

ON PHYSICAL PATTERN OF SPECTRAL LINE SHAPE PERIPHERY

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Some aspects of advancement of the thesis on vital importance of the intermolecular interaction potential for formation of spectral line wings are discussed.

A spectral line wing, its dependence on frequency detuning and thermodynamic parameters are determined by the properties of the intermolecular interaction potential at small distances. This assertion belongs now to the number of "quite obvious" ones, and we would like here merely to pay attention to some details of its formation.

In our publications¹⁻¹⁰ the above conclusion appeared to be a consequence of an *ab initio* analysis of the problem, and, what is the main thing, a result of the interpretation of a large number of measurements of the light absorption in line and band wings. The experimental data taken from current publications pertain to different gas mixtures, spectral regions, and thermodynamic conditions (detailed description of the cases of H₂O-H₂O and H₂O-N₂ can be found in Refs. 1 and 2, NH₃-H₂ and HCl-CO₂ - in Ref. 1, and self-broadened and foreign gas broadened CO₂ and CO - in Refs. 1, 9, and 10). The role of the intermolecular interaction in the formation of the line wing absorption is so important that the inverse problem of retrieving the potential from the spectroscopic data may be solved.^{1,3}

The other scientists dealing with the line wing absorption arrived at the same conclusion later. For example, the highly popular now line mixing concept, which incidentally occurred as even some alternative to our interpretation, leads to the adequate description of the experimental data on the far wings only in the case of indispensable account of the intermolecular interaction.^{11,12} The decisive role of the intermolecular interaction potential was insistently emphasized in Refs. 13-16, and it is quite natural, because the conceptual content of these papers is close to that of Ref. 1, and some formal results obtained in Ref. 1 were simply repeated in part in the above-mentioned papers.

The spectral line wing theory¹ holds that the expression for the absorption coefficient, in addition to the factor of the statistical line theory, line intensity, and factor taking into account the spatial dispersion, includes the factor

$$F = (1/R') \int_0^{R'} R (R'^2 - R^2) \exp(-V(R, T)/kT) dR,$$

$$R' = C / |\omega - \omega_j|^{1/a},$$

where $|\omega - \omega_j|$ is the frequency detuning (ω and ω_j are the field frequency and the frequency of the line center, j represents the appropriate quantum indices); C , a , and k are the constant values; V is the intermolecular interaction potential, which is the function of the

intermolecular separation R and the temperature T . As was shown in Ref. 1, V is the quantum average of $\text{Sp } \rho H_{12}$ type, where H_{12} is the Coulomb interaction energy of molecules and ρ is the Gibbs density matrix with the Hamiltonian $H_1 + H_2 + H_{12}$, in which H_1 and H_2 are the Hamiltonians of colliding molecules.

Properly speaking, it is the function $F(V(R, T))$ that determines a wide variety of the spectral and thermodynamic patterns in the spectral line wing.

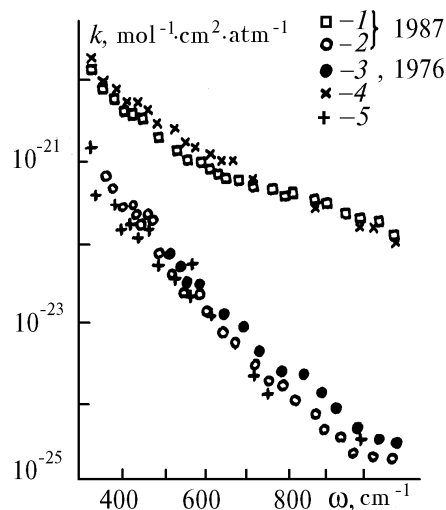


FIG. 1. Water vapor absorption coefficient. The experimental data by Burch reported in Ref. 13: 4) H₂O-H₂O; 5) H₂O-N₂. The calculation¹³: 1) H₂O-H₂O; 2) H₂O-N₂. The calculation by the method of Ref. 1: 3) H₂O-N₂.

These results were first obtained in Refs. 1 and 2 and applied to the calculations of the water vapor absorption coefficient (in the case of self-broadening and N₂ - broadening) in the spectral regions 500-1000 cm⁻¹ and 5-36 cm⁻¹. The accuracy of calculations is illustrated by Fig. 1, and the results of calculations borrowed from Ref. 13 are also depicted for comparison. (We would like to pay attention to the dates; the similar correlations for other cases were presented in Ref. 9.) At that very time the conclusion was reached on the decisive role of F in forming the line wing and, as a consequence, on the dependence of self-broadening coefficient $B = K_{\text{H}_2\text{O}-\text{H}_2\text{O}}/K_{\text{H}_2\text{O}-\text{N}_2}$ (here K is the absorption coefficient of the corresponding gas mixture) upon frequency and temperature (see Fig. 2). The values of B

according to Ref. 1 are given in Fig. 3 together with the values calculated in much more subsequent investigation¹⁶ (see the dates in Fig. 3). We note that in the calculation of Ref. 1 the wing of the H₂O 6.3 μm band was not taken into account resulting in underestimated values of B at frequencies of 900 cm⁻¹ and 1000 cm⁻¹.

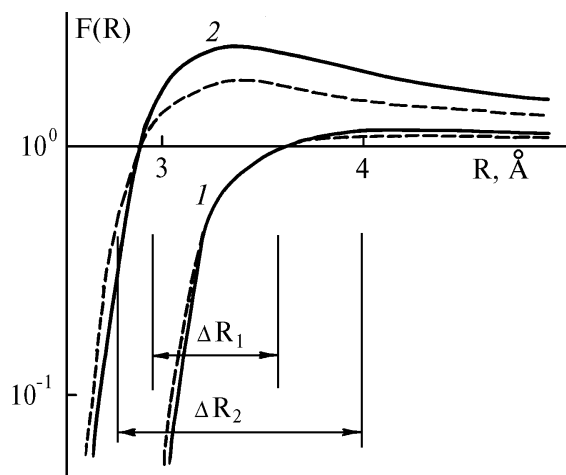


FIG. 2. Factor F as a function of R ; ϵ/k and σ are the constants in the Lennard-Jones potential; ΔR corresponds to the frequency region under study. 1) H₂O-N₂, $\epsilon/k = 217$ K, $\sigma = 3.19$ Å; 2) H₂O-H₂O, $\epsilon/k = 506$ K, $\sigma = 2.71$ Å. Solid curves refer to $T = 300$ K, dashed curves — to $T = 400$ K.

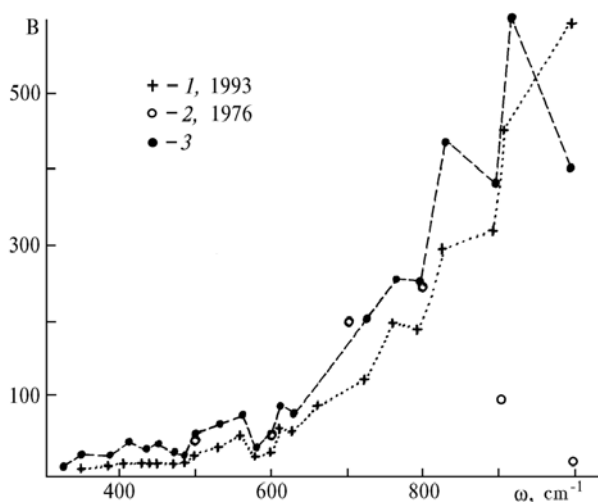


FIG. 3. Self-broadening coefficient: calculations of Refs. 1 and 16 (1, 2) and measurements by Burch (3).

It is needless to say that the example of the water vapor is by no means the only example of this kind, and

we exemplified a number of illustrations of the equally successful description of spectra of different gases. It should be only added that the numerical data discussed here refer to the atmospheric transparency window, where a variety of ways of the description of the continuum (i.e., non-selective water vapor absorption) were tried out (monomer line wings, dimers, ion clusters, and even quantum optics effects). In fact, it may be asserted that the solution of the problem was actually found already in Ref. 1. It should be noted in addition, that already in Ref. 1 the results of the thorough measurements¹⁷ were well reproduced.

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