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CALCULATION OF THE SPECTROSCOPIC CHARACTERISTICS OF BIATOMIC VAN DER WAALS MOLECULES AND IONS: INERT GAS ATOM – HALOGEN-TYPE INERT GAS ION IN THE GROUND STATE

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The interatomic potentials in a system formed by an ion of an inert gas in the ground state and an atom of an inert gas (e.g., Ne^+*,* Ar^+ *–Ne, Ar, Kr, Xe) are calculated on the basis of a calculation of the most important polarization diagrams of perturbation theory in the Thomas–Fermi approximation. The calculation employs the effective pseudopotential method using a new form of the polarization interaction potential. Results are presented from a calculation of the quasimolecular terms of particular van der Waals systems that improve existing data; some of the data were obtained in earlier studies.*

The present study is concerned with the interaction potential of biatomic van der Waals molecular ions, i.e., the system consisting of an ion of a halogen-type inert gas in the ground state and an atom of an inert gas. Knowledge of the corresponding parameters of the unknown potentials proves to be extremely important for the solution of numerous physicochemical problems. The quasimolecular terms of the A–B system constitute the basis for theoretical analysis of elementary processes in slow collisions between atomic particles A both in the ground state and in excited states with other atoms B [1-16]. At the present time, the method of the effective potential and method of the pseudopotential have come to be widely used in calculations of quasimolecular systems. These methods are free of the difficulties typical of traditional quantum-chemical methods, difficulties that usually arise in calculating quasimolecular terms in the region of high and intermediate interatomic distances, a region that is of the greatest interest for analysis of a number elementary processes. The pseudopotential method is most often employed in the approaches developed by Ivanov, Devdariani–Zagrebin, and Baylis (see [5-18]). The key point of any calculation scheme entails a correct choice of the corresponding components of the interatomic potential (see below). Of all the systems that have been the focus of considerable attention either at the theoretical or at the experimental level, those systems containing atoms and ions of the alkali elements, inert gases, and halogens have been subjected to the most intensive study in recent years. Biatomic van der Waals molecular ions such as ions of halogen-type inert gases in a system with an inert gas atom have yet to be the subject of sufficiently extensive research. In fact, sufficiently precise data are available only for light systems with He^+. For other van der Waals systems of this type, either the precision of the available data is low (see [1]) or information is lacking. Many important details about the interatomic potentials have yet to be explained. Thus, it would be extremely important to be able to calculate the spectroscopic parameters of the potentials of specific biatomic systems. Note that, in some sense, singly ionized atoms of inert gases resemble the atoms of alkali elements. As is well known, the latter possess a single outer valence electron over a skeleton of closed electron shells. A singly ionized atom of an inert gas, such as a halogen atom, may be considered as a system consisting of a single vacancy in a skeleton of closed electron shells. This fact has been rather successfully used in certification of well-known techniques for calculating the spectroscopic characteristics of alkali atoms and

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ions in the case of halogen atoms as well as biatomic systems, such as those consisting of a halogen atom in the ground state and an atom of an inert gas (see [18-22]). Below, this fact will also be used in the calculation of the interatomic potentials with an appropriate modification of the method of calculation. Note, too, that a variety of approaches have been used in the calculation of the interatomic interaction potentials of biatomic van der Waals systems, including exchange perturbation theory, the formalism of the density functional, and the pseudopotential method (see [2-18]). In our view, the pseudopotential method in the modification employed by Baylis in calculations of a system consisting of an atom of an alkali element and an atom of an inert gas, or the modification of Duren used in the calculation of Na–Hg and other systems seem to be the most effective (see [8-12]). The essential step in these calculations consists in the application of the Dalgarno-type effective polarization potential [13] to take into account the important effects produced by polarization interaction of an outer electron of an alkali atom with its skeleton expressed in terms of the polarizable atom of an inert gas or mercury. This approach possesses a number of significant drawbacks, however. In particular, it makes it necessary to undertake a preliminary, sufficiently precise determination of dipole, and, in certain cases, quadrupole polarizability (the results usual contain major errors). There are certain other drawbacks as well (see below). In the present study, results are presented from a calculation of the interatomic potentials for the following systems: ion of inert gas in ground state – atom of inert gas: Ne^+, Ar^+–Ne, Ar, Kr, or Xe on the basis of the effective pseudopotential method [9-12] using a new form of the polarization potential obtained by means of an effective calculation of the contributions of the most important polarization diagrams of the theory of Rayleigh–Schrödinger perturbations in the Thomas–Fermi approximation (see [19-24]). The results that are obtained improve the available data for the parameters of the potentials. Since the technique we used for calculation of the interatomic interaction potentials has been discussed in detail in previous studies (see [9-12, 18]), we will confine our analysis to certain distinctive features that are important for this calculation.

The effective potential of a vacancy (henceforth, *quasi particle*) in the skeleton of closed electron shells (the basic configuration of an atom of an inert gas) for a singly ionized atom of an inert gas (henceforth, *halogen-type atom*) within the framework of the pseudopotential method [9-12] is determined as follows:

$$V_1(r, R) = F(r, R) + G(r, R) + W(R), \tag{1}$$

where r describes the coordinate of the quasiparticle relative to the skeleton of the closed electron shells; R is internuclear distance; and G and W are pseudopotentials of the following form, respectively (expressed in terms of ordinary units):

$$\begin{gathered} G(r, R) = (h^2/2m_e)\,[3\pi^2\rho_B(r')]^{2/3} \\ W(R) = (\frac{3}{10}h^2/m_e)\,(3\pi^2)^{2/3}\cdot \int dr[(\rho_A+\rho_B)^{5/3}-\rho_A^{5/3}-\rho_B^{5/3}]. \end{gathered} \tag{2}$$

Here ρ_A and ρ_B are the electron densities of a halogen-type atom and atom of an inert gas, respectively, and r' is the coordinate of the quasiparticle relative to the atom of the inert gas. Expressions of the following form are usually used to take into account interaction determined by the polarizability of the atom of inert gas α_B:

$$\begin{gathered} F(r, R) = -\frac{1}{2}\alpha_B e^2 (R/R^3 - r'/r^3)^2,\ r' \geq r_0, \\ F(r, R) = -\frac{1}{2}\alpha_B e^2 (1/R^4 + 1/r_0^4),\ r' < r_0, \end{gathered} \tag{3}$$

where r_0 is the known cut-off radius for Dalgarno-type potentials. As has been previously emphasized, for example, in [9, 10], the potential F, in fact, describes the induced dipole interaction. In many cases, this approximation proves to be acceptable. A more successful approach assumes terms of higher order than dipole are taken into account in the multipole decomposition; these terms often yield a substantial contribution to interaction. In the latter case, the approximation (3) is sufficiently simple but insufficiently precise. A similar simplification to compensate for the inclusion of r_0 in (3) as a second (i.e., together with α_B) adjusting empirical parameter was proposed in [9]. In view of the limitations of the basis employed here, this approach produced significant errors in the calculations, for example, in the interaction potential of an atom of an alkali atom and mercury, an inert gas. In the present study, a new and theoretically more successful nonparametric form of the potential F is used, a form that lacks the drawbacks referred to. This form was proposed previously in [10-12]:

TABLE 1. Parameters of Interatomic Potentiatials for the Systems Ne^+, Ar^+-A (A = Ne, Ar, Kr, or Xe) (R, Å, E, meV)

Ion	Parameters (published values)	Atom of inert gas			
		Ne	Ar	Kr	Xe
Ne^+ (X 1/2)	E, [1]	1300	—	—	—
	E, pres. study	1390	246	334	430
	R, [1]	1,7	—	—	—
	R, pres. study	1,9	2,3	2.6	2,9
Ar^+ (X 1/2)	E, [1]	—	1340	—	—
	E, pres. study	290	1305	430	644
	R, [1]	—	2,4	—	—
	R, pres. study	2,2	2,5	2,7	3,0

$$
\begin{gathered}
F(\boldsymbol{r}_1 \boldsymbol{r}_2) = X\left(\int d\boldsymbol{r}'\, \rho_B^{(0)1/3}(\boldsymbol{r}') / |\boldsymbol{r}_1 - \boldsymbol{r}'| \cdot |\boldsymbol{r}' - \boldsymbol{r}_2| - \right. \\
\left. - \left(\int d\boldsymbol{r}'\, \rho_B^{(0)1/3}(\boldsymbol{r}') / |\boldsymbol{r}_1 - \boldsymbol{r}'| \int d\boldsymbol{r}''\, \rho_B^{(0)1/3}(\boldsymbol{r}'') / |\boldsymbol{r}'' - \boldsymbol{r}_2|\right) / <\rho_B^{(0)1/3}> \right); \\
<\rho_B^{(0)1/3}> = \int d\boldsymbol{r}\, \rho_B^{(0)1/3}(\boldsymbol{r}),
\end{gathered}
\tag{4}
$$

where X is a numerical coefficient (see [10] for a detailed derivation of (4)). The effect of skeletal polarization is taken into account in the Thomas–Fermi approximation. In this approximation the polarization of all the multipolarities is taken into account. Of course, in each particular case the selection rules, which are based on angular symmetry, leave unchanged the contributions of a finite number of terms of the multipole decomposition. Note, too, that the region of low r, where application of the Dalgarno-type potentials (3) is not, in general, justified, is eliminated by means of the truncating factor. Meanwhile, this region is extremely important for particles with orbitals that penetrate the region of the polarizable atom and is taken into account in [4]. We wish to emphasize that we have successfully employed expressions such as (4) in high-precision calculations of the energies of excited states, the forces of oscillators in atoms and ions, and other types of van der Waals systems (see [18-22, 26]). Except for the use of the new form for the polarization potential, our calculation scheme otherwise corresponds to the calculation scheme of the standard pseudopotential approach (see [8-12]).

Let us now present results from a calculation of the parameters of the interatomic potentials for the following systems: Ne^+, Ar^+-A (A = Ne, Ar, Kr, or Xe). Note, too, that the matrix elements of the effective potential are calculated in terms of wave functions for the single-quasiparticle Hamiltonian function of a halogen-type atom. Expression (2) was numerically integrated to obtain the contribution of W.

The values of the basic parameters of the interatomic potentials (equilibrium distances R, depth of potential pit E) of the systems we are studying are presented in Table 1, which, for purposes of comparison, also includes the data recommended in [1]. Some agreement with the reference data of [1] may be noted in analyzing the results obtained for a system of the form Ne^+-Ne or Ar^+-Ar. There are no precise data for the parameters of the potentials for the other ions available in the literature. In conclusion, we would like to note that, though one advantage of the present study is the fact that it employs a precise procedure for taking into account the polarization effects, the use of a rather limited basis in the calculations obviously led to some error in the results. It will, therefore, be important in future studies, especially in experimental studies, to investigate the systems employed here, taking into account the important role which these types of systems play in a host of applications, including plasma chemistry, laser physics, etc.

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