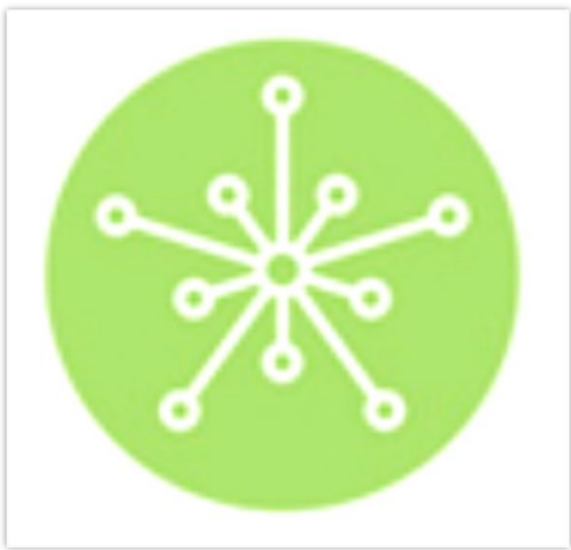


# TIME-EFFICIENT NUMERICAL SIMULATION OF DIATOMIC MOLECULES' EMISSION AND ABSORPTION SPECTRA



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We developed a full quantum mechanical procedure for calculating the emission and absorption spectra of diatomic molecules in dense weakly ionized plasma at high temperatures. Discrete and continuous spectrum contributions, which are the result of transitions between bound, free, and quasi-bound states of diatomic molecules were treated on the same footing. The reduced absorption coefficient is given by the equation

$$k(E, T) = a(\mu, T, E) \sum_J (2J+1) \sum_{v', v''} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | D(R) | \Phi_{v', v''} \rangle \right|^2 g(E - E_{v'})$$

where the rovibrational energies and wave functions were determined using the Fourier grid Hamiltonian method [1].

Lam, Gallagher, and Hessel [2], using analytical summation over the angular momenta  $J$ , got the approximate expression for the absorption coefficient (LGH approximation):

$$k(E, T) = a(\mu, T, E) \sum_{v', v''} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | D(R) | \Phi_{v', v''} \rangle \right|^2 \exp\left(-\frac{B_{v', v''}(E - E_{v'})}{B_{v', v''} k_B T}\right) \frac{\Theta\left(\frac{E - E_{v'}}{B_{v', v''}}\right)}{|B_{v', v''}|}$$

This approximation described extremely well the discrete spectrum structure due to the transitions from deeply bound rovibrational states, but less correctly the one due to transitions from weakly bound and free states. Using the stationary-phase approximation and the classical Franck-Condon principle we have shown that:

$$k(E, T) \approx a(\mu, T, E) \frac{2ik_B T}{h^2} \int_{\sigma_{\min}}^{\infty} d\sigma \exp\left(-\frac{\sigma^2}{k_B T}\right) \left| \langle \Phi_{v', v''} | RD(R) | \Phi_{v', v''} \rangle \right|^2$$

The semiclassical approximation (SCA) [3] does not give the rovibrational molecular structure of the spectrum bands, but agrees perfectly with the averaged out quantum mechanical spectra.

Using "good" analytical properties of the semiclassical approximation, we developed a computationally efficient "semiquantum" approximation of the reduced absorption coefficient (SQA):

$$k(E, T) = a(\mu, T, E) \frac{2ik_B T}{h^2} \sum_{v', v''} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | RD(R) | \Phi_{v', v''} \rangle \right|^2 g(E - E_{v'})$$

This approximation is in very good agreement with full quantum calculations, while its consumption of computer time is lower by three orders of magnitude. A disadvantage of this method is a not sufficiently good description of the discrete structure of molecular bands.

To take advantage of good properties of both the LGH approximation and the semiquantum one, we propose a hybrid approximation (HA) in which the reduced absorption coefficient is calculated from the relation

$$k(E, T) = a(\mu, T, E) \left[ \frac{2ik_B T}{h^2} \sum_{v', v''}^{\text{free}} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | RD(R) | \Phi_{v', v''} \rangle \right|^2 g(E - E_{v'}) + \sum_{v', v''}^{\text{bound}} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | D(R) | \Phi_{v', v''} \rangle \right|^2 \exp\left(-\frac{B_{v', v''}(E - E_{v'})}{B_{v', v''} k_B T}\right) \frac{\Theta\left(\frac{E - E_{v'}}{B_{v', v''}}\right)}{|B_{v', v''}|} + \mathfrak{R}(E, T) \right]$$

where

$$\mathfrak{R}(E, T) = \left[ \frac{2ik_B T}{h^2} \sum_{v', v''}^{\text{bound}} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | RD(R) | \Phi_{v', v''} \rangle \right|^2 g(E - E_{v'}) - \sum_{v', v''}^{\text{bound}} \exp\left(-\frac{E_{v', v''}}{k_B T}\right) \left| \langle \Phi_{v', v''} | D(R) | \Phi_{v', v''} \rangle \right|^2 \exp\left(-\frac{B_{v', v''}(E - E_{v'})}{B_{v', v''} k_B T}\right) \frac{\Theta\left(\frac{E - E_{v'}}{B_{v', v''}}\right)}{|B_{v', v''}|} \right] * L(E, T)$$

The results of the hybrid approximation are in excellent agreement with full quantum calculations, and the time efficiency is more than two orders of magnitude higher, which is very suitable for application in the analysis of experimental results.

For the calculation of the absorption spectrum of the BX transition at the temperature of 985 K, the computer time required (quad-core 3 GHz processor, 8 GB RAM) amounts to 2675 s for the full quantum calculations, 59 s for the LGH approximation, 2 s for the hybrid one, 0.17 s for the semiclassical, and 0.16 s for the semiquantum.

Theoretical results we obtained were tested by comparison with experimental absorption spectra of potassium molecules at different temperatures. [4]. It was found that our theoretical approach gives much better results than recent studies by other authors [5].

If accurate molecular electronic potential curves and corresponding electronic transition dipole moments are known, it is possible, by using the fast "semiquantum" approach and comparing the obtained theoretical spectra with experimental data, to determine the temperature and number density of molecules in real time.

[1] V. Kokoouline et al, Phys. Rev. A **62**, 0022504 (2000)

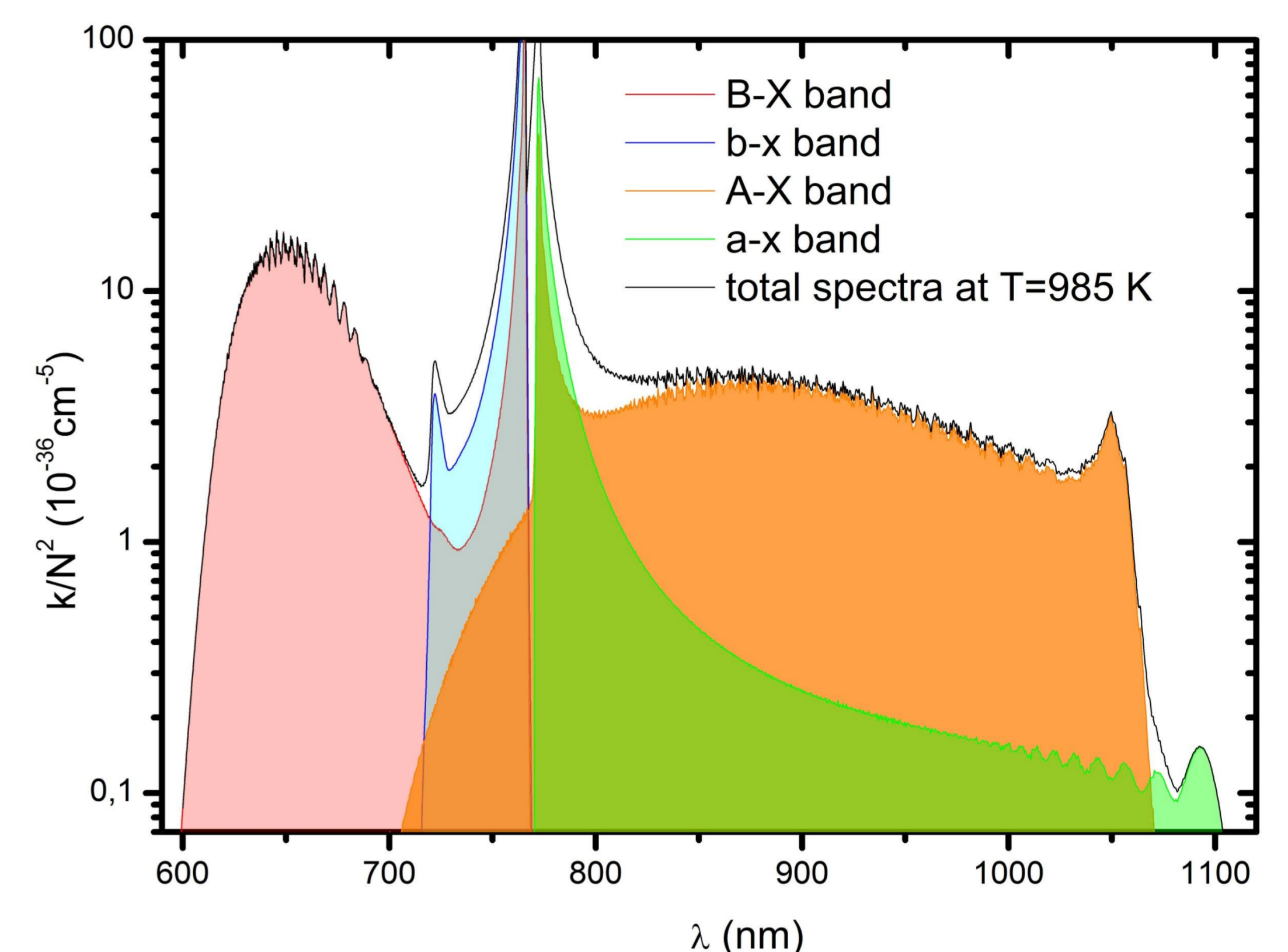
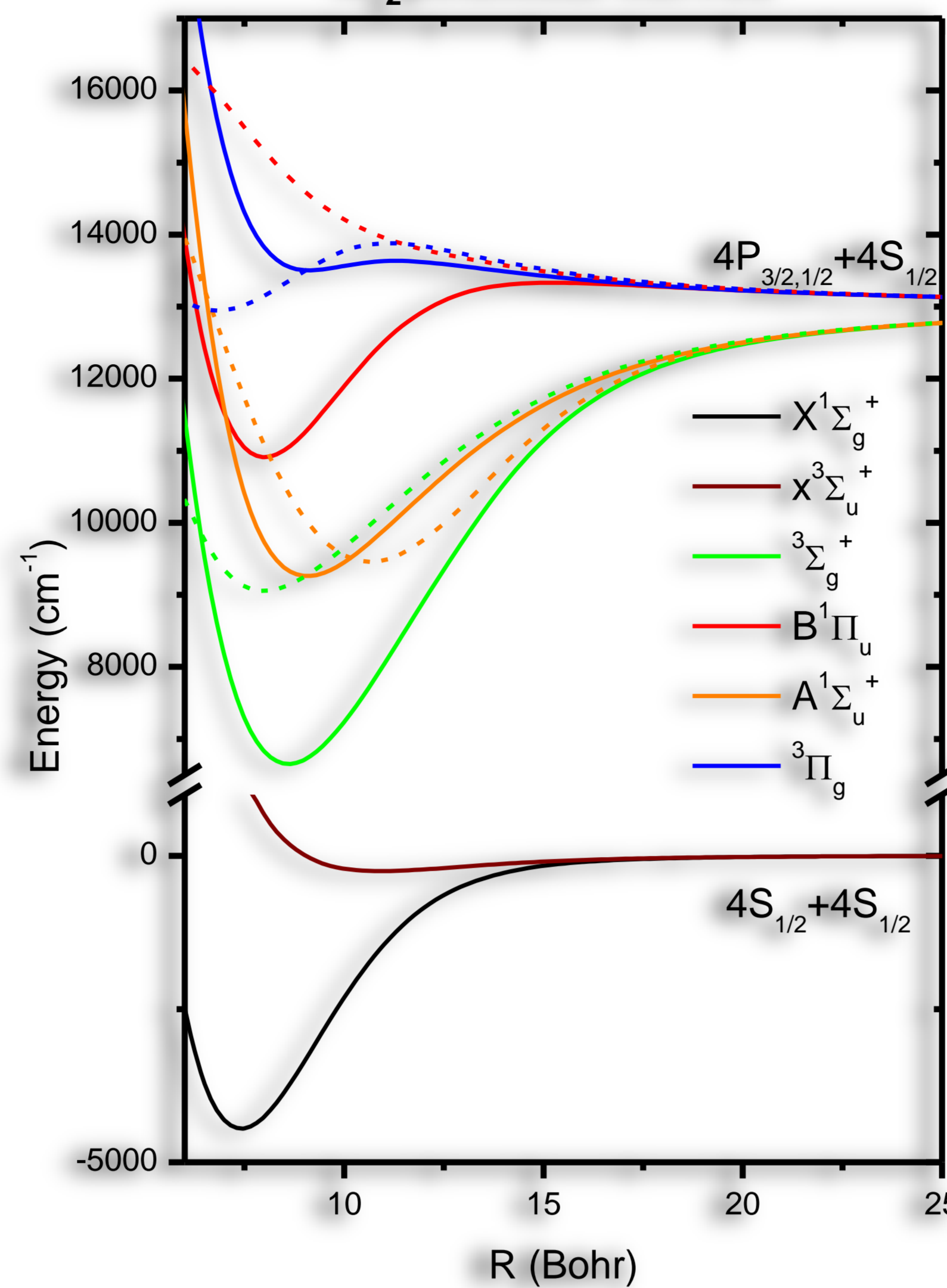
[2] L. K. Lam et al, J. Chem. Phys., **66**, 3550-3556 (1977)

[3] R. Beuc et al, J. Phys. B: **43**, 215210 (2010)

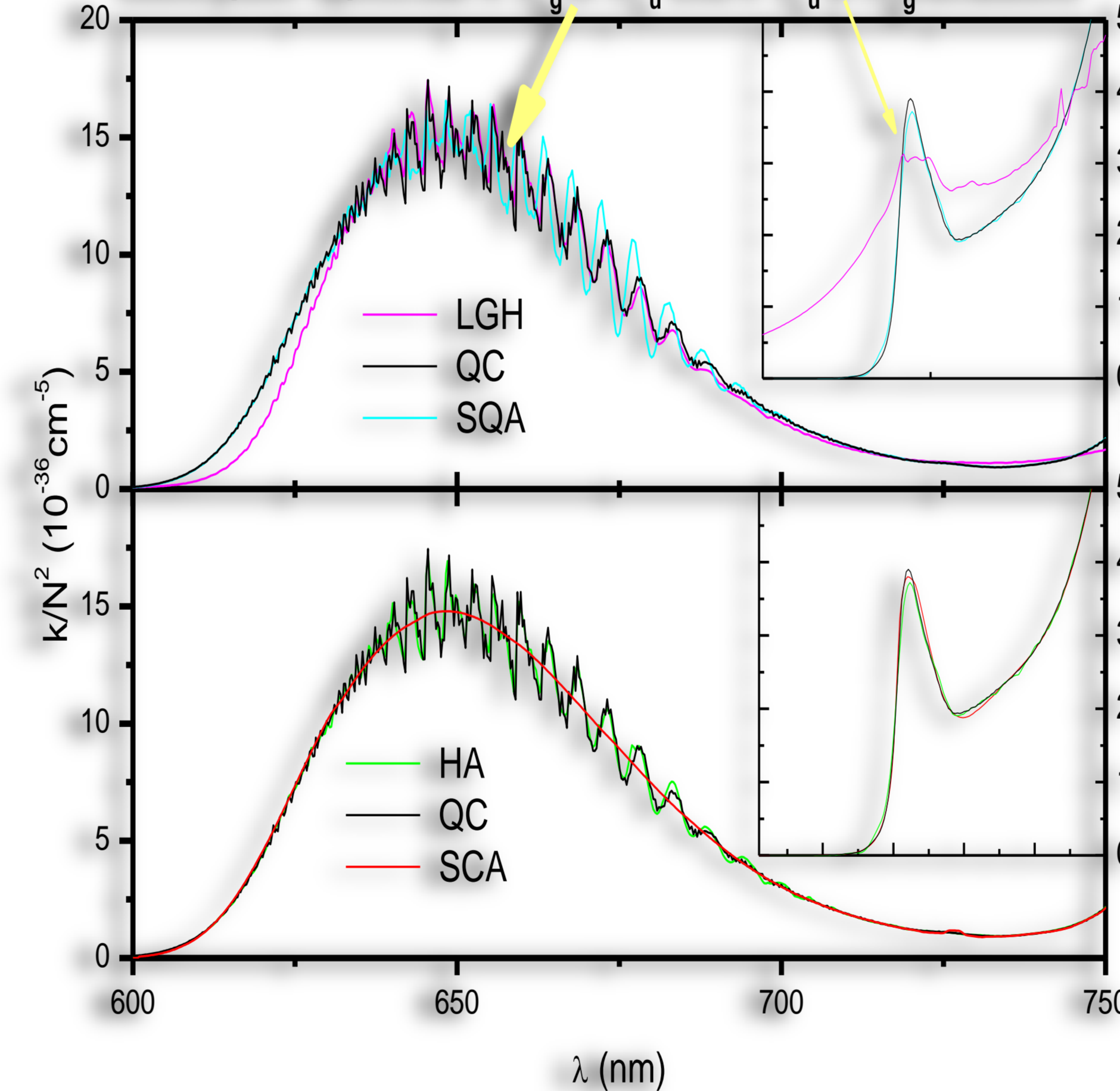
[4] C. Vadla et al, Eur.Phys.J.D, **37**(2006)

[5] F. Talbi et al, Eur.Phys.J.D **50**, 141-151(2008)

**K<sub>2</sub> potential curves**



**absorption spectrum X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>-B<sup>1</sup>Π<sub>u</sub><sup>+</sup> and X<sup>3</sup>Σ<sub>u</sub><sup>+</sup>-b<sup>3</sup>Π<sub>g</sub> transitions**



**absorption spectrum X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>-A<sup>1</sup>Σ<sub>u</sub><sup>+</sup> and X<sup>3</sup>Σ<sub>u</sub><sup>+</sup>-a<sup>3</sup>Σ<sub>g</sub><sup>+</sup> transitions**

