

Spectra of Diatomic Molecules: From Cold to Hot

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Outline

Diatomic molecules have been an object of very intensive investigation for different physical conditions. I shall discuss theoretical aspects of some investigations in a wide range of temperatures.

- Overview of theoretical methods used in the analysis of spectra of diatomic molecules
- Formation of ultracold molecules in magneto-optical traps using photoassociation method $T = 10^{-4} \text{ K}$
- Spectroscopy of alkali diatomic molecules adsorbed on the surface of helium droplets $T = 0.37 \text{ K}$
- Optical spectra of carbon monoxide molecule at room temperature $T \approx 300 \text{ K}$
- Spectroscopy of hot vapors $T > 300 \text{ K}$
 - Potassium resonance lines pressure broadened by helium atoms
 - Absorption and thermal emission of superheated cesium vapor at high temperatures ($1000 - 1300 \text{ K}$)

Introduction

The absorption cross section from a rovibrational state of the lower electronic state (v'', J'', Λ'') to the rovibrational state of the upper electronic state (v', J', Λ') (Lam et al. 1977, Chung et al. 1999) is given by

$$\sigma_{v'' J'' \Lambda''}^{v' J' \Lambda'}(\nu) = \frac{8\pi^3 \nu}{3hc} w_{\Lambda''} \frac{S_{J'' \Lambda''}^{J' \Lambda'}}{2J''+1} \left| \langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \rangle \right|^2 g(\nu - \nu_{tr})$$

and the spontaneous emission rate from the state (v', J', Λ') to (v'', J'', Λ'') is

$$A_{v' J' \Lambda'}^{v'' J'' \Lambda''}(\nu) = \frac{64\pi^4 \nu^3}{3hc^3} w_{\Lambda'} \frac{S_{J' \Lambda'}^{J'' \Lambda''}}{2J'+1} \left| \langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \rangle \right|^2$$

$D(R)$ is the electronic transition dipole moment, μ the molecular reduced mass, $g(\nu - \nu_{tr})$ the line-shape function, $S_{J'' \Lambda''}^{J' \Lambda'}$ the Hönl-London factor, $h\nu_{tr} = E_{v', J', \Lambda'} - E_{v'', J'', \Lambda''}$ the transition energy, and $w_{\Lambda} = \frac{2 - \delta_{0, \Lambda + \Lambda'}}{2 - \delta_{0, \Lambda}}$ the statistical factor dependent on the symmetry of electronic states.

The energies $E_{v, J, \Lambda}$ and radial wave functions $\phi_{vJ\Lambda}$ can be obtained from the Schrödinger equation

$$\left(E - V_{\Lambda}(R) - \frac{\hbar^2}{2\mu} \frac{J(J+1) - \Lambda^2}{R^2} + \frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} \right) \phi(R) = 0$$

where $V_{\Lambda}(R)$ is the potential of the electronic state Λ .

If one of the transition states is a free continuum state, instead of unity-normalized wave functions $\Phi_{v,J,\Lambda}$ the energy-normalized wave functions $\Phi_{\varepsilon,J,\Lambda}$ are used.

In the Fourier grid Hamiltonian method, rovibrational wave functions are represented on a finite number of grid points R_i ($i=1,\dots,N$), uniformly spaced by ΔR . The Hamiltonian is represented by an $N \times N$ matrix

$$H_{i,j} = \frac{\hbar^2}{2\mu\Delta R^2} \left\{ \begin{array}{ll} \frac{\pi^2}{3} - \frac{1}{2i^2} & i = j \\ (-1)^{i-j} \frac{8ij}{(i^2 - j^2)^2} & i \neq j \end{array} \right\} + \left[V_{\Lambda}(R_i) + \frac{\hbar^2}{2\mu} \frac{J(J+1) - \Lambda^2}{R_i^2} \right] \delta_{i,j}$$

The *infinite* set of rovibrational states is represented on the grid by a *finite* set of states whose energies $E_{v,J,\Lambda}$ and wave functions $\Phi_{v,J,\Lambda}$ are the eigenvalues and eigenvectors of the Hamiltonian matrix. The *continuum* of free states is represented by a *discrete* set of unity-normalized wave functions having a node at the outer grid boundary $R_N = N \Delta R$.

The **absorption coefficient** $K(\nu)$ is obtained by averaging over initial rovibrational levels with weighting factors $\rho(\nu'', J'', \Lambda'')$ and summing over all transitions, multiplied by the molecular number density N_{AB} .

$$K(\nu) = N_{AB} \frac{1}{Z_{\Lambda''}} \sum_{\nu'' J'' \Lambda''} \rho(\nu'', J'', \Lambda'') \sigma_{\nu'' J'' \Lambda''}^{\nu' J' \Lambda'}(\nu)$$

where Z_{Λ} is the partition function of the molecular state Λ , $Z_{\Lambda} = \sum_{\nu, J} \rho(\nu, J, \Lambda)$

The **emission coefficient** $\epsilon(\nu)$ is obtained by averaging over upper rovibrational levels with weighting factors $\rho(\nu', J', \Lambda')$ and summing over all transitions.

$$\epsilon(\nu) = N_{AB} \frac{1}{Z_{\Lambda'}} \sum_{\nu' J' \Lambda'} \rho(\nu', J', \Lambda') A_{\nu' J' \Lambda'}^{\nu J \Lambda}(\nu)$$

Assuming **thermodynamic equilibrium**, the weighting factor is:

$$\rho(\nu, J, \Lambda) = \omega_J (2J + 1) \exp\left(-\frac{D_{\Lambda} + E_{\nu J \Lambda} - E_{\Lambda}}{k_B T}\right) \quad Z_{\Lambda} = \sum_{\nu, J} \omega_J (2J + 1) \exp\left(-\frac{D_{\Lambda} + E_{\nu J \Lambda} - E_{\Lambda}}{k_B T}\right)$$

where ω_J is a statistical factor dependent on nuclear spin I with the values $I/(2I + 1)$ for even J and $(I + 1)/(2I + 1)$ for odd J , D_{Λ} is the dissociation energy of the state Λ , and $E_{\Lambda} = V_{\Lambda}(R \rightarrow \infty)$

According to the mass action law at thermodynamic equilibrium,

$$\frac{N_{AB}}{N_A N_B} = \frac{(2S+1)(2\Lambda+1)}{(2S_A+1)(2L_A+1)(2S_B+1)(2L_B+1)} (2\pi\mu kT)^{-3/2} e^{\frac{D_e}{kT}} Z_\Lambda$$

$N_{A,B}$ is the atom number density, $S_{A,B}$ is spin, $L_{A,B}$ the angular momentum of atom A,B. The **absorption coefficient $K(\nu, T)$** :

$$K(\nu, T) = \frac{8\pi^3\nu}{3hc} w_{\Lambda''} C(\Lambda'', T) \sum_{\nu'' \nu' J'' J'} \omega_{J''} e^{-\frac{E_{\nu'' J'' \Lambda''}}{kT}} S_{J'' \Lambda''}^{J' \Lambda'} \left| \langle \phi_{\nu'' J'' \Lambda''} | D(R) | \phi_{\nu' J' \Lambda'} \rangle \right|^2 g(\nu - \nu_{ij})$$

The **emission coefficient $\varepsilon(\nu, T)$** :

$$\varepsilon(\nu, T) = \frac{64\pi^4\nu^3}{3hc^3} w_{\Lambda'} C(\Lambda', T) \sum_{\nu'' \nu' J'' J'} \omega_{J''} e^{-\frac{E_{\nu'' J'' \Lambda''}}{kT}} S_{J'' \Lambda''}^{J' \Lambda'} \left| \langle \phi_{\nu'' J'' \Lambda''} | D(R) | \phi_{\nu' J' \Lambda'} \rangle \right|^2 g(\nu - \nu_{tr})$$

$$C(\Lambda, T) = \left\{ \begin{array}{l} N_A N_B \exp\left(\frac{E_\Lambda}{k_B T}\right) \frac{(2S+1)(2\Lambda'+1)}{(2S_A+1)(2L_A+1)(2S_B+1)(2L_B+1)} (2\pi\mu kT)^{-3/2} \\ N_{AB} \frac{1}{\tilde{Z}_\Lambda = \sum_{\nu, J} \omega_J (2J+1) \exp\left(-\frac{E_{\nu J \Lambda}}{k_B T}\right)} \end{array} \right\}$$

The **thermal emission** from a uniform layer of thickness L is related to the absorption coefficient **$K(\nu, T)$** by Kirchhoff's law of thermal radiation [Horvatić et al. 2015]. Spectral radiance **$I(\nu, T)$** can be written as

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

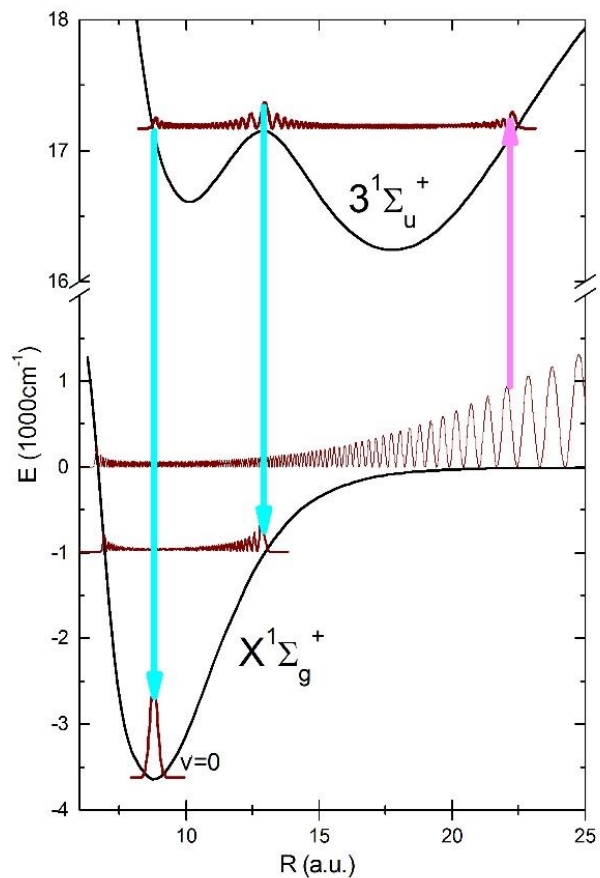
Ultracold $T = 10^{-4}$ K



Formation of ultracold Cs₂ molecules

M.Pichler, W.C.Stwalley , R.Beuc and G.Pichler., Phys. Rev A **69** : 013403 (2004)

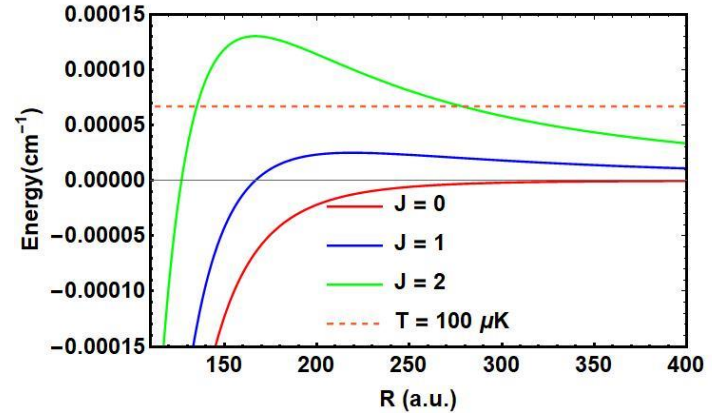
At ultracold conditions (100 μK) in a magneto-optical trap (MOT) cold molecules can be produced by two-photon photoassociation process of colliding atom pairs. I shall describe one of the scenarios for the formation of cold Cs₂ molecules by photoassociation.



- From the ultracold free state described by the wave function $\Phi(E, X^1\Sigma_g^+)$ that scatters within the ground $X^1\Sigma_g^+$ state (energy of the free state corresponds to the average relative kinetic energy of the collision of 100 μK), the absorption of a photon produces excitation into the bound vibrational state v' of the excited $3^1\Sigma_u^+$ electronic state (photoassociation).
- By spontaneous photon emission ($3^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition), the bound vibrational states v'' of the ground electronic state $X^1\Sigma_g^+$ are produced.

The ground electronic state potential curve for $J>0$ has a long-range barrier, so only the colliding pairs of atoms with $J=0,1$ can reach the short-range region.

$$V(R, J) = -\frac{C_6}{R^6} + \frac{\hbar^2}{2\mu} \frac{J(J+1)}{R^2}$$



The probability of photoassociation, $P_{PA}(E, \nu')$, from the free $\Phi(E, X^1\Sigma_g^+)$ state into the bound $\nu'(3^1\Sigma_u^+)$ state, is proportional to the square of the modulus of the matrix element for the electronic transition dipole moment $D(R)$ for this transition,

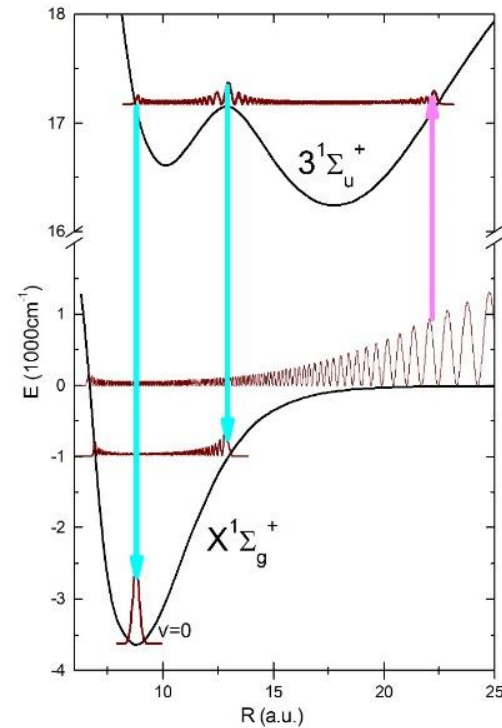
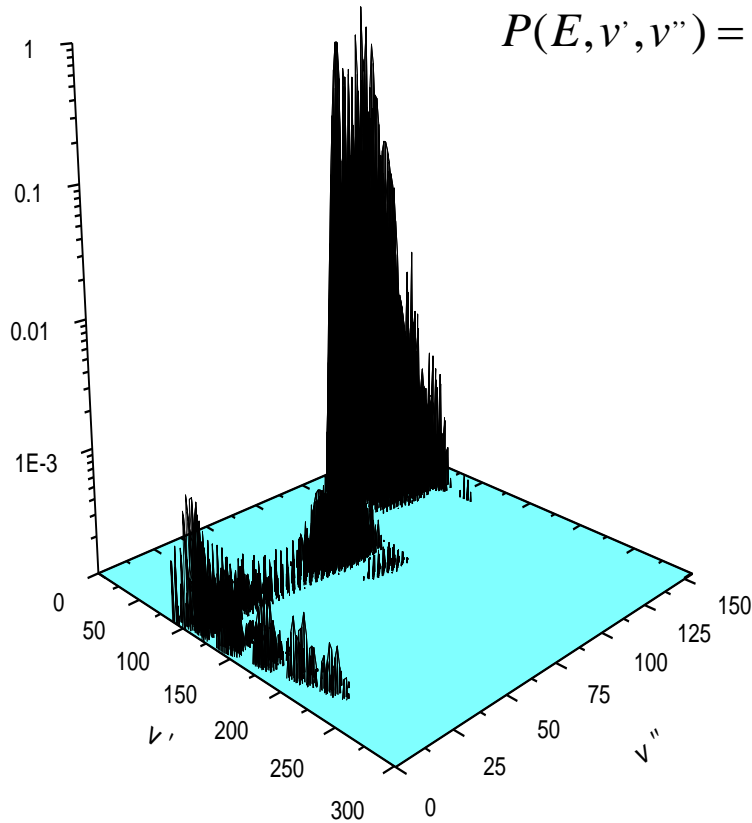
$$P_{PA}(E, \nu') \propto \left| \langle E, X^1\Sigma_g^+ | D(R) | \nu', 3^1\Sigma_u^+ \rangle \right|^2$$

The probability of spontaneous emission from bound states ν' of the excited electronic state $3^1\Sigma_u^+$ into bound states ν'' of the ground electronic state $X^1\Sigma_g^+$

$$P_{SE}(\nu', \nu'') \propto \left| \langle \nu'', X^1\Sigma_g^+ | D(R) | \nu', 3^1\Sigma_u^+ \rangle \right|^2$$

Probability of formation of ultracold molecules in v'' states of the ground electronic $X^1\Sigma_g^+$ state in dependence of photoassociation into bound states v' of the excited electronic $3^1\Sigma_u^+$ state

$$P(E, v', v'') = P_{PA}(E, v') P_{SE}(v', v'')$$



Molecules formed in the ground electronic $X^1\Sigma_g^+$ state by photoassociation are translationally and rotationally cold because only low partial-wave collisions (s-wave and p-wave) of cold atoms contribute to the process. However, generally they are not vibrationally cold.

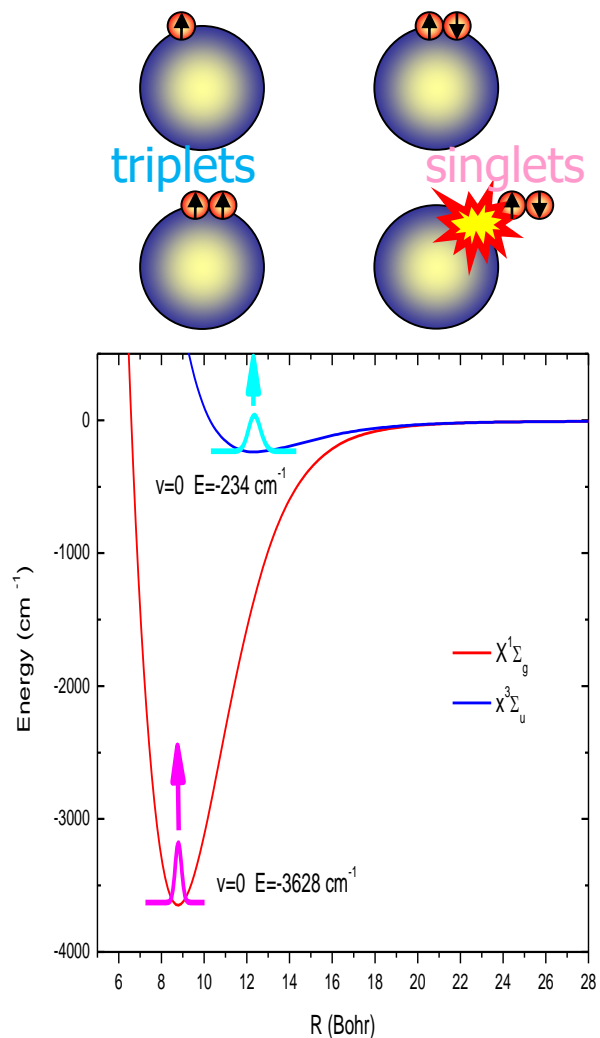
Cold $T = 0.37 \text{ K}$



Cesium dimer spectroscopy on helium droplets

W.E.Ernst; R. Huber; S. Jiang; R. Beuc; M. Movre; G. Pichler:
J. Chem. Phys. **124** (2006)

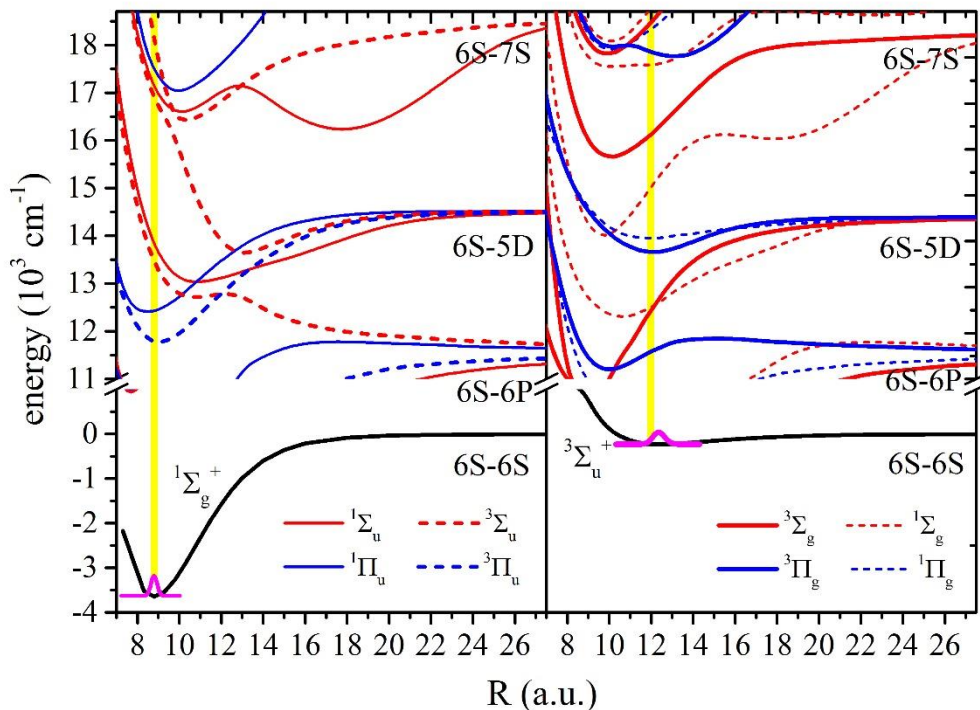
Cold nanodroplets of about 10^4 helium atoms provide a weakly interacting, low-temperature environment (cryostat) of 0.37 K for the formation and spectroscopy of molecules. Cesium atoms picked up by a beam of helium nanodroplets remain on the helium surface where they "skate" and form molecules in cold collisions. Energy of excited rovibrational states is released into the surrounding helium cluster and causes evaporation of helium atoms, one helium atom for every 5 cm^{-1} of energy. As a result, helium droplets loaded with weakly bound molecules $a^3\Sigma^+_u$ ($\Delta E_{\text{vib}}=10.8\text{ cm}^{-1}$) are observed at larger abundance downstream in the helium cluster beam than droplets loaded with strongly bound molecules $X^1\Sigma^+_g$ ($\Delta E_{\text{vib}}=44.8\text{ cm}^{-1}$).



All adsorbed Cs_2 molecules are in $v'' = 0$ vibrational state. Only a few rotational levels within the lowest vibrational level are populated. In that case one can safely neglect the J dependence of the matrix elements and put $J' = J'' = 0$.

$$K(\nu, T) = N \frac{8\pi^3\nu}{3hc} w_{\Lambda''} \sum_{v''} \left| \langle \phi_{00\Lambda''} | D(R) | \phi_{v''0\Lambda''} \rangle \right|^2 g(\nu - \nu_{ij})$$

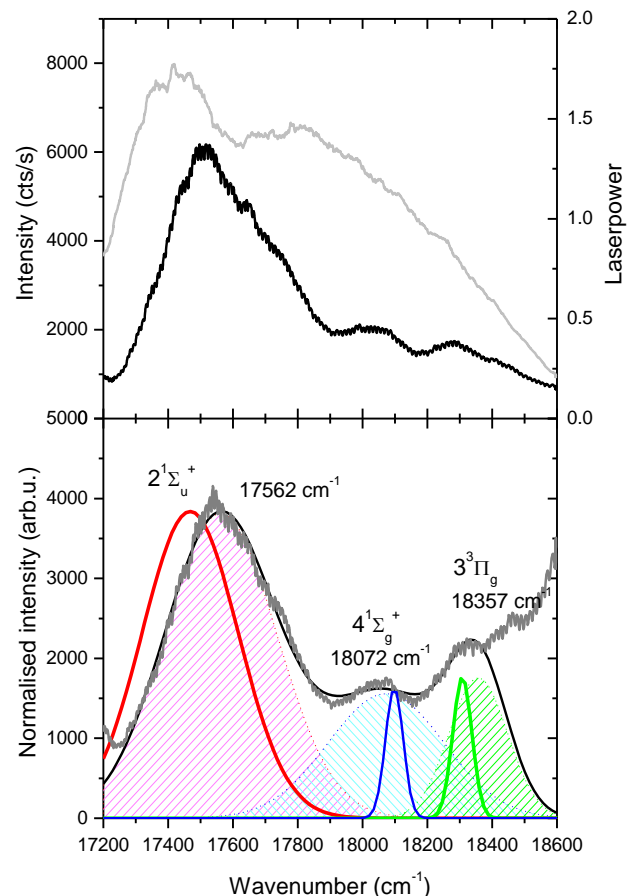
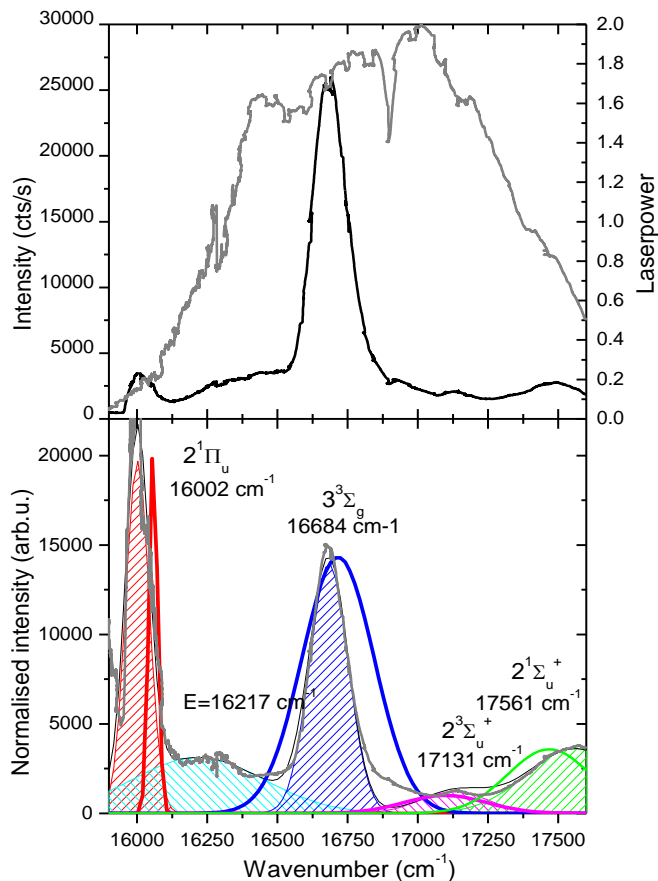
The small vibrational spacings in the bands of the heavy alkali diatoms are usually not resolved because of the helium-induced line broadening, and we replace the summation over v with an integral over energy. Using the reflection approximation [Beuc et al. 2007] one gets the absorption coefficient in the form:



$$K(\nu, T) = N \frac{8\pi^3\nu}{3c} w_{\Lambda''} D(R_0)^2 \frac{\sqrt{2}}{w^{3/2}} e^{-\frac{2}{w}(E-h\nu)}$$

$$w = \left| \frac{2V'_e(R_0)\sqrt{\hbar}}{4\sqrt{\mu V''_g(R_0)}} \right| \quad E_0 = V_e(R_0) - V_g(R_0)$$

R_0 position of ground state minimum



Spectra of cesium molecules on helium droplets (Rh6G and Rh110 dye laser). Upper panels show observed spectra of laser-induced fluorescence and the simultaneously recorded relative laser intensity.

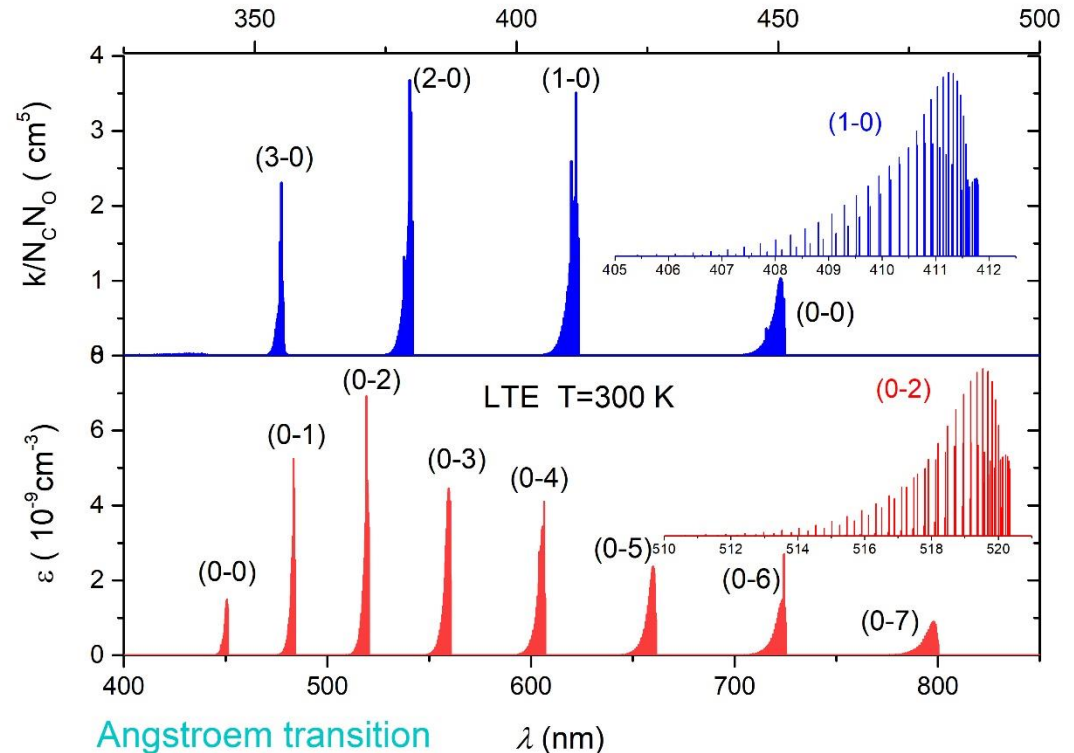
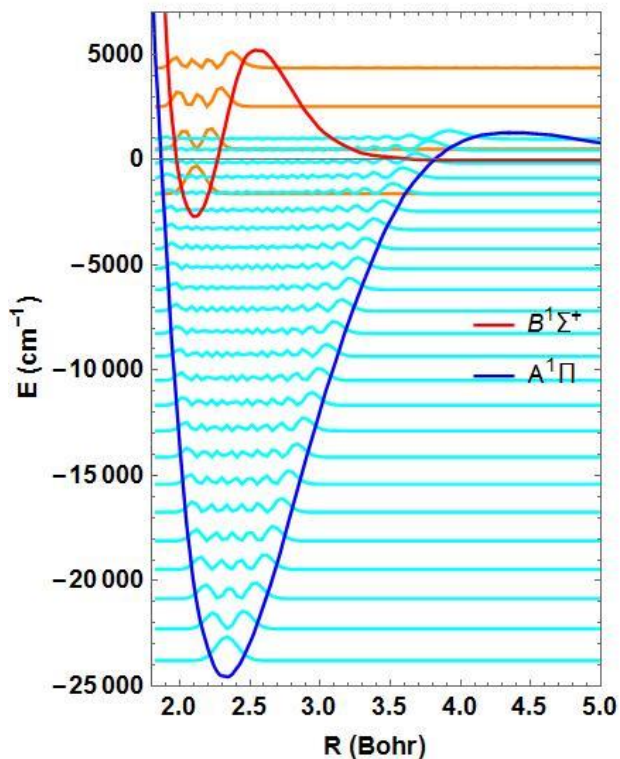
Lower panels show normalized spectra and Gaussian fits to the band maxima, as well as the positions of the bands. All observed spectral features are identified by comparison with theoretical spectra simulations based on the simple reflection formula .

Room temperature $T \approx 300 \text{ K}$



Spectra of the CO molecule

CO is the second most common molecule (after H_2) in the interstellar medium. The CO molecule spectra have been the subject of many studies of Earth atmosphere, especially greenhouse gas remediation. We calculated the quantum-mechanical absorption and emission spectra for the $B^1\Sigma^+ \rightarrow A^1\Pi$ Angström transition of CO molecule at room temperature (300 K). This transition is suitable for plasma diagnostics in the study of cold and low-density plasmas, performed by the group of S. Milošević at my Institute.

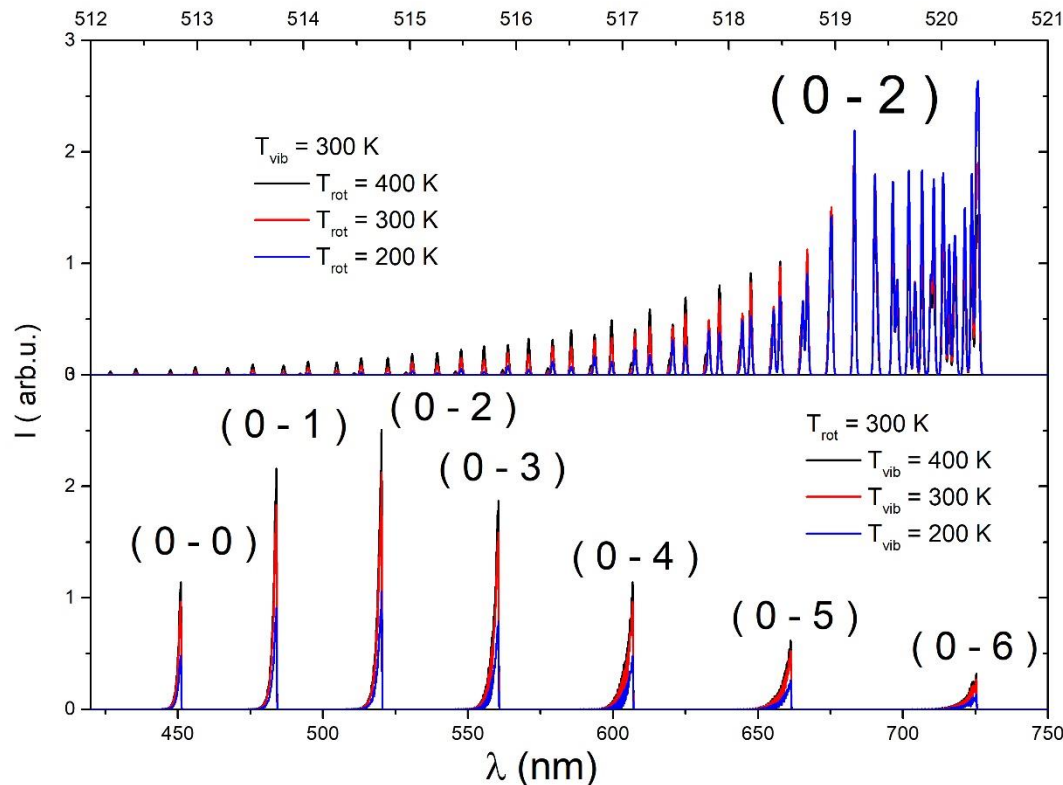


In order to simulate the plasma emission spectra in non-LTE condition, the rovibrational levels weighting factor can be approximated by the relation

$$\rho(v, J, \Lambda, T_{vib}, T_{rot}) = \omega_J (2J + 1) \exp\left(-\frac{E_{v\Lambda vib}}{k_B T_{vib}} - \frac{E_{vJ\Lambda rot}}{k_B T_{rot}}\right)$$

The emission intensity is

$$I(v, T_{vib}, T_{rot}) \propto \frac{v^4}{\tilde{Z}_\Lambda(T_{vib}, T_{rot})} \sum_{v', J', \Lambda'} \rho(v', J', \Lambda', T_{vib}, T_{rot}) S_{J'' \Lambda''}^{J' \Lambda'} \left| \langle \phi_{v'' J'' \Lambda''} | D(R) | \phi_{v' J' \Lambda'} \rangle \right|^2 g(v - v_{tr})$$



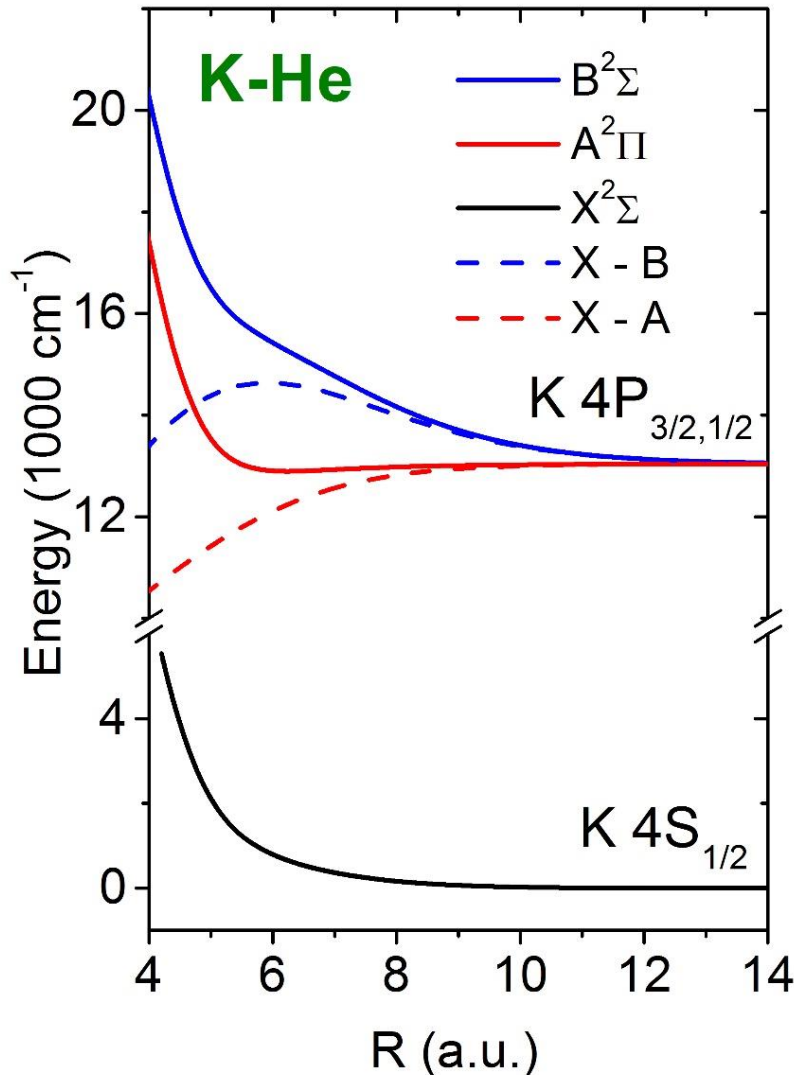
$$\tilde{Z}_\Lambda(T_{vib}, T_{rot}) = \sum_{v, J} \rho(v, J, \Lambda, T_{vib}, T_{rot})$$

where $E_{v\Lambda vib}$ and $E_{vJ\Lambda rot}$ are vibrational and rotational energies of the rovibrational state and T_{vib} and T_{rot} are the vibrational and rotational temperatures.

Hot $T > 300$ K



Potassium resonance lines pressure broadened by helium atoms



R. Beuc, G. Peach, M. Movre, B. Horvatić; X SBAC 2016, AApTr?

- Potential curves, difference potential curves (dashed lines) of the ground **X²Σ⁺** and the excited **B²Σ⁺** and **A²Π** states. Potential curves are predominantly repulsive, exhibiting just a shallow well.
- **X-A** transition has a monotonic difference potential curve and contributes to the "red" wing of the first resonant line.
- **X-B** transition has a difference potential curve with one maximum and contributes to the "blue" wing and the "blue" satellite band.

In LTE, assuming the Q-branch approximation ($\Delta J=0$) and $\omega_J = 1/2$, the **absorption coefficient** has the form (Chung et al. 2001, Beuc et al. 2012):

$$K(\nu, T) = \frac{4\pi^3\nu}{3hc} w_{\Lambda''} C(\Lambda'', T) \sum_{\nu'' \nu' J''} (2J'' + 1) e^{-\frac{E_{\nu'' J'' \Lambda''}}{kT}} \left| \langle \phi_{\nu'' J'' \Lambda''} | D(R) | \phi_{\nu' J' \Lambda'} \rangle \right|^2 g(\nu - \nu_{ij})$$

In the case of a K-He dimer, the free-free transitions dominate the optical spectra and the motion of the atoms can be described by a classical trajectory $R = R(t)$. Using the **semiclassical approximation** and the standard stationary phase approximation, one obtains:

$$K(\nu, T) = \frac{16\pi^4\nu}{3c} w_{\Lambda''} C(\Lambda'', T) \sum_{c=1}^n \frac{R_c^2 D(R_c)^2}{|\Delta'(R_c)|} \exp\left(-\frac{V_{\Lambda''}(R_c)}{k_B T}\right)$$

Summation is over the **Condon points** R_c

$$\Delta(R_c) = V_{\Lambda'}(R_c) - V_{\Lambda''}(R_c) = h\nu$$

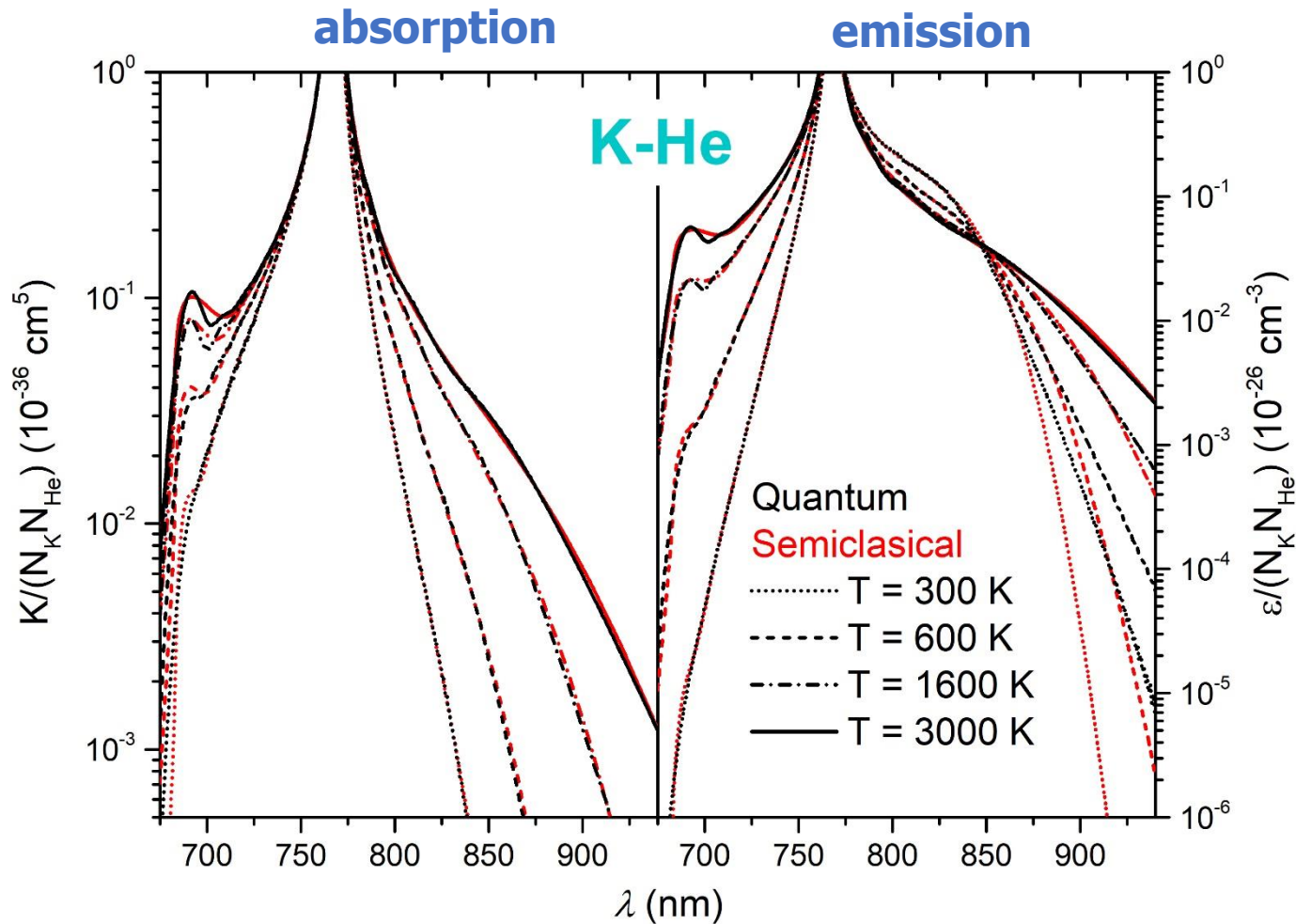
Divergence at the difference potential extremes can be removed by **uniform Airy approximation** [Sando et al. 1973, Szudy et al 1975, Beuc et al. 1992]

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

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

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

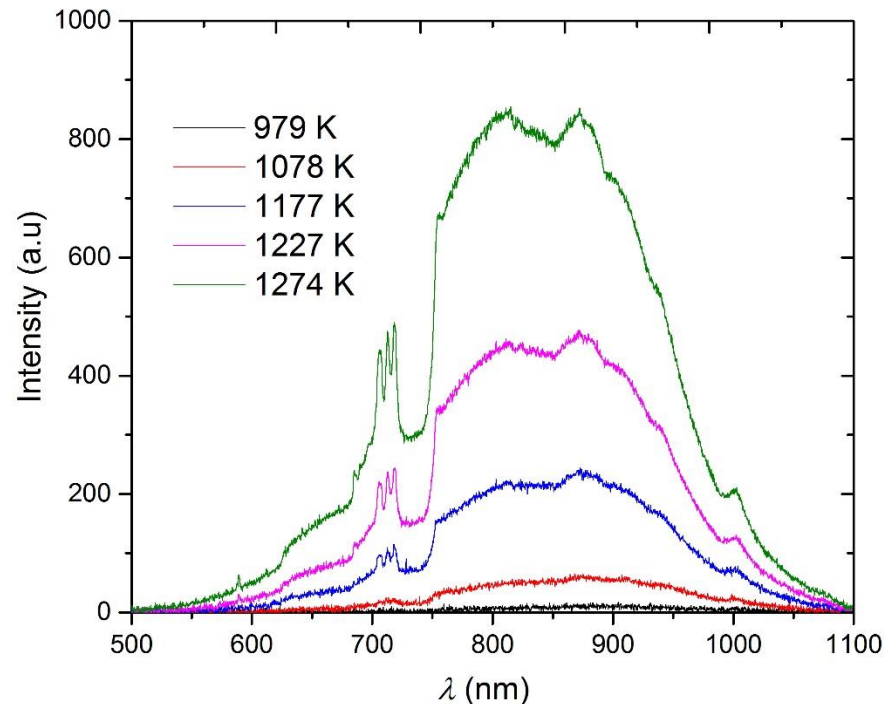
$$\zeta \approx \left(\frac{4\pi^2 h \mu}{k_B T |\Delta''(R_e)|} \right)^{1/3} \sigma(\nu_e - \nu)$$



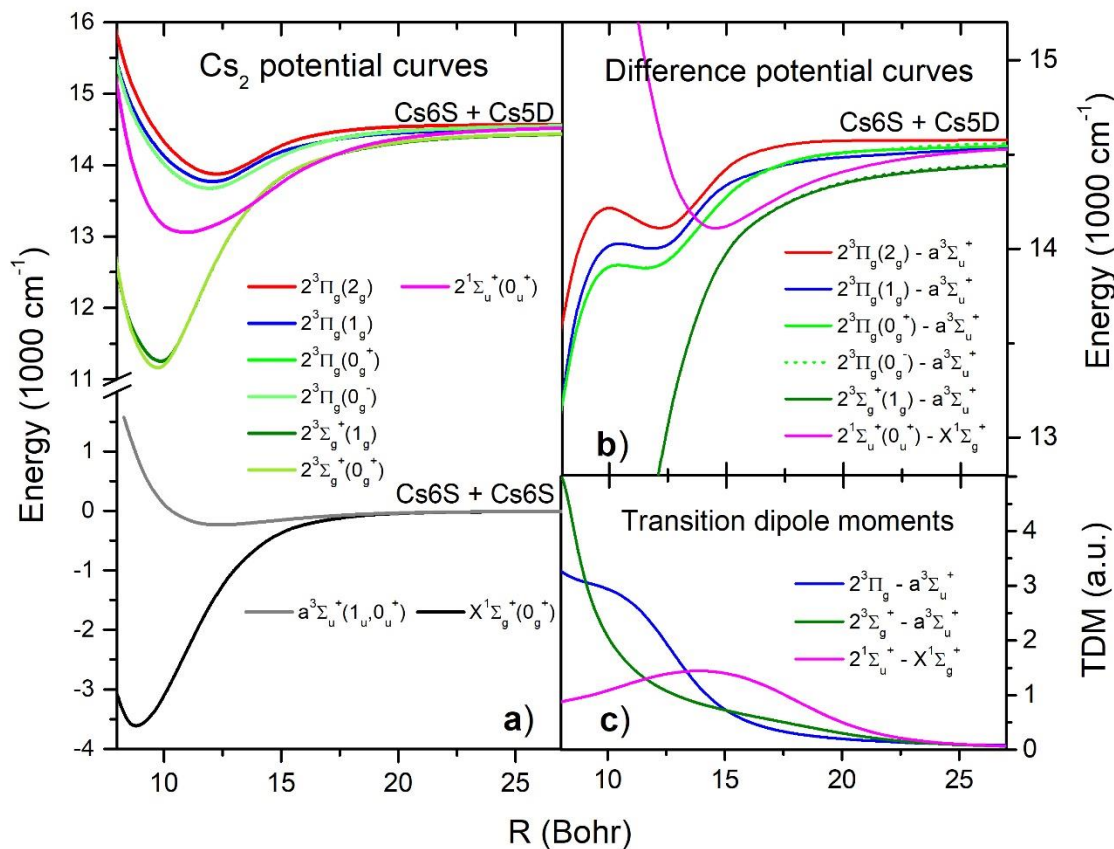
We calculate the reduced absorption coefficient $\frac{K}{N_K N_{He}}$ and the reduced emission coefficient $\frac{\varepsilon}{N_K N_{He}}$ using the fully **quantum-mechanical** and the **semiclassical approach** in the wide range of temperatures (300 – 3000 K), typical for the atmospheres of brown dwarfs and giant exoplanets.

Absorption and thermal emission of cesium vapor at high temperatures

Pichler G, Makdisi Y, Kokaj J, Thomas N, Mathew J and Beuc R, J. Phys. B, 2016; Pichler G, Makdisi Y, Kokaj J, Mathew J, Rakić M and Beuc R, J. Phys: Conf. Series, 2017



Absorption and thermal emission of superheated cesium vapor was studied in the all-sapphire cell at very high temperatures (1000 - 1300 K). The measured spectra of the Cs₂ diffuse band around 710 nm were compared with theoretical simulations.



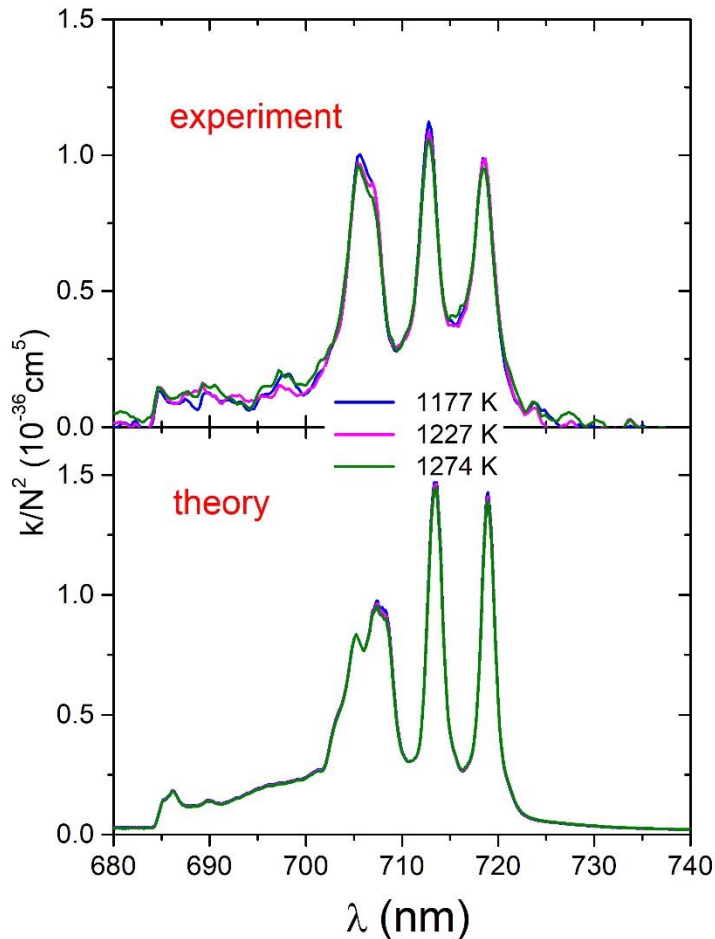
Three groups of optical transitions contribute to the emission and absorption in the spectral region between 680 nm and 740 nm; two triplet transitions and one singlet transition. Potential curves of these electronic states given by [Spies, 1989] are shown in Fig. a.

Difference potential curves for the relevant transitions are shown in Fig b. All difference potentials of triplet transitions have two extrema (minima and maxima).

In Fig c we present the relevant transition dipole moments calculated without the spin-orbit interaction [Allouche et al. 2012].

Absorption spectra

$$K(\nu, T) = \frac{4\pi^3\nu}{3hc} w_{\Lambda''} C(\Lambda'', T) \frac{2\mu k_B T}{\hbar^2} \sum_{v''v'} e^{-\frac{E_{v''0\Lambda''}}{kT}} \left| \langle \phi_{v''0\Lambda''} | RD(R) | \phi_{v'0\Lambda'} \rangle \right|^2 g(\nu - \nu_{ij})$$

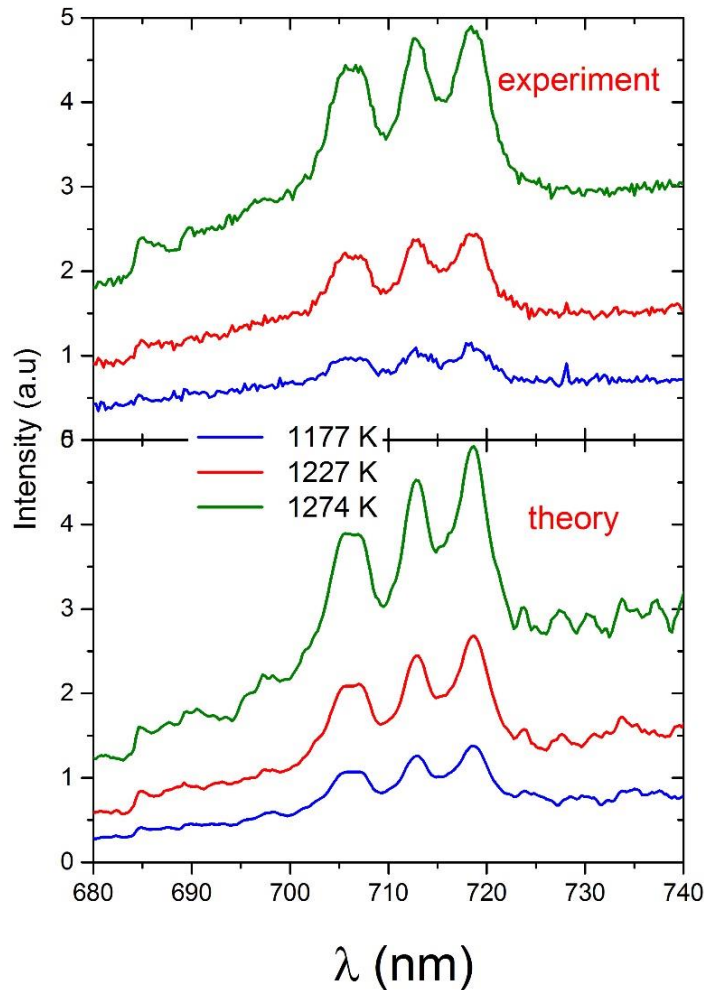


Because of the small vibrational and rotational energy splitting in the Cs_2 molecule, in our calculations we used the **semiquantum** approach [Beuc et al. 2012]. In order to evaluate the absorption coefficient, one needs to know the vibrational energies and the corresponding wave functions for $J = 0$ only. If several electronic transitions contribute to the absorption in the same frequency range, the total absorption coefficient is

$$K(\nu, T) = \sum_{i,j} K_{\Lambda_i'', \Lambda_j'}(\nu, T)$$

Emission spectra

$$I(\nu, T) = A \frac{2h\nu^3}{c^2} \frac{1 - e^{-LK(\nu, T)[1 - \exp(-h\nu/k_B T)]}}{e^{h\nu/k_B T} - 1} + B \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T} - 1}$$



There are two distinct contributions to the measured emission spectra. The first one is the emission of superheated cesium vapor, and the second is the „blackbody” radiation of the oven, heater and sapphire cell. Parameters A and B are optimized in order to obtain the best fit to the observed emission profile.

Acknowledgments

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- **Wolfgang Ernst, Institut fur Experimentalphysik TU Graz**
- **William C. Stwalley, Marin Pichler, University of Connecticut, Storrs**

Thank you for your attention

XI - Serbian Conference on Spectral Line
Shapes in Astrophysics
August 21 - 25, 2017
Šabac, Serbia

XI SCSLSA

The image features a spectral line plot on the right side, with a line that transitions through a rainbow spectrum from purple to red. The plot shows several distinct peaks of varying heights. Below the plot is a horizontal bar that also transitions through a rainbow spectrum, matching the colors of the spectral line. The background of the entire graphic is a light, textured surface with a subtle pattern of small, dark spots, resembling a star field or a nebula.