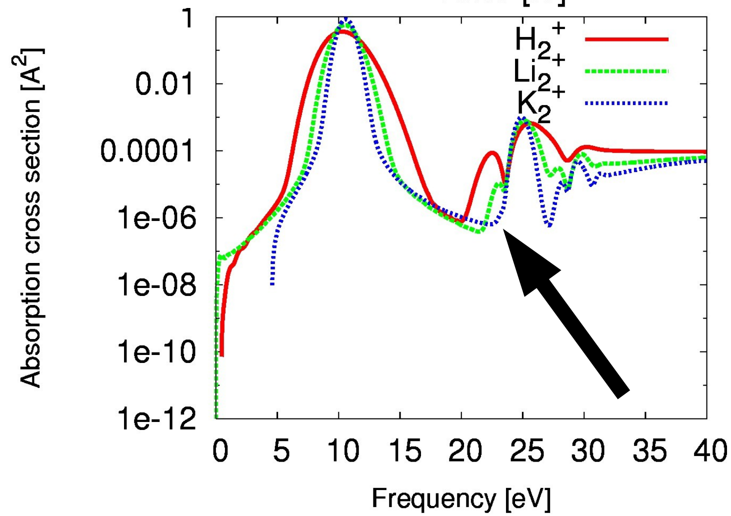
$$\sigma(\omega)=\lim_{k\to\infty}\frac{4\pi\alpha\omega}{k}\Im\left[\int_0^\infty dt\,e^{-i\omega t}(d(t)-d(0))\right]$$

Optical spectra: BOA vs Full









Lorentzian

m_I **no peak shift**

Gaussian

m_I **peak shift**

NEW PEAK !

BOA theoretical analysis

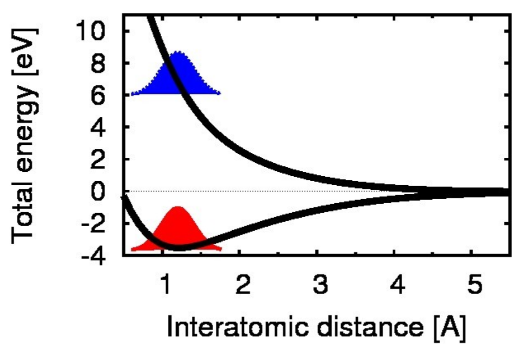
$$\psi_{BOA}(R,r,t)\approx\chi_0(R)\varphi_0^{(R)}(r)e^{\frac{H_e t}{i\hbar}}+ik\sum_{i>0}d_{i0}\varphi_i^{(R)}(r)\chi_i(R,t)$$

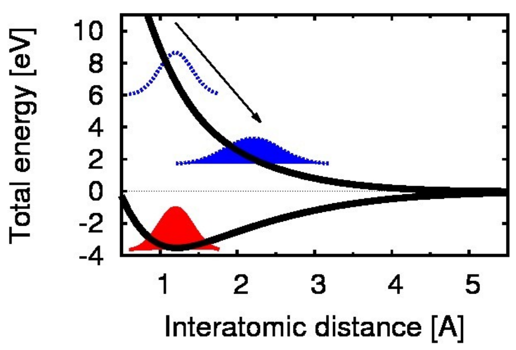
$$\chi_i(R,t)=N\,e^{-\alpha_i(R-R_i)^2-\frac{1}{i\hbar}(R-R_i)P_i-\frac{1}{i\hbar}\gamma_i}$$

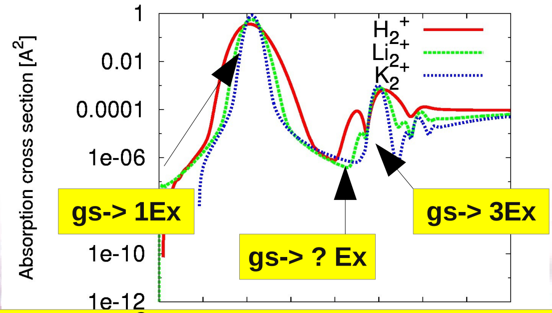
$$\chi_0(R,t)=N\,e^{-\alpha_0(R-R_0)^2}e^{\frac{E_0 t}{i\hbar}}$$

$$i\hbar\frac{\partial}{\partial t}\chi_i(R,t)=\left(-\frac{\hbar^2}{2\mu_I}\frac{\partial^2}{\partial R^2}-F_i(R-R_i)+\varepsilon_i(R_i)\right)\chi_i(R,t)$$

$$E_0\chi_0(R)=\left(-\frac{\hbar^2}{2\mu_I}\frac{\partial^2}{\partial R^2}-\frac{1}{2}K(R-R_0)^2+\varepsilon_0(R_0)\right)\chi_0(R)$$







$$d(t)=\int\psi_{eI}^*(R,r,t)\,r\,\psi_{eI}(R,r,t)$$

BOA theoretical analysis

$$d(t)=\int \psi^{*}_{BOA}(R,r,t)\, r\, \psi_{BOA}(R,r,t)$$

$$d(t)=2\mathrm{k}\sum_{i>0} d^{2}_{i0}\,\Im\int dR\, e^{-\frac{E_0 t}{i\hbar}}\chi^{*}_{0}(R)\chi_{i}(R,t)$$

$$d(t)=2\mathrm{k}\sum_{i>0} d^{2}_{i0}\,\Im\left(e^{-\frac{F_i^2\sigma_0^2}{2\hbar^2}t^2-\omega_i t+\frac{F_i^2}{12\hbar\mu_I}t^3}\right)$$

ONLY ADIABATIC EFFECTS

BOA theoretical analysis

$$\psi_{eI}(R,r,t)=\sum_i c_i(t)\chi_i(R,t)\varphi_i^R(r)$$

$$<\chi_n(R,t)\varphi_n(R,r)|i\hbar\frac{\partial\psi}{\partial t}-H\psi>=0$$

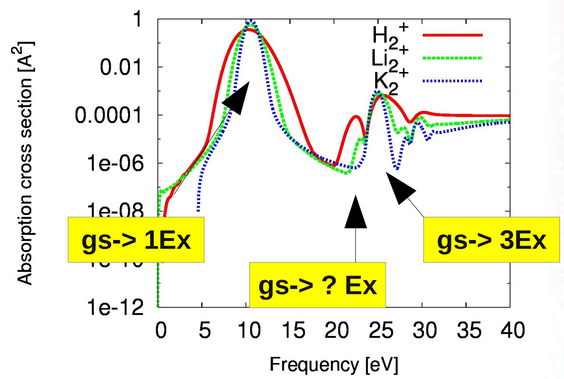
$$i\hbar\dot{c}_n=\frac{P_n}{\mu_I}\sum_i I_{\mathrm{ni}}A_{\mathrm{ni}}c_i+\frac{2i\hbar\alpha_0}{\mu_I}\sum_i I_{\mathrm{ni}}^{(i)}A_{\mathrm{ni}}c_i-\frac{1}{2\mu_I}\sum_i I_{\mathrm{ni}}B_{\mathrm{ni}}c_i$$

$$I_{\mathrm{ni}}=\int dR\,\chi_n^*(R,t)\chi_i(R,t) \qquad I_{\mathrm{ni}}^{(i)}=\int dR\,\chi_n^*(R,t)(R-R_i)\chi_i(R,t)$$

$$A_{\mathrm{ni}}=-i\hbar<\varphi_j(R)|\frac{\partial\varphi_i(R)}{\partial R}> \qquad B_{\mathrm{ni}}=-\hbar^2<\varphi_j(R)|\frac{\partial^2\varphi_i(R)}{\partial R^2}>$$

BOA theoretical analysis

$$V_{dark} = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \qquad V_{bright} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \longrightarrow \begin{pmatrix} 0 & 23 & 24 \\ 32 & 0 & 34 \\ 42 & 43 & 0 \end{pmatrix}$$



$$g \begin{pmatrix} 0 & \sin\frac{(\theta)}{\sqrt{2}} & 2\cos(\theta) \\ \sin\frac{(\theta)}{\sqrt{2}} & 0 & \sin\frac{(\theta)}{\sqrt{2}} \\ 2\cos(\theta) & \sin\frac{(\theta)}{\sqrt{2}} & 0 \end{pmatrix} = g \begin{pmatrix} 0 & \sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \begin{pmatrix} v_{bright} \\ v_{dark} \end{pmatrix}$$

$$V = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$ **evolution ?**

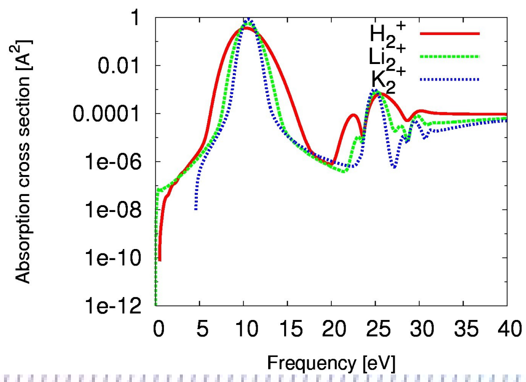
BOA theoretical analysis

$$i\hbar\frac{\partial v}{\partial t}=g\begin{pmatrix}0 & \sin(\theta)\\ \sin(\theta) & \cos(\theta)\end{pmatrix}v \longrightarrow v(t)$$

$$c_3(t)=\langle v_{bright}|v(t)\rangle=\cos^2\left(\frac{\theta}{2}\right)e^{-2ig\sin^2\left(\frac{\theta}{2}\right)/\hbar}+\sin^2\left(\frac{\theta}{2}\right)e^{2ig\cos^2\left(\frac{\theta}{2}\right)/\hbar}$$

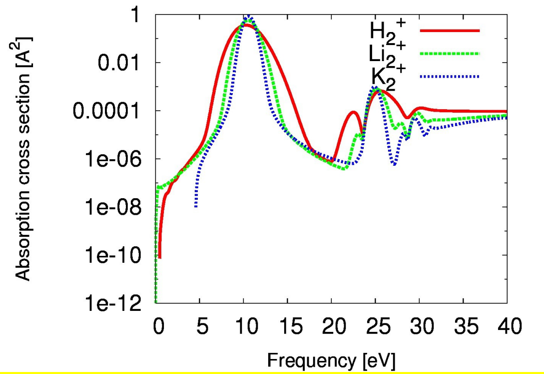
$$d_1(t)=\int\psi^*_{0(BOA)}(R,r,t)\,r\,\psi_{1(BOA)}(R,r,t)$$

$$d_3(t)=\int\psi^*_{0(BOA)}(R,r,t)\,r\,c_3(t)\,\psi_{3(BOA)}(R,r,t)$$



BOA theoretical analysis

$$d(t)=2k\sum_{i=1,3} d_{i0}^2\,\Im\int dR\, e^{-\frac{E_0 t}{i\hbar}}\chi_0^*(R)c_3(t)\chi_i(R,t)$$



only 3rd peak

peak shift — new 2nd peak

$$d(t)=2k\sum_{i=1,3} d_{i0}^2\,\Im\left(e^{-\frac{F_i^2\sigma_0^2}{2\hbar^2}t^2-\left(\omega_i+2g\sin^2\left(\frac{\theta}{2}\right)-2g\right)t+\frac{F_i^2}{12\hbar\mu_I}t^3}\right)$$

$$\sigma_0=\frac{\hbar^{1/2}}{2^{1/2}\mu_I^{1/4}K^{1/4}}$$

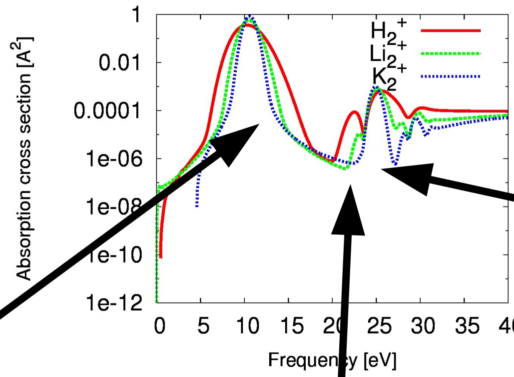
$$\omega_i=\hbar(\varepsilon_i(R_0)-\varepsilon_0(R_0))-\frac{\hbar K^{1/2}}{4\mu_I^{1/2}}$$

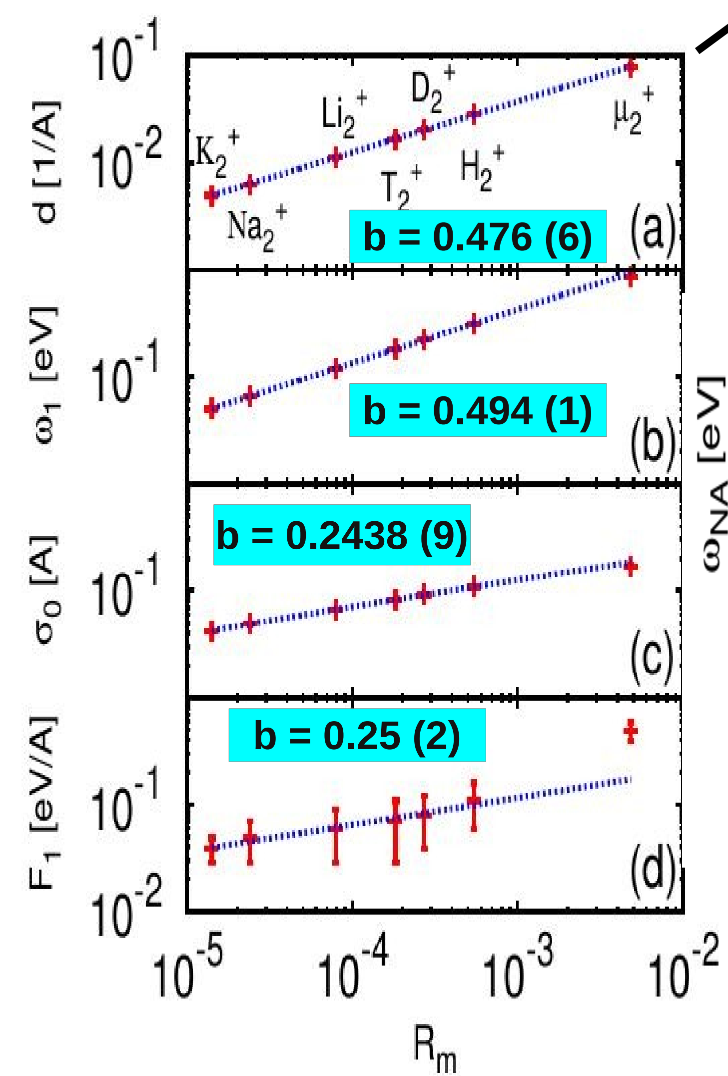
$$F_i=\frac{\hbar^{1/2}K^{3/4}}{2^{1/2}\mu_I^{1/4}}$$

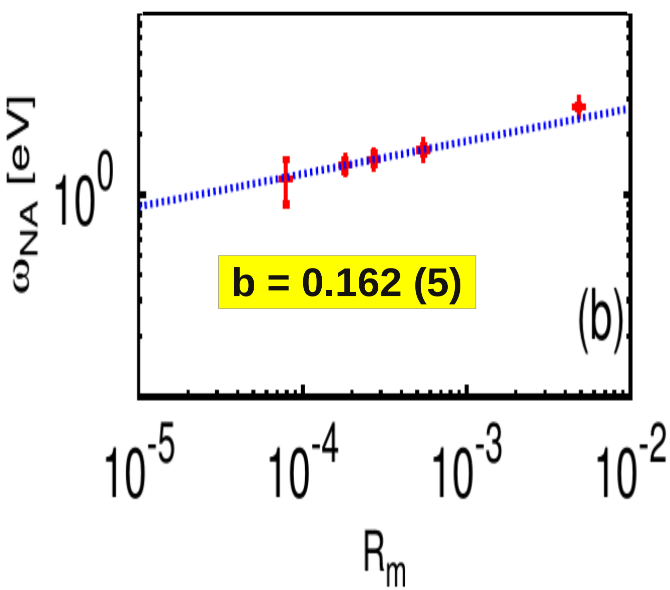
$$d_{i0}=\int\varphi_i^{*(R)}(r)\,r\,\varphi_0^{(R)}(r)\rightarrow\varphi\left(E_0=\varepsilon_0(R_0)+\frac{1}{2}\hbar\frac{K^{1/2}}{\mu_I^{1/2}}\right)$$

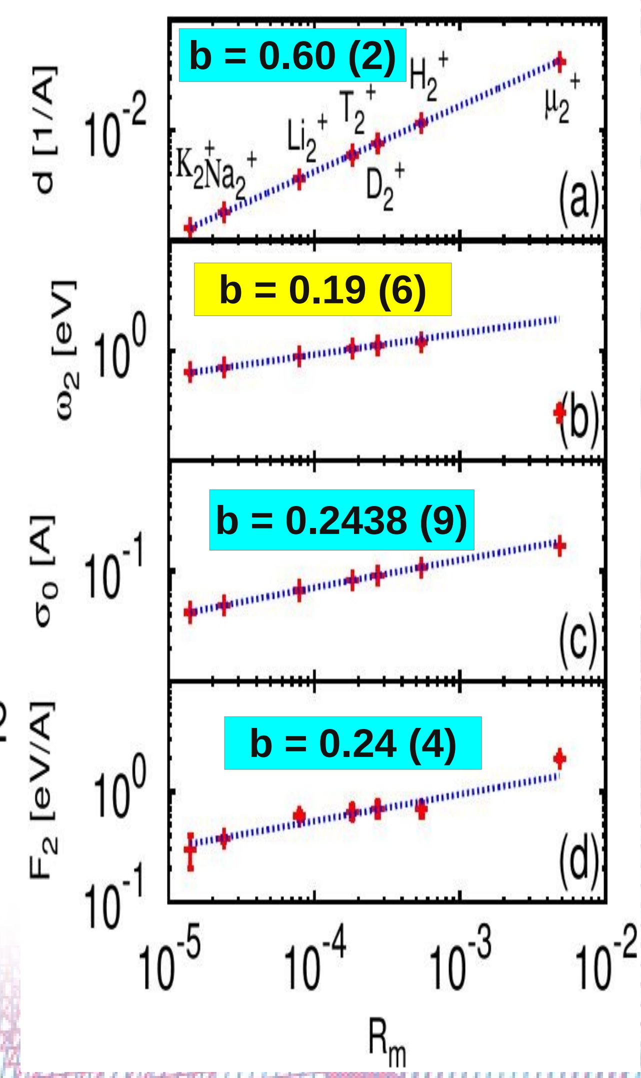
BOA theoretical analysis

$y = ax^b$









Conclusions

- Non adiabatic effects
  - Gaussian lineshape
  - Peaks shift with ionic mass
  - New non-adiabatic peak
- Theoretically analysed with BOA (fits)
- Electron-ion coupling (BOA not good)
- Other systems ?

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