The interaction of excited atoms and molecules with the surface of condensed media determines the character of many physicochemical phenomena, in particular, heterogeneous reactions on a surface and catalytic reactions. However, the processes of conversion of the electronic excitation energy of particles near the surface of transparent dielectrics are poorly studied. In [1], we have found that some part of the electronic excitation energy of Cs atoms colliding with a sapphire surface is transferred to their translational movement. As this took place, another part of the excitation energy is converted into oscillations of the sapphire lattice.

To reveal the character of interaction of an excited Cs atom with sapphire, we have studied [2] the luminescence spectrum of Cs atoms flying up to approaching the sapphire surface. In the experiment, we recorded the luminescence of atoms excited resonantly near the sapphire window of the cell. The interaction with sapphire shifts the atomic energy levels and the frequencies of interlevel transitions. This can be seen in the absorption and luminescence spectra near a resonance line corresponding to a certain transition.

It was found in that study that the luminescence spectrum in the far wings (at the detuning $\Delta = \lambda_0 - 1/\lambda_0 = \pm(5–50) \text{ cm}^{-1}$ from $\lambda_0 = 852 \text{ nm}$—the center of the $D2$ line) differed significantly in shape from that predicted by the theory of quasistatic wings. The spectrum obtained was described well by the exponential dependence on the detuning. The intensities in the red and green parts of the spectrum differed severalfold (see figure).

The wings of the $D2$ atomic line in this detuning range are formed by the van der Waals interaction between Cs and sapphire. According to the data of [3], this interaction should cause the red shift of the line by $\sim z^{-3}$, where $z$ is the separation of the atom from the sapphire surface. According to the standard theory of far wings [4], such an interaction should form an intense red wing and a weak blue wing and the spectrum of the red wing should be described by the power function: $S_\Delta \sim (-\Delta)^{-4/3}$.

In this paper, we will interpret the abnormal shape of the spectrum under consideration and present the phe-
nomenological theory of the shape of the line wings for atoms near the surface of an ionic crystal.

In the static theory, the luminescence spectrum, as well as the absorption spectrum, is determined by the probability of transition between two atomic states, when the transition frequency, shifting in time, falls into resonance with the emitted (absorbed) quantum of the field. The shape of the spectrum is described by the equation [4]

\[ S_w = \left| \int_0^\infty dt \exp\left( -i \int_0^t dt' \nu(t') + i\omega t \right)^2 \right|, \]

in which \( \nu(t) \) is the atomic frequency of transition measured from the D2 line at the time \( t \) and determined by the separation of the atom from the surface \( z(t) \), \( w = 2\pi c\Delta \), and \( \langle \dots \rangle \) denotes the averaging over positions of all moving particles.

In the case that the atom is under the action of the van der Waals forces, \( \nu(z) = C/z^3 \). According to the data of [3], \( C = -2.4 \times 10^{12} \) s\(^{-1} \) nm\(^{-3} \) (80 cm\(^{-3} \) nm\(^{-3} \)) for the transition 6S\(_{1/2}\) - 6P\(_{3/2}\). From the condition of resonance \( w = \nu(z) = -Cz^3 \), we can determine the position of the atom emitting a photon with the frequency detuned from the atomic line by \( w \). The quanta with \( w = -2\pi c(5-50 \) cm\(^{-1} \)) are emitted in the range \( z = 0.64-1.36 \) nm beyond the range of the action of molecular forces.

In the one-speed approximation, it is believed that atoms move to the surface with the speed \( v \sim 10^4 \) cm/s that is comparable with the thermal speed, and \( v \sim -0.1 \times (10^{-7}/\hbar)^3 \) s\(^{-1} \). The calculation by Eq. (1) with this data completely disagrees with the experimental spectrum.

In this description, the wing shape is determined only by the van der Waals interaction, connected with the high-frequency electronic polarizability of sapphire, while the motion of the sites of its lattice was assumed insignificant. Indeed, the ionic contribution to the polarizability of a transparent crystal at optical frequencies is much smaller than the electronic contribution. However, the motion of sites in an ionic crystal gives rise to an incoherent irregular electric field near the crystal surface. This field can act upon an atom flying near the surface. The presence of an atom at a distance of about 1 nm from the crystal surface does not affect both the motion of sites and this field.

The characteristic frequencies of the fluctuating field are determined by the natural frequencies of site oscillations, that is, by phonon frequencies, which are small compared to the frequency of the atomic transition. Therefore, this field can be considered as quasistatic and its action on the atom reduces to the dynamic low-frequency Stark effect. The field with the strength \( E(t, z) \) acting upon a two-level system induces the blue Stark shift of the transition frequency

\[ \nu_S(t) = (dE)^2/\hbar^2 \omega_0. \]

Here, \( d \) is the dipole moment of the transition at the resonance frequency \( \omega_0 \).

An irregular change in the frequency of the atomic transition gives rise to the phase relaxation, which manifests itself in the broadening of the shifting line of the atom approaching the surface. In other words, this broadening of the luminescence spectrum is connected with the creation–annihilation of phonons.

The electric field generated by moving sites of the crystal lattice is determined by the equation

\[ E(r, t) = \sum_n \nabla(r_n p_n(t)/r_n^3), \]

where \( r_n \) determines the position of the crystal lattice cell with the dipole moment \( p_n \) with respect to the position \( r \) of the atom.

The average field \( \langle E(r, t) \rangle = 0 \). If the oscillations of dipoles in the cells are assumed statistically independent, which is justified in the high-temperature approximation, then the average density of the field energy is approximately given by

\[ \langle E(z, t)^2 \rangle = \sum_{m, n} \langle p_m(t)p_m(t)\rangle/r_n^3 r_m^3 \rightarrow n\langle p(t)^2\rangle/z^3 \]

at \( z > n^{-1/3} \), where \( n \) is the concentration of dipoles. As in the commonly recognized van der Waals description of the interaction between an atom and a crystal, here, we also neglect the cell structure.

Since \( p = ql \), where \( l \) is the amplitude of oscillations of the charges \( q \), and the oscillation energy \( M\Omega_i^2/\langle l^2 \rangle = T \) (\( M \) is the reduced mass, \( \Omega_i \) is the oscillator frequency, and \( T \) is the temperature of the crystal), the mean Stark shift can be estimated as

\[ \langle \nu_S(t) \rangle \sim T d^2 n q^2 M\Omega_i^2 z^3 h^2 \omega_0. \]

At \( T = 0.03 \) eV, \( d = 10^{-17} \) esu, \( n = 2 \times 10^{22} \) cm\(^{-3} \), \( q = e \), \( M = 4 \times 10^{-21} \) g, \( \Omega_i = 10^{13} \) s\(^{-1} \), and \( h\omega_0 = 1.5 \) eV at a distance \( z = 1 \) nm, we obtain the shift \( -3 \times 10^{-12} \) s\(^{-1} \) (100 cm\(^{-1} \)), which is comparable with the shift induced by the van der Waals interaction.

This estimate, overestimated due to the use of the high-temperature approximation, indicates, however, that the luminescence spectrum of atoms near the surface of an ionic crystal is formed not only by the van der Waals forces, but also by the electric field produced by the motion of the sites of the ionic crystal. It should be noted that, with the distance from the surface, the density of this field decreases proportionally to \( z^{-3} \), as well as the van der Waals potential does.