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Self- and foreign water vapor continuum absorption in the 8-12 and 3-5 μm transmission windows

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In accordance with the asymptotic line wing theory, the transmission windows absorption is determined by the joint impact of the far wings of strong lines pertaining near monomer bands. In the theory, the semiclassical representation method is used to solve the total quantum problem of interaction of the absorbing and the broadening molecules. This method separates rigorously the center of mass motion which is considered further as classical. The method also allows retaining the classical interaction potential in the density matrix. Then the kinetic equation for the correlation function is solved on assumption of the large frequency detunings that also provides the asymptotic evaluation of the time integral. In the asymptotic line wing theory an expression for the absorption coefficient includes the classical and quantum intermolecular interaction potentials. Both potentials are then parameterized. The parameters are found from the comparison between the measured and calculated absorption coefficients.

Asymptotic line wing theory

$$H_0 = H_1(x_1) + H_2(x_2) + T(p) + U(x_1, x_2, q)$$ - Hamiltonian of the quantum system of two interacting molecules

S - the evolution operator in the total quantum problem

Within the semiclassical representation method the overall quantum problem is rigorously divided into classical and quantum parts
The motion of the centres of mass is considered to be classical

$$i\hbar\,\partial C / \partial t = \left(H_1(x_1) + H_2(x_2) + U(x, q(t))\right)C \qquad S = BCG \qquad i\hbar\,\partial B / \partial t = \left(T(\hat{p}) + V(\hat{q})\right)B$$

U(x,q(t)) –quantum potential of intermolecular interaction

V(q) – classical potential of intermolecular interaction

$$\rho = \rho^{(1)}\rho^{(2)}\rho_3 = \rho_{quant}\,F_{cl}(q, p)$$

Absorption coefficient in the far line wing is obtained from the solution of the kinetic equation with the further asymptotic evaluation of the time integral
Classical and quantum potentials are parameterized

Line shape in the far wing

$$\kappa^W_{a_j}(\omega) = D_{a_j}\frac{1}{|\omega-\omega_j|^{1+3/a_j}}\frac{1}{r_{a_j}}\int_0^{r_{a_j}}\frac{e^{-V(r,\Theta)/k\Theta}}{\sqrt{r_{a_j}^2 - r^2}}r\,dr = D_{a_j}\frac{1}{|\omega-\omega_j|^{1+3/a_j}}F(r_{a_j})$$

Absorption coefficient of individual line

$$V(r, \Theta_0) = \frac{4\varepsilon}{k\Theta_0}\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right)$$

Classical potential of intermolecular interaction

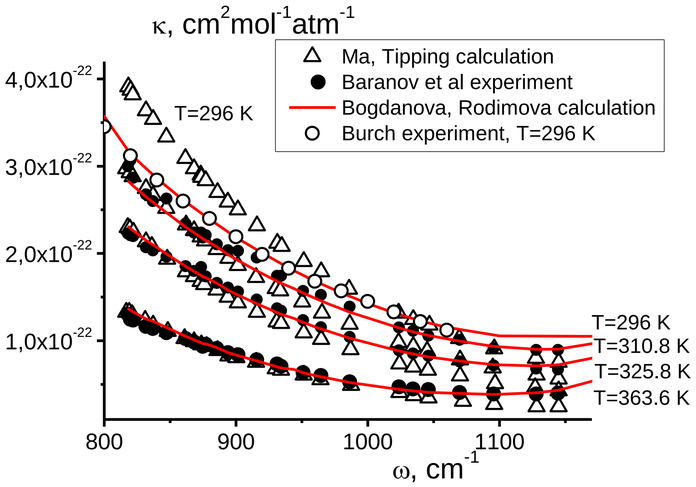
$$r_{a_j} = \frac{C_{a_j}}{|\omega-\omega_j|^{1/a_j}}$$

Quantum potential of intermolecular interaction

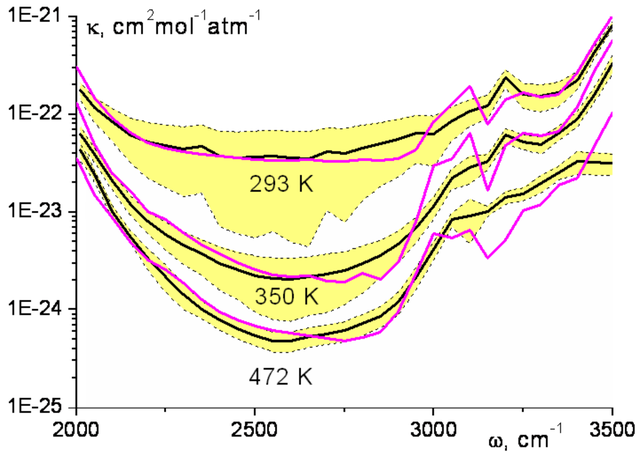
Comparison of calculation and experiment

Self - broadening

8-12 μm

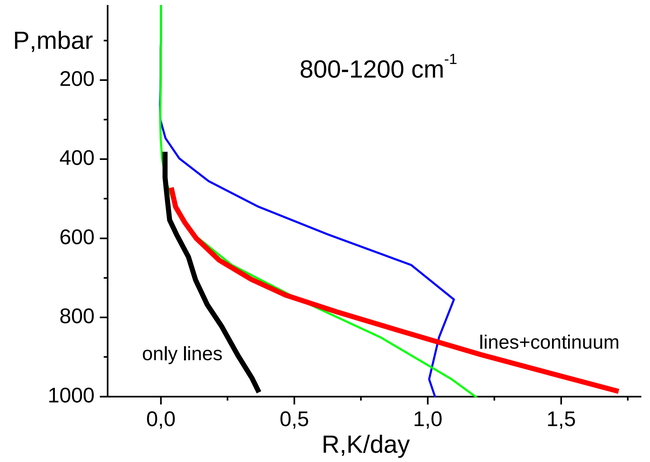


3-5 μm



Experimental data by **Ptashnik et al** JGR, 2011 (black lines)
Calculation results by **Klimeshina, Rodimova** JQSRT, 2013 (magneta lines)

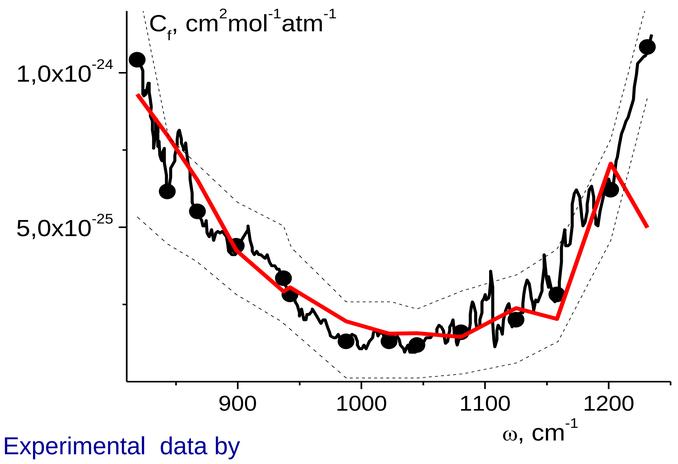
Cooling rates



calculation **Schwarzkopf, Fels** JGR, 1991
calculation with line shape for describing MT_CKD
calculation with line shape for describing **Baranov, Lafferty** Phil. Trans. Roy. Soc. A., 2012

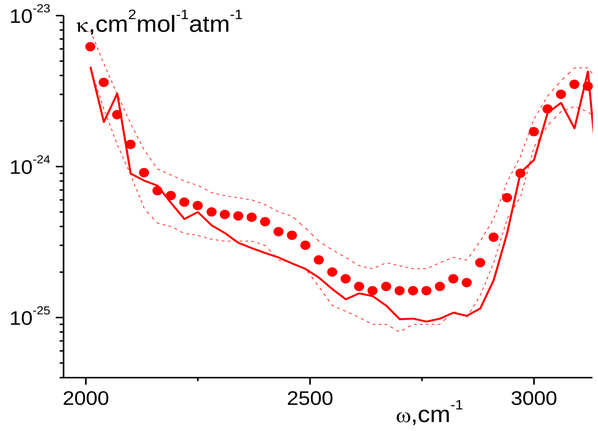
N_2 - broadening

8-12 μm



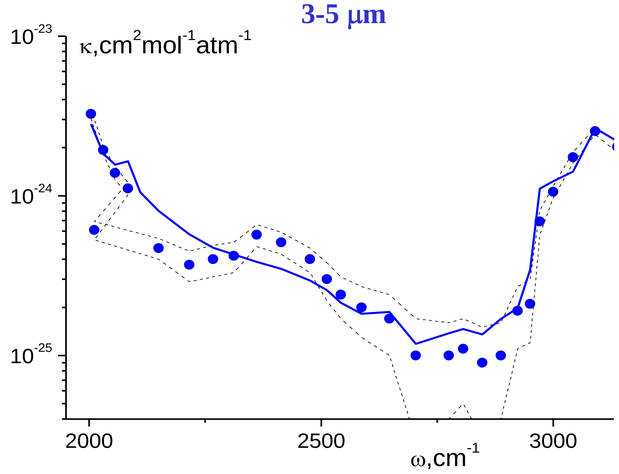
Experimental data by
Baranov, Lafferty Phil. Trans. Roy. Soc. A., 2012
(black lines and circles)
Calculation results (red line)

3-5 μm



Experimental data by **Ptashnik et al** Phil. Trans. R. Soc. A, 2012
(red circles), T=402 K
Calculation results (red line)

3-5 μm



Experimental data by
Baranov, Lafferty Phil. Trans. Roy. Soc. A., 2012
(blue circles), T=326 K
Calculation results (blue line)

Conclusions

1. Line Wings Theory allowed to obtain the line shape describing the water vapor absorption coefficient in case of N_2-continuum in the 8-12 microns region received in recent experiments NIST

2. Line Wings Theory allowed obtaining the shape of line describing the water vapor absorption coefficient in case of self-continuum and N_2-continuum in the 3-5 microns region received in recent experiments CAVIAR and NIST

3. The value of measured H_2O-N_2 absorption coefficient exceeds the value of the absorption coefficient calculated by the model MT CKD in the 800-1200 cm^{-1} spectral region. The increase of the H_2O-N_2 absorption coefficient leads to the appearance of a maximum in the altitude behavior of cooling rate in this region

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