

High temperature optical spectra of diatomic molecules: quantum-mechanical, semiquantum and semiclassical approach

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Outline

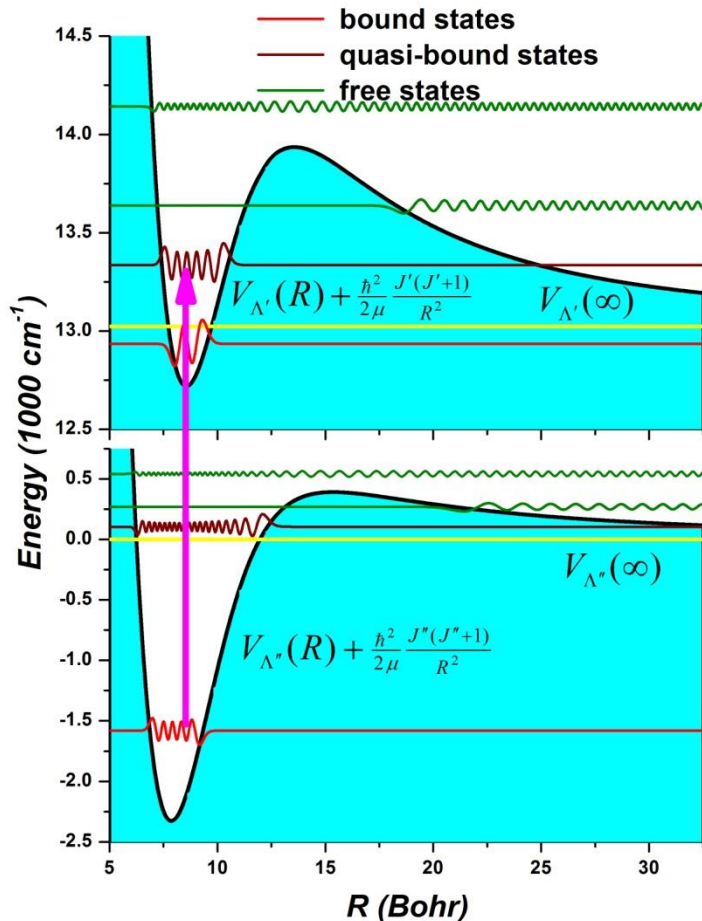
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Reduced absorption coefficient of a dimer

According to the Beer-Lambert law, in terms of binary collisions, the transmittance $\tau(\nu, T)$ of a uniform atomic gas layer with a number density of atoms n and length L is $\tau(\nu, T) = \exp(-n^2 k(\nu, T)L)$ where $k(\nu, T)$ is the reduced absorption coefficient of atomic dimer, ν is frequency of absorbed photon and T is temperature.

$$k(\nu, T) = \sum_{i,j} k_{\Lambda''_i, \Lambda'_j}(\nu, T)$$

Λ'' and Λ' label the lower and the upper electronic state. $V_{\Lambda}(R)$ is the *interaction* potential



Bound (quasi-bound) states: energy $E_{v,J,\Lambda}$, unity-normalized wave function $\Phi_{v,J,\Lambda}$, v vibrational and J rotational quantum number

Free states: asymptotic kinetic energy ε , energy-normalized wave functions $\Psi_{\varepsilon,J,\Lambda}$

$$\left(-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{\Lambda}(R) + \frac{\hbar^2}{2\mu} \frac{J(J+1) - \Lambda^2}{R^2} \right) \Phi(R) = E\Phi(R)$$

$$k_{\Lambda'', \Lambda'}(\nu, T) \propto \sum_{\text{transition}} \left[\begin{array}{c} v''(\varepsilon'') \rightarrow v'(\varepsilon') \\ J'' \rightarrow J' = J'', J'' \pm 1 \end{array} \right]$$

Neglecting the differences between *even* and *odd* J , assuming the applicability of the Q -branch approximation $\Delta J=0$, the thermally averaged absorption coefficient [H.-K. Chung, K. Kirby, J.F. Babb, Phys. Rev. A, 1999, 2001]:

$$k_{\Lambda'',\Lambda'}(\nu, T) = k_{bb}(\nu, T) + k_{bf}(\nu, T) + k_{fb}(\nu, T) + k_{ff}(\nu, T)$$

bound (quasi-bound) - bound (quasi-bound) transitions: $h\nu_{tr} = E_{\nu',J,\Lambda'} - E_{\nu'',J,\Lambda''}$

$$k_{bb}(\nu, T) = w_{\Lambda'',\Lambda'} \frac{8\pi^3\nu}{3hc} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_J (2J+1) \sum_{\nu'',\nu'} \left| \langle \Phi_{\nu''J\Lambda''} | D(R) | \Phi_{\nu'J\Lambda'} \rangle \right|^2 \exp\left(-\frac{E_{\nu''J\Lambda''}}{k_B T}\right) g(h\nu - h\nu_{tr})$$

bound (quasi-bound) - free transition: $\varepsilon' = E_{\nu'',J,\Lambda''} + h\nu$

$$k_{bf}(\nu, T) = w_{\Lambda'',\Lambda'} \frac{8\pi^3\nu}{3hc} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_J (2J+1) \sum_{\nu''} \left| \langle \Phi_{\nu''J\Lambda''} | D(R) | \Psi_{\varepsilon'J\Lambda'} \rangle \right|^2 \exp\left(-\frac{E_{\nu''J\Lambda''}}{k_B T}\right)$$

free - bound (quasi-bound) transitions: $\varepsilon'' = E_{\nu',J,\Lambda'} - h\nu$

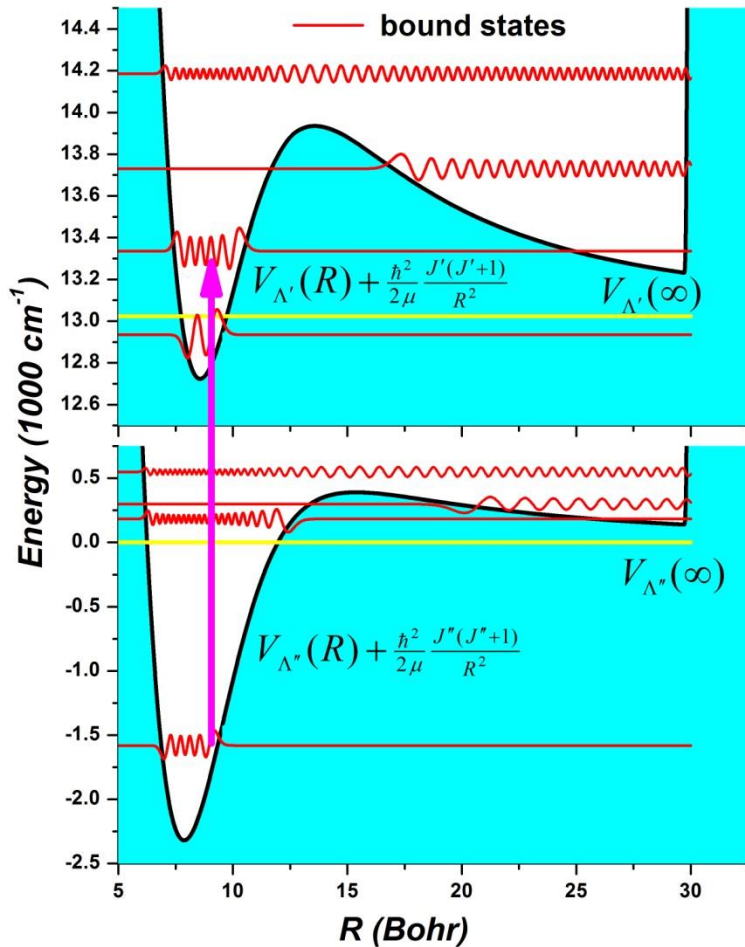
$$k_{fb}(\nu, T) = w_{\Lambda'',\Lambda'} \frac{8\pi^3\nu}{3hc} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_J (2J+1) \sum_{\nu'} \left| \langle \Psi_{\varepsilon''J\Lambda''} | D(R) | \Phi_{\nu'J\Lambda'} \rangle \right|^2 \exp\left(-\frac{\varepsilon''}{k_B T}\right)$$

free-free transitions: $\varepsilon' = \varepsilon'' + h\nu$

$$k_{ff}(\nu, T) = w_{\Lambda'',\Lambda'} \frac{8\pi^3\nu}{3hc} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_J (2J+1) \int_{D_e} d\varepsilon'' \left| \langle \Psi_{\varepsilon''J\Lambda''} | D(R) | \Psi_{\varepsilon'J\Lambda'} \rangle \right|^2 \exp\left(-\frac{\varepsilon''}{k_B T}\right)$$

$D(R)$ is electronic transition dipole moment, w is statistical factor dependent on the symmetry of electronic states, μ is molecular reduced mass, g line profile.

Quantum calculation on the Fourier grid (QC)



The FGR method can be considered as a special case of Discrete Variable Representation where functions are represented on finite number of grid points R_i ($i=1\dots N$). We used a grid of uniformly spaced points, $R_{i+1} - R_i = \Delta R$, [D.T. Colbert, W.H. Miller, J. Chem. Phys. 1992]. Energies and wave functions can be determined by diagonalization of $N \times N$ Hamiltonian matrix $H=T+P$:

$$T_{i,j} = \frac{\hbar^2}{2\mu\Delta R^2} \begin{cases} \frac{\pi^2}{3} - \frac{1}{2i^2} & i = j \\ (-1)^{i-j} \frac{8ij}{(i^2-j^2)^2} & i \neq j \end{cases}$$

$$V_{i,j} = \left[V_{\Lambda}(R_i) + \frac{\hbar^2 J(J+1) - \Lambda^2}{2\mu R_i^2} \right] \delta_{i,j}$$

The method yields only a discrete set of continuum energies, but in the range spanned by the grid the corresponding unity-normalized wave functions do represent the states of a true continuum.

Solving the relevant radial Schrödinger equation on the grid one obtains a set of discrete energies effectively describing a *confined* molecule, “a molecule in a box”, and the entire spectrum is of the bound–bound type.

$$k(\nu, T) = w \frac{8\pi^3 \nu}{3hc} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_{J=0}^{J_{\max}} (2J+1) \sum_{\nu'', \nu'} \left| \langle \Phi_{\nu'', J, \Lambda''} | D(R) | \Phi_{\nu', J, \Lambda'} \rangle \right|^2 \exp\left(-\frac{E_{\nu'', J, \Lambda''}}{k_B T}\right) g(h\nu - h\nu_{tr})$$

The matrix elements of the transition dipole moment $D(R)$ are computed as:

$$\langle \Phi_{\nu'', J, \Lambda''} | D(R) | \Phi_{\nu', J, \Lambda'} \rangle = \sum_{i=1}^{N_p} \Phi_{\nu'', J, \Lambda''}^*(R_i) D(R_i) \Phi_{\nu', J, \Lambda'}(R_i)$$

The parameters of the grid are estimated in the following way:

$$\Delta R = \frac{2\pi\hbar}{n_B \sqrt{2\mu\epsilon_{kin}}} \quad n_B \text{ is the number of grid points per de Broglie wavelength at maximal expected kinetic energy } \epsilon_{kin}.$$

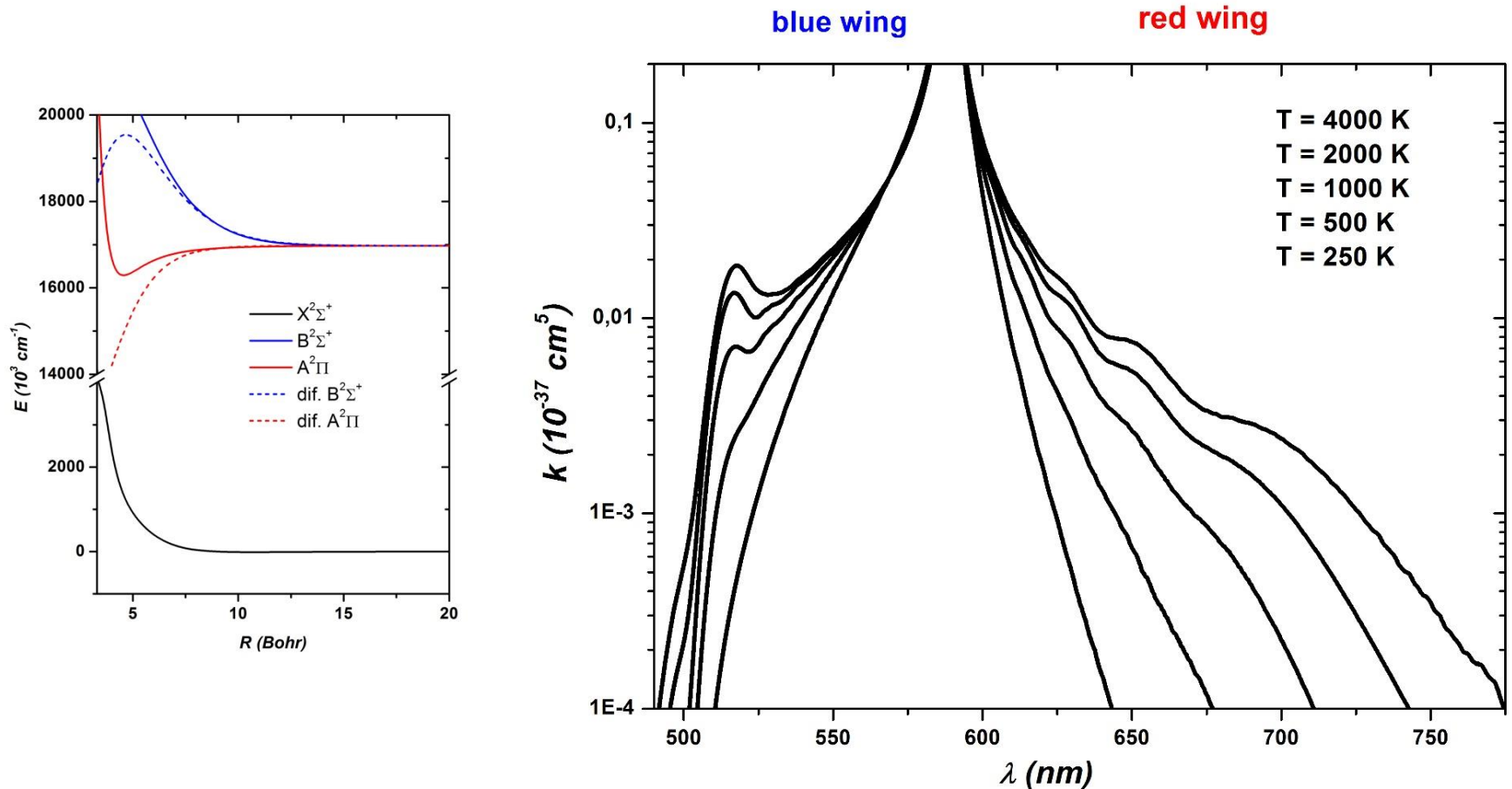
R_N was chosen in order to get closer to the atomic line centre.

$$J_{\max} \approx \frac{R_N}{\hbar} \sqrt{2\mu k_B T}$$

Line profile g can be approximated with a normalized rectangular instrumental profile: $1/\Delta(h\nu)$

Fully quantum-mechanical procedure based on the Fourier grid Hamiltonian method, is numerically robust but time consuming.

Sodium resonance 3s-3p line pressure broadened by helium atoms

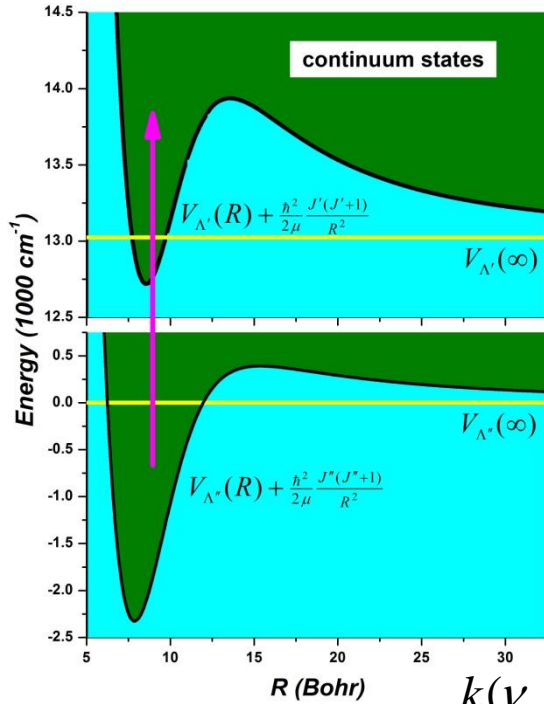


Good agreement with:

C. Zhu, J. F. Babb and A. Dalgarno, Phys.Rev. A:2006

K Alioua , M Bouledroua ,A R Allouche and M Aubert-Frécon, J. Phys. B: 2008

Semiclassical approximation (SCA)



Introducing a continuous variable $Y = \mathcal{X}(J + 1)$ and change $\sum_J (2J + 1) \rightarrow \int_0^\infty dY$

Any unity-normalized wave function Φ_ν can be turned into an energy-normalized wave function $\Psi_\varepsilon = \frac{1}{\sqrt{\left| \frac{\partial E_{\nu, J, \Lambda}}{\partial \nu} \right|}} \Phi_\nu$ and the sum can be changed into the integral

$$\sum_\nu \rightarrow \int_{\varepsilon_{\min}}^\infty \frac{\partial \nu}{\partial \varepsilon} d\varepsilon$$

The absorption coefficient can be written as:

$$k(\nu, T) \approx w \frac{8\pi^3 \nu}{3c} \left(\frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \int_{\varepsilon_{\min}}^\infty d\varepsilon'' \exp\left(-\frac{\varepsilon''}{k_B T}\right) \int_0^\infty dY \left| \langle \Psi_{\varepsilon'', Y, \Lambda''} | D(R) | \Psi_{\varepsilon'' + h\nu, Y, \Lambda'} \rangle \right|^2$$

Using energy-normalized wave functions in the WKB form, and the standard approximations, one obtains:

$$\langle \Psi_{\varepsilon, Y, \Lambda''} | D(R) | \Psi_{\varepsilon + h\nu, Y, \Lambda'} \rangle \approx \frac{\sqrt[4]{2\mu}}{\sqrt{2\pi\hbar}} \sum_i \frac{D(R_i)}{\sqrt[4]{\varepsilon - V_{\Lambda''}(R_i, Y)} \sqrt{|\Delta'(R_i)|}} \cos(\varphi(Y, \varepsilon, \nu, R_i) - \sigma_i \frac{\pi}{4})$$

Difference potential: $\Delta(R) = V_{\Lambda'}(R) - V_{\Lambda''}(R)$ $\Delta'(R) = \frac{d}{dR} \Delta(R)$ $\sigma_i = \text{sgn}[\Delta'(R_i)]$

Sumation is over the **Condon points** R_i satisfying the condition $\Delta(R_i) = h\nu$.

Neglecting the rapidly oscillating terms , one obtains **coherent quasi-static** formula of the reduced absorption coefficient :

$$k(\nu, T) = w \frac{32\pi^4 \nu}{3c} \left[\sum_{i=1}^n \frac{R_i^2 D(R_i)^2}{|\Delta'(R_i)|} \exp\left(-\frac{V_{\Lambda^*}(R_i)}{k_B T}\right) + \sum_{i=1}^{n-1} 2 \frac{R_{ii}^2 D(R_i) D(R_{i+1})}{\sqrt{|\Delta'(R_i)| |\Delta'(R_{i+1})|}} \exp\left(-\frac{V_{\Lambda^*}(R_{ii})}{k_B T}\right) M_i(\nu, T) \right]$$

Quasi-static formula generally gives a good description of the absorption coefficient, but diverges in difference potential extremes (classical singularity).

This divergence can be removed by mapping of the semi-classical canonic integral phase, into the characteristic form of the elementary "fold" or "cusp" catastrophe.

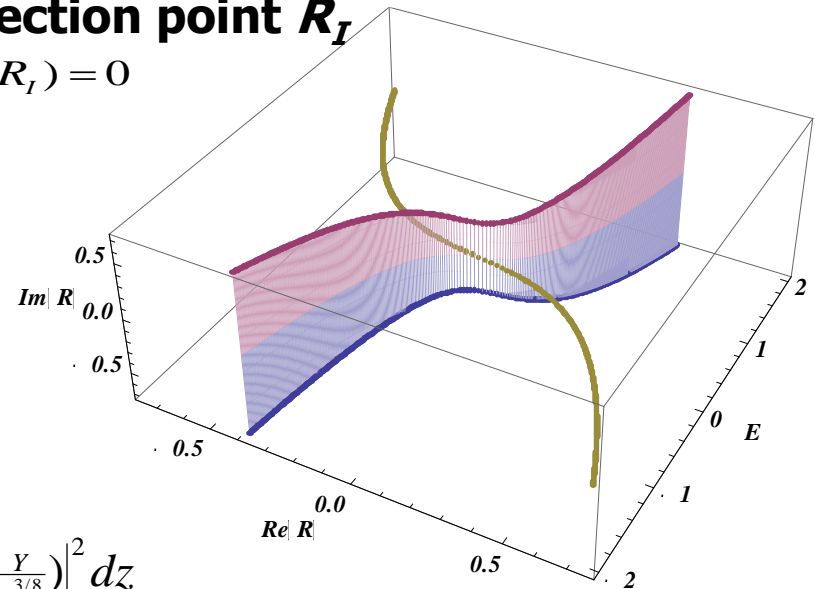
Elementary profile type:

1. Difference potential $\Delta(R)$ is a monotonic function, one real Condon point R_1
2. Difference potential $\Delta(R)$ is a monotonic function, one inflection point R_I , one real Condon point R_1 and complex pair of Condon points $R_{2,3}$
3. Difference potential $\Delta(R)$ has extrema , two Condon points $R_{1,2}$

If difference potential $\Delta(R)$ has more extremes, absorption profile can be obtained by combining the elementary profiles.

2. Difference potential $\Delta(R)$ has one inflection point R_I transitive Pearcey approximation $\Delta''(R_I) = 0$

$$k(\nu, T) = w \frac{32\pi^4 \nu}{3c} \frac{R_I^2 D(R_I)^2}{|\Delta'(R_I)|} \exp\left(-\frac{V_{\Delta''}(R_I)}{k_B T}\right) L_c(\nu, T)$$



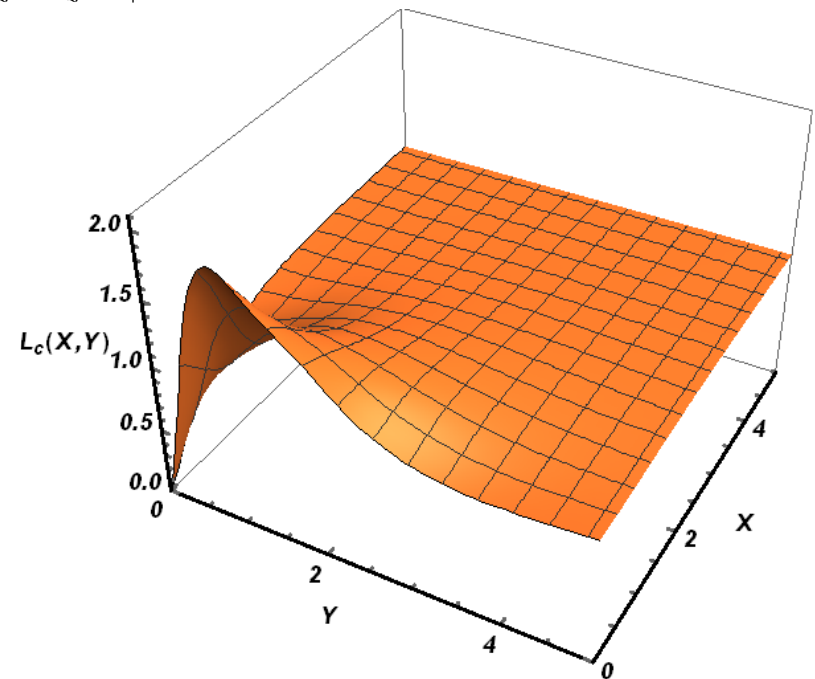
$$L_c(X, Y) = \frac{\left(\sqrt{\frac{8}{27}X^3+Y^2}-Y\right)^{\frac{2}{3}} + \left(\sqrt{\frac{8}{27}X^3+Y^2}+Y\right)^{\frac{2}{3}} - \frac{2}{3}X}{\pi^{3/2}} \int_0^{\infty} \frac{\exp(-z)}{z^{3/4}} \left|P\left(\frac{X}{z^{1/4}}, \frac{Y}{z^{3/8}}\right)\right|^2 dz$$

$$P(x, y) = \int_{-\infty}^{\infty} e^{i(u^4+xu^2+yu)} du \quad \text{Pearcey integral}$$

$$X(T) = |\Delta'(R_I)| \sqrt{\frac{3}{|\Delta'''(R_I)|}} \left(\frac{2\mu}{\hbar^2 k_B T}\right)^{1/4}$$

$$Y(\nu, T) = |\Delta(R_I) - h\nu| \sqrt[4]{\frac{3}{|\Delta'''(R_I)|}} \left(\frac{2\mu}{\hbar^2 k_B T}\right)^{3/8}$$

If $Y(\nu, T) > 5$ or $X(T) > 5$, what is the most common case, $L_c(\nu, T) \rightarrow 1$



3. Difference potential $\Delta(R)$ has extrema in point R_e

J.N.L. Connor, R.A. Marcus, *J. Chem. Phys.* 1971

K.M. Sando, J.C. Wormhoudt, *Phys. Rev. A* 1973

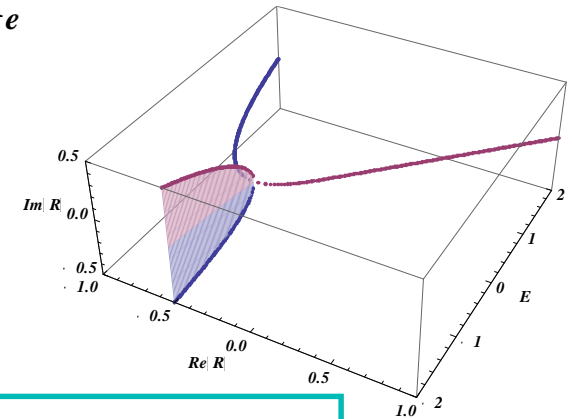
J. Szudy, W.E. Baylis, *JQSRT* 1975

P.A. Vicharelli, C.B. Collins, *SLS* 1983

R. Beuc and V. Horvatic: *J. Phys. B*: 1992

R. Beuc, B. Horvatić, M. Movre, *J. Phys. B*, 2010

$$\Delta''(R_e) = 0$$



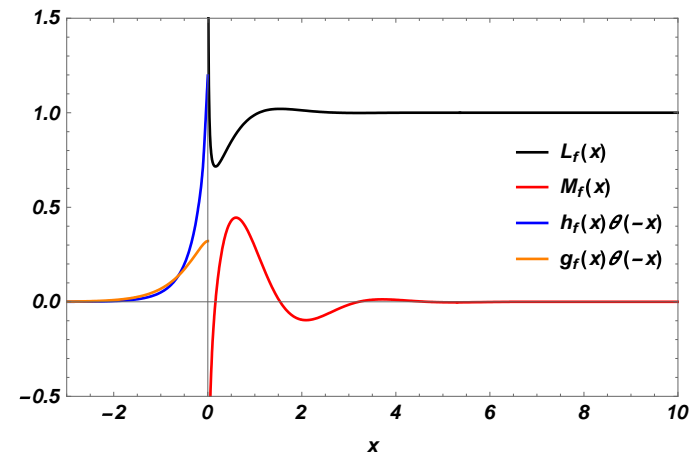
uniform Airy approximation

$$k(\nu, T) = w \frac{32\pi^4 \nu}{3c} \left\{ \left[\frac{R_1^2 D(R_1)^2}{|\Delta'(R_1)|} \exp\left(-\frac{V_{\Lambda^*}(R_1)}{k_B T}\right) + \frac{R_2^2 D(R_2)^2}{|\Delta'(R_2)|} \exp\left(-\frac{V_{\Lambda^*}(R_2)}{k_B T}\right) \right] L_f(\zeta) \right. \\ \left. + 2 \frac{R_1^2 D(R_1) D(R_2)}{\sqrt{|\Delta'(R_1)| |\Delta'(R_2)|}} \exp\left(-\frac{V_{\Lambda^*}(R_1)}{k_B T}\right) M_f(\zeta) \right. \\ \left. + \left(\frac{8m}{\hbar^2 k_B T} \right)^{\frac{1}{3}} \frac{R_e^2}{|\Delta''(R_e)|^{2/3}} e^{-\frac{V(R_e)}{k_B T}} \left[D(R_e)^2 h(\zeta) + \left(\frac{\hbar^2 k_B T}{8m} \right)^{\frac{1}{3}} \frac{4 \left[D'(R_e) - D(R_e) \frac{\Delta'''(R_e)}{6\Delta''(R_e)} \right]^2}{|\Delta''(R_e)|^{\frac{2}{3}}} g(\zeta) \right] \right\}$$

$$L_c(\zeta) = \sqrt{\zeta} h(\zeta) + \frac{1}{\sqrt{\zeta}} g(\zeta) \quad M_c(\zeta) = \sqrt{\zeta} h(\zeta) - \frac{1}{\sqrt{\zeta}} g(\zeta)$$

$$h(\zeta) = \sqrt{\pi} \int_0^{\infty} \frac{Ai\left[\frac{-\zeta}{x^{1/3}}\right]^2}{x^{2/3}} e^{-x} dx \quad g(\zeta) = \sqrt{\pi} \int_0^{\infty} \frac{Ai\left[\frac{-\zeta}{x^{1/3}}\right]}{x^{1/3}} e^{-x} dx$$

$$\zeta = \zeta(\nu, T) \approx \left(\frac{4\pi^2 \hbar \mu}{k_B T |\Delta''(R_e)|} \right)^{\frac{1}{3}} \sigma(\nu_e - \nu)$$



The standard semiclassical approximation does not give the rovibrational structure of the molecular bands, neglects the effects of turning points, but agrees perfectly with the averaged-out quantum-mechanical spectra. Also, the semiclassical theory can give a physical interpretation of the results obtained by fully quantum-mechanical calculations (W. H. Miller).

Semiquantum approximation (SQA)

Using standard semiclassical approximations, we calculated integral :

$$\int_{\varepsilon_{\min}}^{\infty} d\varepsilon \exp\left(-\frac{\varepsilon}{k_B T}\right) \left| \left\langle \Psi_{\varepsilon,0,\Lambda''} \left| RD(R) \right| \Psi_{\varepsilon+h\nu,0,\Lambda'} \right\rangle \right|^2$$

By comparison with the semi-classical form of reduced absorption coefficient, we get expression:

$$k(\nu, T) \approx w \frac{32\pi^4 \nu}{3c} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{\frac{1}{2}} \int_{\varepsilon_{\min}}^{\infty} d\varepsilon'' \exp\left(-\frac{\varepsilon''}{k_B T}\right) \left| \left\langle \Psi_{\varepsilon'',0,\Lambda''} \left| RD(R) \right| \Psi_{\varepsilon''+h\nu,0,\Lambda'} \right\rangle \right|^2$$

Turning energy-normalized wave functions to unity-normalized wave functions one obtains

$$k(\nu, T) \approx w \frac{32\pi^4 \nu}{3c} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{1/2} \int_0^{\infty} d\nu'' \int_0^{\infty} d\nu' \exp\left(-\frac{E_{\nu'',0,\Lambda''}}{k_B T}\right) \left| \left\langle \Phi_{\nu'',0,\Lambda''} \left| RD(R) \right| \Phi_{\nu',0,\Lambda'} \right\rangle \right|^2 \delta(h\nu - h\nu_{tr})$$

One can approximate the integrals by sums

and obtain a quantum-like (“quasiquantum” or “**semiquantum**”) expression.

$$k(\nu, T) \approx W \frac{32\pi^4 \nu}{3c} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{1/2} \sum_{\nu'', \nu'} \exp\left(-\frac{E_{\nu'', \Lambda''}}{k_B T}\right) \left| \langle \Phi_{\nu'', 0, \Lambda''} | RD(R) | \Phi_{\nu', 0, \Lambda'} \rangle \right|^2 g(h\nu - h\nu_{tr})$$

In order to evaluate this relation, one needs to know the vibrational energies and the corresponding wave functions for $J = 0$ only.

Semiquantum approximation gives good results if the distance between the vibrational transitions $h\nu_{tr} = E_{\nu', \Lambda'} - E_{\nu'', \Lambda''}$ is comparable or less than the width of the instrumental profile g .

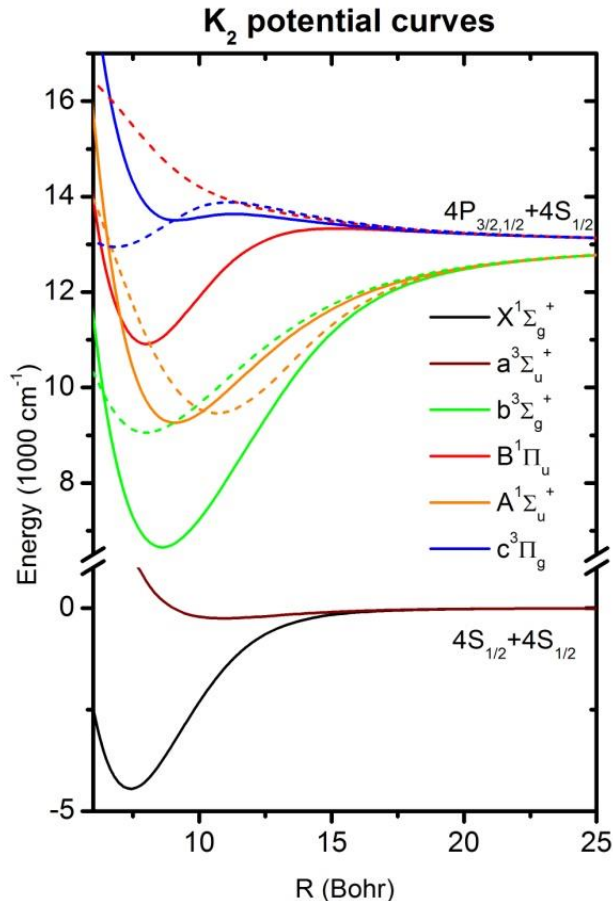
The semiquantum spectrum was collected in bins of the size $\Delta h\nu = 10 \text{ cm}^{-1}$ and smoothed out with a simple unity-normalized triangular profile having a width of 50 cm^{-1} .

The semiquantum approximation is in very good agreement with fully quantum calculations, while its computer time consumption can be lower by four orders of magnitude.

A disadvantage of this method is an unsatisfactory description of the discrete structure of molecular bands.

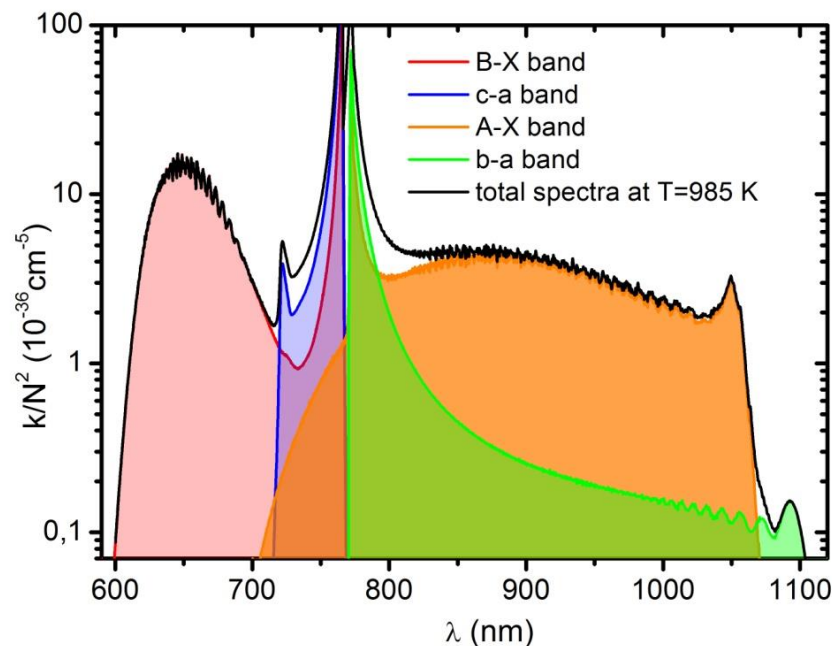
However, even the low-resolution absorption spectroscopy may serve as a valuable tool for checking the accuracy of molecular electronic structure calculations, and for gas temperature and number density diagnostics .

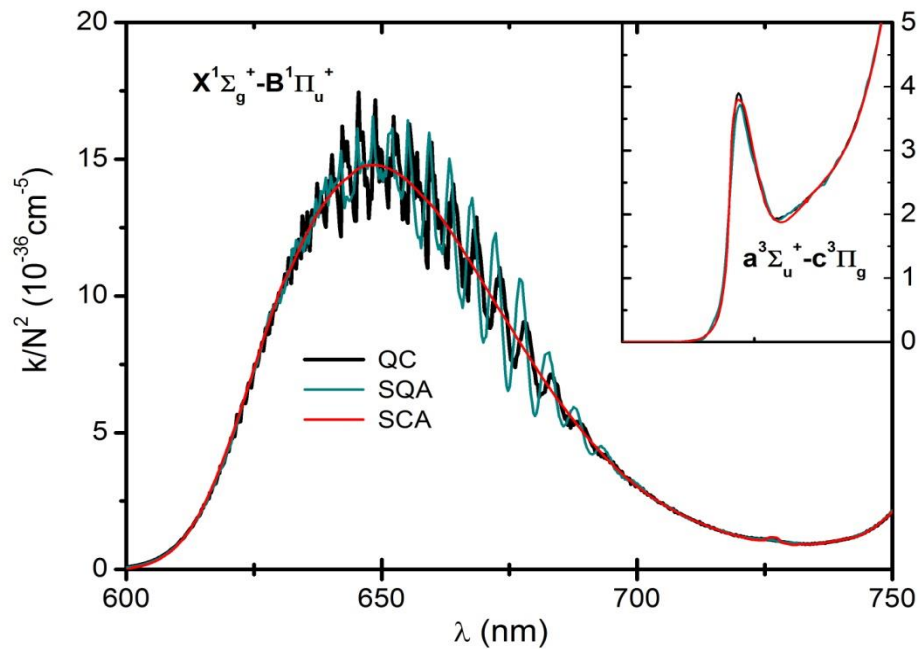
Absorption spectra of potassium molecule



The quantum-mechanical calculation for temperature $T = 985$ K.

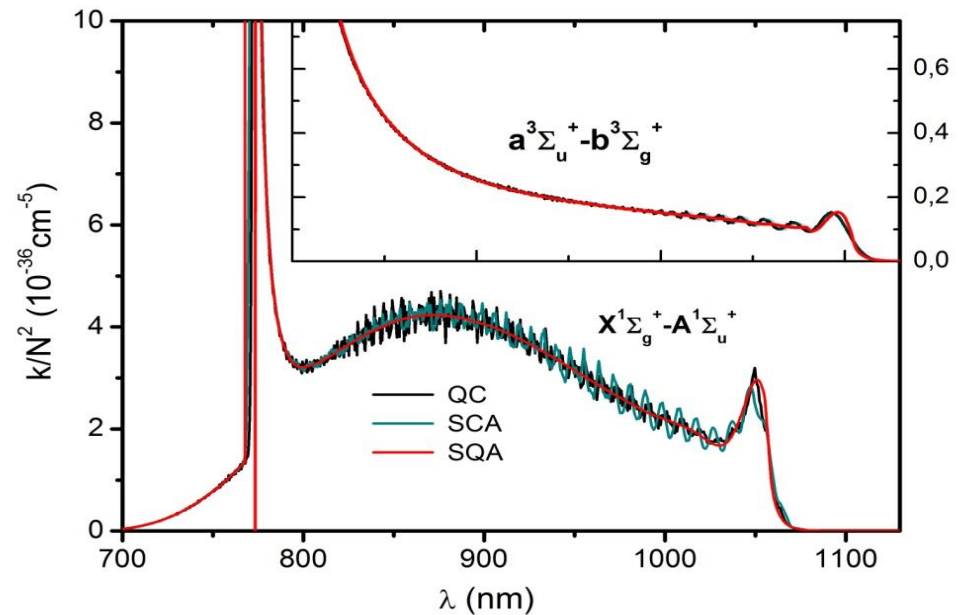
R. Beuc, M. Movre, B. Horvatić, Eur. Phys. J. D, 2014
 In the theoretical simulation we used *ab initio* potential energy functions and the relevant transition dipole moments [L. Yan, W. Meyer, unpublished results], experimentally determined potential functions for the singlet transitions [C. Amiot, J. Mol. Spectrosc. (1991) and C. Amiot, J. Vergès, C.E. Fellows, J. Chem. Phys. (1995)], and the long-range calculation [M. Marinescu, A. Dalgarno, Phys. Rev. A (1995)].

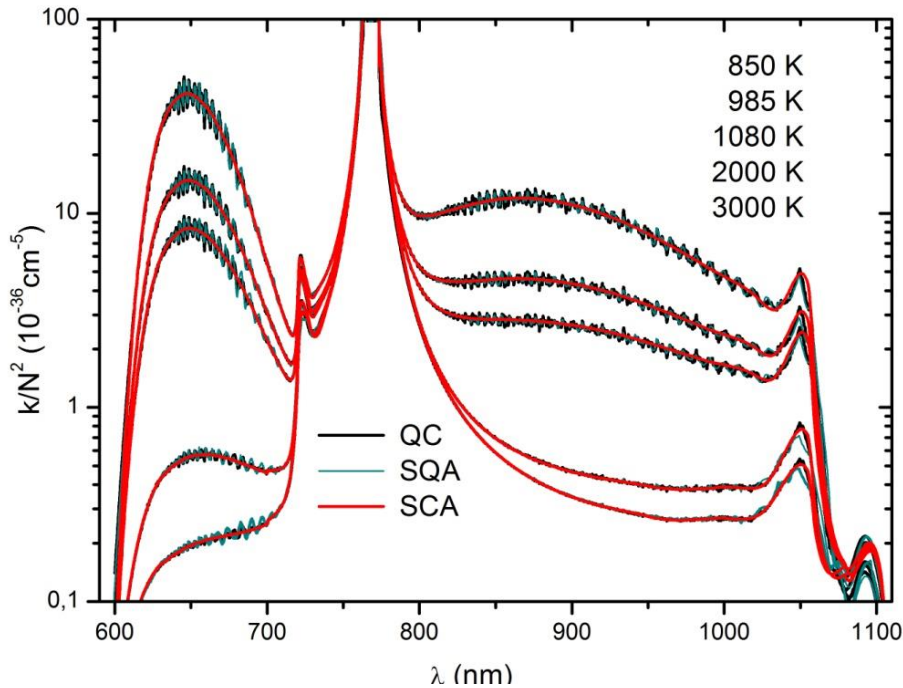




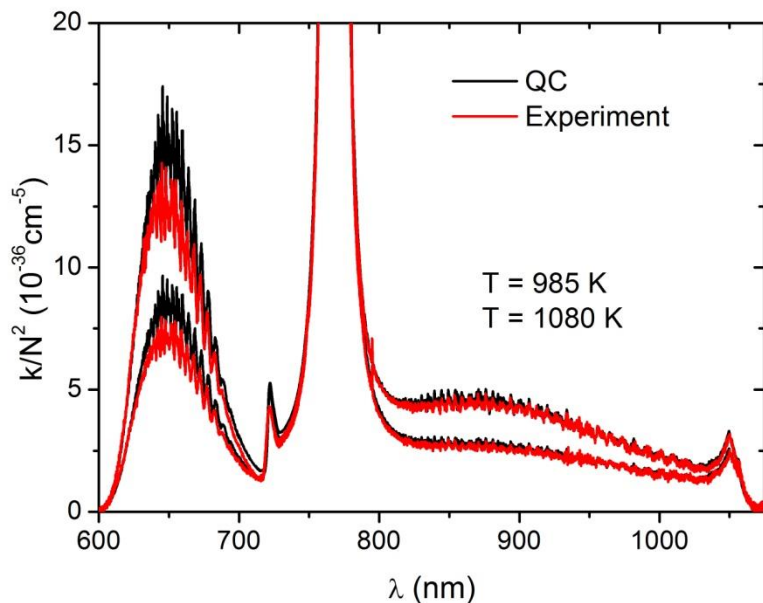
Comparison of QC, SQA and SCA for vapor temperature $T = 985$ K.

For the calculation of the absorption spectrum of the $B-X$ transition, the computer time was:
 3000 s for the QC
 0.2 s for the SQA and SCA.





Comparison of QC, SQA and SCA for a range of temperatures.



We compare experiment [C. Vadla, R. Beuc, V. Horvatic, M. Movre, A. Quentmeier, K. Niemax, Eur. Phys. J. D,2006] and QC for two experimental temperatures. A slight increase in the simulated $B-X$ band intensity may be attributed to the uncertainty in the *ab initio* transition dipole moments.

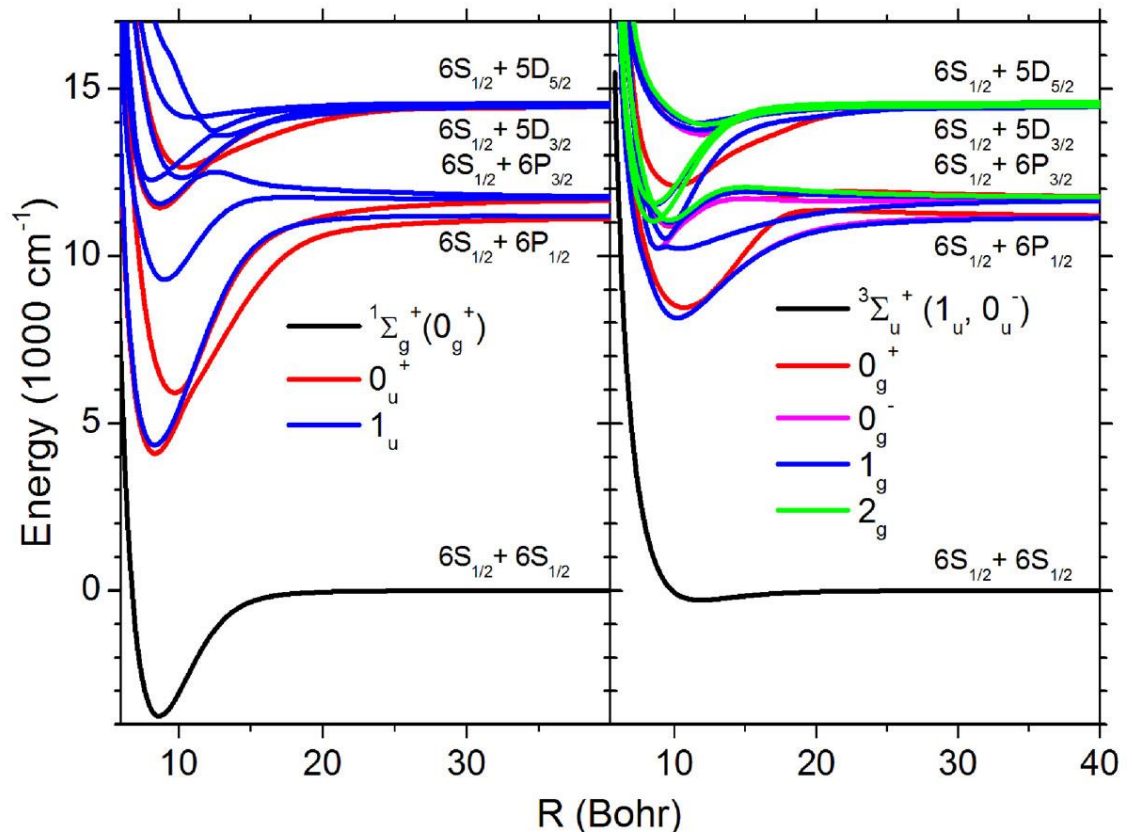
Cesium emission and absorption spectra

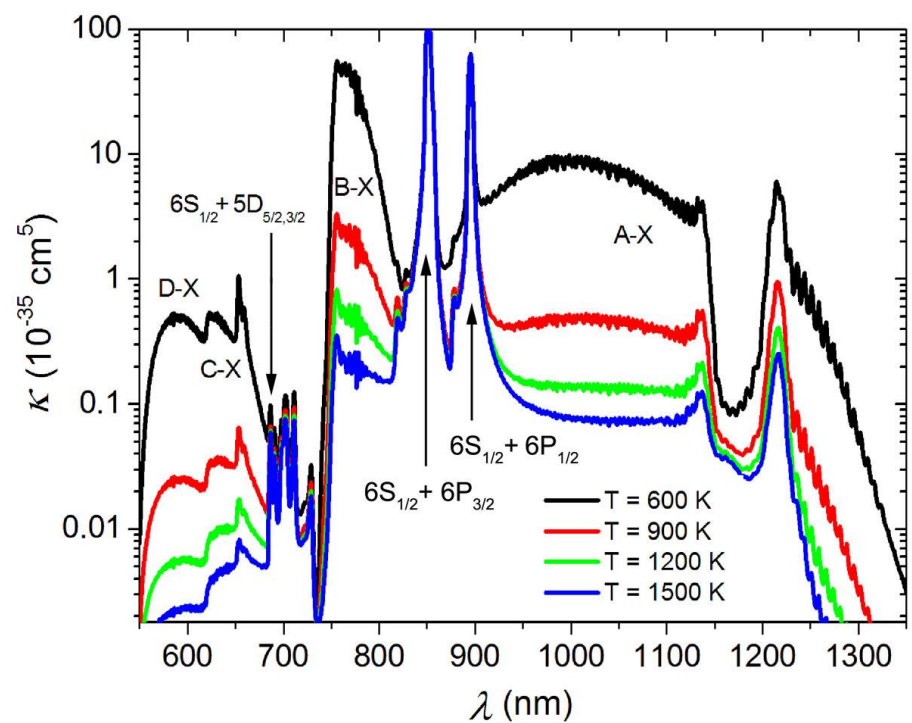
B. Horvatić, R. Beuc, M. Movre, Eur. Phys. J. D, 2015

A recent *ab initio* [A. R. Allouche, M. Aubert-Frécon, J. Chem. Phys. 2012] calculation of Cs₂ electronic potential curves and electronic transition dipole moments provided us with an input for the numerical simulation of Cs₂ spectra.

We investigated the red and near-infrared (600 – 1300 nm) absorption and emission spectrum of a cesium vapor for temperatures within the range 600 – 1500 K using SQA.

11 singlet and 19 triplet electronic transitions $\Lambda'' \rightarrow \Lambda'$ contribute to the absorption spectrum. The computing time was 6 – 60 seconds, depending on the temperature.

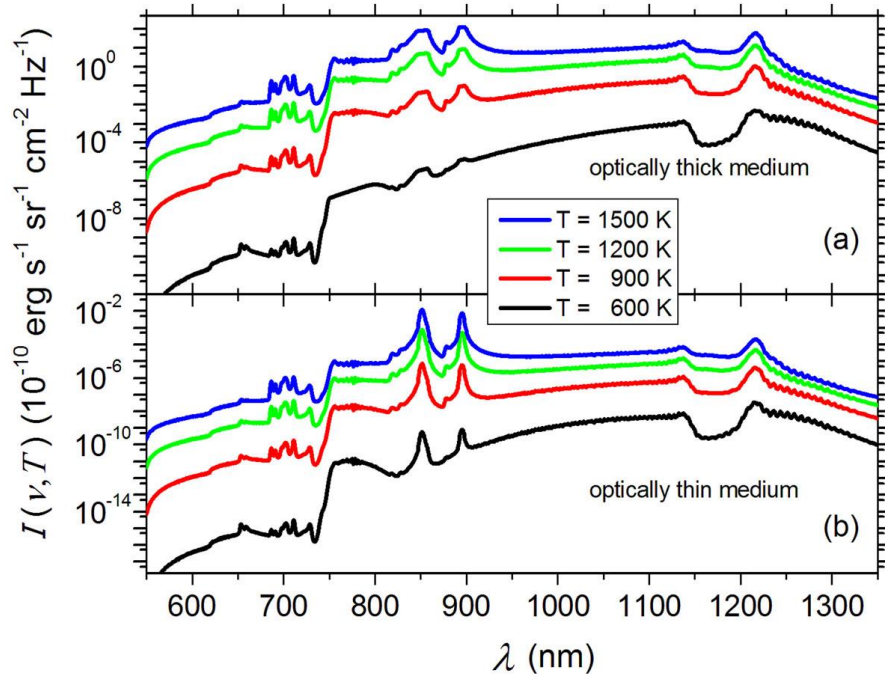




Absorption spectra for a range of temperatures.

In the LTE approximation, the spectral radiance of a uniform emitting layer (thickness L , atomic number density N) is:

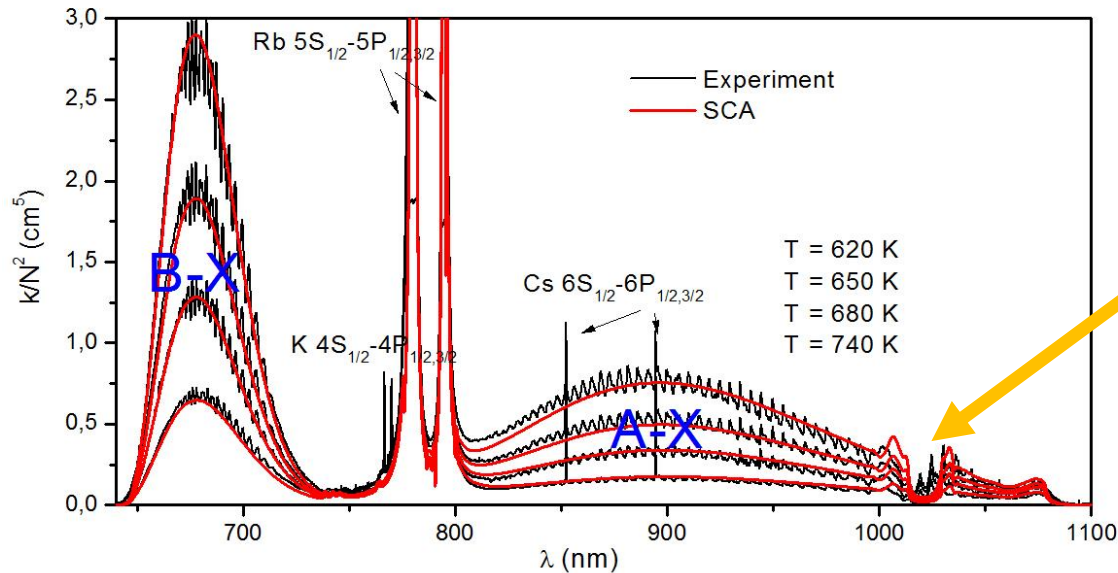
$$I(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1 - e^{-N^2 L k(\nu, T) [1 - \exp(-h\nu/k_B T)]}}{e^{h\nu/k_B T} - 1}$$



- (a) optically thick medium
 $\kappa N^2 L \gg 1$, $N^2 L = 3 \cdot 10^{34} \text{ cm}^{-5}$
- (b) optically thin medium
 $\kappa N^2 L \ll 1$, $N^2 L = 10^{29} \text{ cm}^{-5}$

Absorption spectra of rubidium dimer

R. Beuc, M. Movre, V. Horvatic, C. Vadla, O. Dulieu and M. Aymar, Phys.Rev. A, 2007

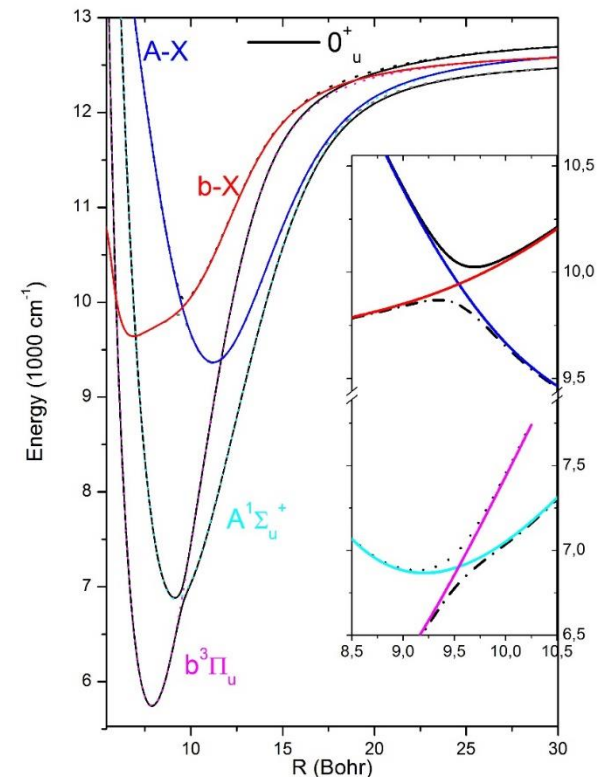


A-X absorption band is formed by a transition from ground $0^+_g(X^1\Sigma^+_g)$ state to excited states $0^+_u(A^1\Sigma^+_u)$ and $0^+_u(b^1\Pi_u)$ coupled by spin-orbit interaction $V_{so}(R)$.

In the framework of FGH method, energies and wave functions for coupled states can be determined by diagonalization of $2N \times 2N$ matrix H

$$H = \begin{pmatrix} T & 0 \\ 0 & T \end{pmatrix} + \begin{pmatrix} V_A & V_{so} \\ V_{so} & V_b \end{pmatrix} \quad T_{i,j} = \frac{\hbar^2}{2\mu\Delta R^2} \begin{cases} \frac{\pi^2}{3} - \frac{1}{2i^2} & i = j \\ (-1)^{i-j} \frac{8ij}{(i^2 - j^2)^2} & i \neq j \end{cases}$$

$$(V_{A,b})_{i,j} = \left[V_{A,b}(R_i) + \frac{\hbar^2}{2\mu} \frac{J(J+1)}{R_i^2} \right] \delta_{i,j} \quad (V_{so})_{i,j} = V_{so}(R_i) \delta_{i,j}$$



If the dominant contribution to the spectrum consists of bound-bound transitions, and if the distance between the rotational lines is less than the width of the instrumental profile, the absorption coefficient can be determined using the **vibrational band continuum approximation (VBCA)**; [R.W. Patch, W.L. Shackleford, S.S. Penner. JQSRT, 1962, L.K. Lam, A. Gallagher, and M.M. Hessel, J.Chem.Phys. 1977].

$$k_{b,b}(\nu, T) = w \frac{8\pi^3 \nu}{3c} \left(\frac{h^2}{2\pi\mu k_B T} \right)^{3/2} \sum_{v'', v'}^{bound} \exp\left(-\frac{E_{v'', \Lambda''}}{k_B T}\right) \frac{\left| \langle \Phi_{v'', 0, \Lambda''} | D(R) | \Phi_{v', 0, \Lambda'} \rangle \right|^2}{|B_{v'} - B_{v''}|} \exp\left(-\frac{B_{v'}(E_{v', v''} - h\nu)}{(B_{v'} - B_{v''})k_B T}\right)$$

VBCA gives good results, if the dominant contribution comes from the transition between the lowest vib-rotational states, where following conditions are satisfied

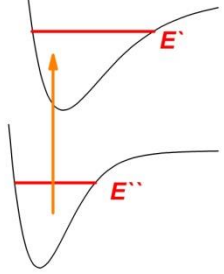
$$\left| \langle \Phi_{v'', J, \Lambda''} | D(R) | \Phi_{v', J, \Lambda'} \rangle \right| \approx \left| \langle \Phi_{v'', 0, \Lambda''} | D(R) | \Phi_{v', 0, \Lambda'} \rangle \right| \quad E_{v, J, \Lambda} \approx E_{v, \Lambda} + B_v J(J + 1)$$

Hybrid approximation

Using good properties of SQA and VBCA, we introduced a **hybrid approximation** (HA) of the reduced absorption coefficient:

$$k(\nu, T) = w \frac{8\pi^3 \nu}{3c} \left(\frac{\hbar^2}{2\pi\mu k_B T} \right)^{3/2} \sum_{\nu'', \nu'} \exp\left(-\frac{E_{\nu'', \Lambda''}}{k_B T}\right) \frac{|\langle \Phi_{\nu'', 0, \Lambda''} | D(R) | \Phi_{\nu', 0, \Lambda'} \rangle|^2}{|B_{\nu''} - B_{\nu'}|} \exp\left(-\frac{B_{\nu'}(E_{\nu', \nu'} - h\nu)}{(B_{\nu'} - B_{\nu''})k_B T}\right) G(E'', E'', \nu'', \nu', \nu) +$$

$$+ w \frac{32\pi^4 \nu}{3c} \left(\frac{\hbar^2}{2\pi\mu k_B T} \right)^{1/2} \sum_{\nu'', \nu'} \exp\left(-\frac{E(E'', E', \nu'', \nu')}{k_B T}\right) \left| \langle \Phi_{\nu'', 0, \Lambda''} | RD(R) | \Phi_{\nu', 0, \Lambda'} \rangle \right|^2 g(h\nu - h\nu_{ir})$$



$$G(E'', E'', \nu'', \nu', \nu) = \theta\left(\frac{h\nu - E_{\nu', \nu'}}{B_{\nu'} - B_{\nu''}}\right) \theta\left(\min\left[\frac{E'' - E_{\nu'', \Lambda''}}{B_{\nu''}}, \frac{E' - E_{\nu', \Lambda'}}{B_{\nu'}}\right] - \frac{h\nu - E_{\nu', \nu'}}{B_{\nu'} - B_{\nu''}}\right)$$

$$E(E'', E'', \nu'', \nu') = E_{\nu'', \Lambda''} \left[1 - \theta(E'' - E_{\nu'', \Lambda''}) \theta(E' - E_{\nu', \Lambda'}) \right] + \min[E'', E' - E_{\nu', \Lambda'} + E_{\nu'', \Lambda''}] \theta(E'' - E_{\nu'', \Lambda''}) \theta(E' - E_{\nu', \Lambda'})$$

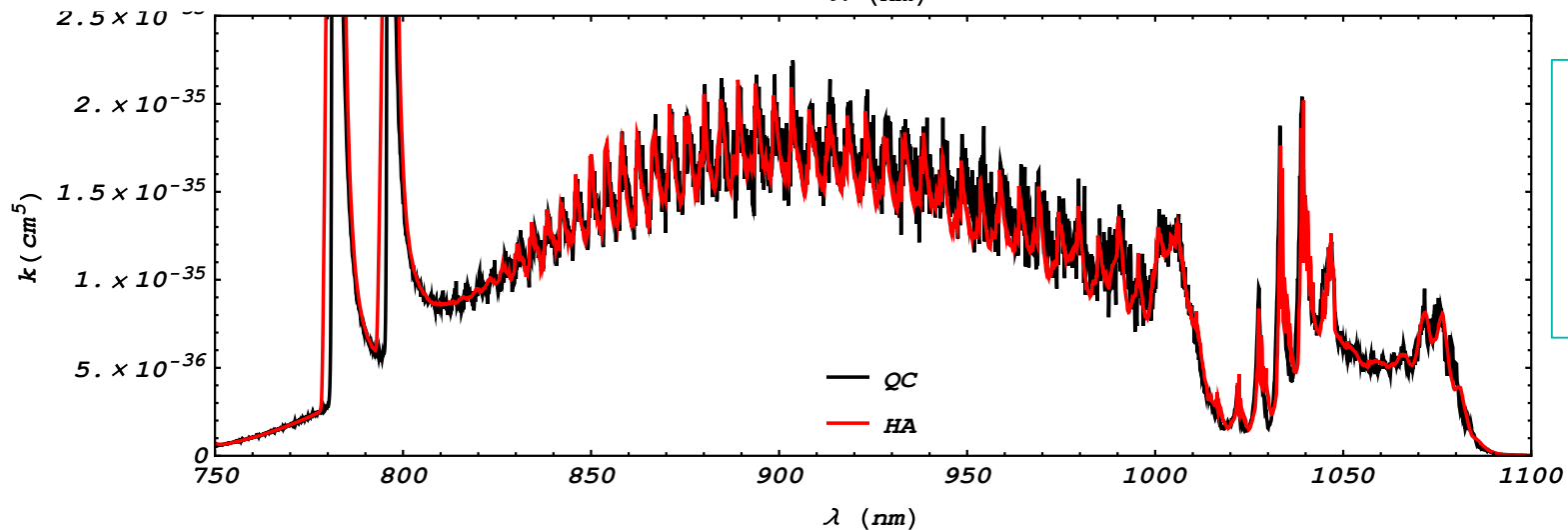
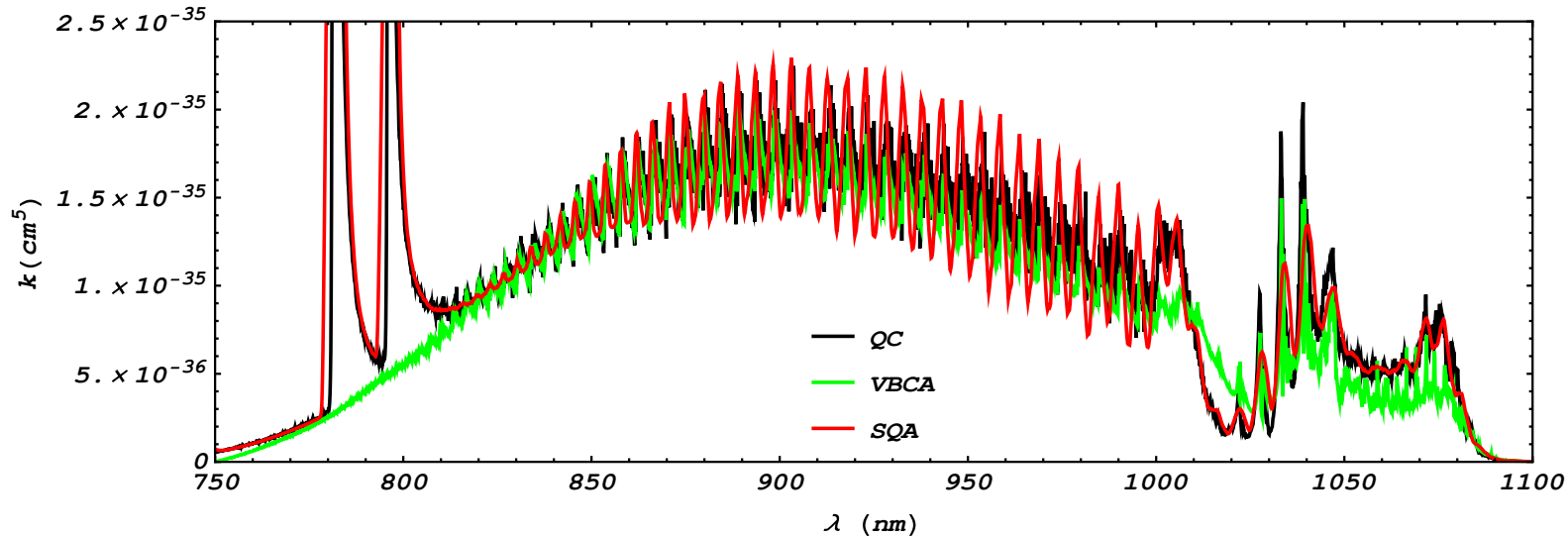
The first contribution to $k(\nu, T)$ is the VBCA of transitions for which $E'' \geq E_{\nu'', J, \Lambda''}$ and $E' \geq E_{\nu', J, \Lambda'}$, and the second contribution is the SQA of all other transitions.

$$E'' = E_{0, \Lambda''} + x \frac{B_{\nu''=0}^2}{D_{\nu''=0}} \quad E' = E_{0, \Lambda'} + x \frac{B_{\nu'=0}^2}{D_{\nu'=0}}$$

$$E'' \geq E_{\nu'', J, \Lambda''} \quad E_{\nu'', J, \Lambda''} = E_{\nu'', \Lambda''} + B_{\nu''} J(J+1) \quad \Phi_{\nu'', J, \Lambda''} \approx \Phi_{\nu'', 0, \Lambda''}$$

$$E' \geq E_{\nu', J, \Lambda'} \quad E_{\nu', J, \Lambda'} = E_{\nu', \Lambda'} + B_{\nu'} J(J+1) \quad \Phi_{\nu', J, \Lambda'} \approx \Phi_{\nu', 0, \Lambda'}$$

Theoretical simulations of rubidium A-X band at a temperature of 740 K.



Comp. time:
QC=2618 s
VBCA=126 s
HA=16 s
SQA=0.3 s

The hybrid approximation improves the description of the molecular bands structure at a cost of an acceptable increase of the computer time.

Thank you for your attention

