

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

S. V. Malinovskaya,* S. V. Dan'kov, A. I. Drozdov,
A. F. Kivganov, A. N. Polevoi, and V. N. Khokhlov

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Based on the effective-pseudopotential method with the use of a new form of the polarization-interaction potential, obtained on the basis of calculating the most important polarization diagrams of the perturbation theory in the Thomas-Fermi approximation, the authors calculated interatomic potentials in the inert-gas ion in the ground state-inert-gas atom system: Ne^+ , Kr^+ -Ne, Ar, Kr, Xe. The results of calculating on its basis quasi-molecular terms of the sought van der Waals systems that refine the available data are given; a part of the results is obtained for the first time.

Key words: *interaction potential, quasi-molecular term, pseudopotential, atom, ion, inert gas.*

Introduction. The present work seeks to study the interaction potentials of diatomic van der Waals (VDW) molecular ions: halogen-type inert-gas ion in the ground state-inert-gas atom (IGI-IGA). Knowledge of the corresponding parameters of the potentials sought proves very important for many applications. A basis for the analysis of elementary processes in slow collisions of atomic particles (A) both in the ground and excited states with other atoms (B) is provided by quasi-molecular terms of the A-B system [1-16]. At present, the methods of effective potential and pseudopotential (PP) for calculation of quasi-molecular systems have been widely accepted; these methods are free of the difficulties that are common with traditional quantum chemical methods and are associated with calculating quasi-molecular terms in the region of large and medium interatomic distances that are of greatest interest for analysis of different elementary processes. The PP method was employed most frequently in the variants of Ivanov, Devdariani-Zagrebin, and Baylis [5-18]. The key feature of each computational scheme involves the correct choice of the components of the interatomic potential (see below). In recent years, systems that contain atoms and ions of alkaline elements, inert gases, and halogens have particularly been actively studied among the systems that have received sufficient attention in terms of both theory and experiment. The IGI-IGA-type diatomic systems have not been completely studied to date. In fact, sufficiently accurate data are available only for simple systems with He^+ and He. For the remaining similar systems, the accuracy of the available data is either low (see [1]) or there is no information. In this connection, the problem of calculating their spectroscopic parameters seems pressing. We note that singly ionized IGAs resemble in a sense the atoms of alkaline elements. The latter are known to have one outer valence electron above the skeleton of closed electron shells. A singly ionized IGA, just as a halogen atom, can be considered as a system with one vacancy in the skeleton with closed electron shells. This fact was quite successfully used in evaluation of the known computational procedures for spectroscopic characteristics of alkaline atoms and ions to calculate halogen atoms and the halogen atom in the ground state-IGA-type diatomic systems [18-22]. It will also be used in what follows in calculating interatomic potentials with the corresponding modification of the calculation method. Next we note that, to calculate the interatomic potentials of

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the interaction of VDW systems, use was made of different approaches: the exchange perturbation theory (PT), formalism of the density functional, and the PP method [2-18]. In our opinion, the PP method in the variant employed by Baylis in calculations of the alkaline-element atom-IGA systems, by Duren in calculating Na-Hg, and others, seems the most efficient [8-12]. An important point of these calculations is the use of the Dalgarno-type effective polarization PP [13] to allow for the effects of the polarization interaction of the outer electron of the alkaline atom with the skeleton via the polarized IGA or mercury atom. This PP has a number of drawbacks; in particular, we need to quite accurately predetermine dipole and quadrupole polarizations. In this work, we give the results of calculating interatomic potentials for the Ne^+ , Kr^+ -Ne, Ar, Kr, Xe IGI-IGA systems on the basis of the effective-PP method [9-12] with the use of a new form of the polarization potentials, obtained by calculating efficiently the contributions from the most important polarization diagrams of PT of the Rayleigh-Schrödinger type in the Thomas-Fermi approximation [19-24]. The results obtained refine the available data for potential parameters: since the computational procedure used was presented in detail earlier (see [9-12, 18]), we dwell here only on some features that are important for this calculation.

Calculation Method and Results. The effective potentials of a vacancy (in what follows, a quasi-particle) in the skeleton of closed electron shells (the ground configuration of IGA) for a singly ionized IGA (in what follows, a halogen-type atom) within the framework of the PP approach [9-12] is determined as

$$V_1(r, R) = F(r, R) + G(r, R) + W(R), \quad (1)$$

where r describes the coordinate of the quasi-particle in relation to the skeleton of the closed electron shells; R is the internuclear distance; G and W are the PP of the form (in conventional units)

$$G(r, R) = (\hbar^2/2m_e) [3\pi^2 \rho_B(r')]^{2/3} \quad \text{and}$$

$$W(R) = \left(\frac{3}{10} \hbar^2/m_e \right) (3\pi^2)^{2/3} + \int dr [(\rho_A + \rho_B)^{5/3} - \rho_A^{5/3} - \rho_B^{5/3}].$$

Here ρ_A and ρ_B are the electron densities of the halogen-type atom and IGA, respectively; r' is the quasi-particle coordinate in relation to the IGA. To allow for the interaction determined by the IGA polarization α_B , use is usually made of expressions of the form

$$F(r, R) = -\frac{1}{2} \alpha_B e^2 (R/R^3 - r'/r^3)^2, \quad r' \geq r_0$$

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

where r_0 is the known cutoff radius for the Dalgarno potentials. As was emphasized, for example, in [9, 10], the potential F describes, in fact, the induced dipole interaction. In many cases, this approximation proves acceptable. A more consistent approach assumes allowance for terms of a higher order than the dipole in multipole expansion that often make a substantial contribution to the interaction. In the latter case, approximation (3) is insufficiently correct. In [9], it was proposed to compensate for a similar simplification by considering, along with α_B in (3), r_0 as the second fitting empirical parameter, which, with allowance made for the limitedness of the basis used caused significant errors in determining, for example, the interaction potential for the atom of an alkaline element and mercury, IGA. In the present work, we use the new, more consistent theoretically, nonparametric form of the potential F , devoid of the above drawbacks and proposed earlier in [10-12]:

$$F(r_1, r_2) = X \left(\int dr' \rho_B^{(0)1/3}(r') / |r_1 - r_2| |r' - r_2| - \right. \\ \left. - \left(\int dr' \rho_B^{(0)1/3}(r') / |r_1 - r'| \int dr'' \rho_B^{(0)1/3}(r'') / |r'' - r_2| \right) / \langle \rho_B^{(0)1/3} \rangle \right),$$

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

Ion	Parameter	Information source	Inert-Gas Atom			
			Ne	Ar	Kr	Xe
Ne^+ (X 1/2)	E	[1]	1300	-	-	-
	E	present work	1390	246	334	430
	R	[1]	1.7	-	-	-
	R	present work	1.9	2.3	2.6	2.9
Kr^+ (X 1/2)	E	[1]	-	-	1210	-
	E	present work	375	508	1230	856
	R	[1]	-	-	2.6	-
	R	present work	2.4	2.6	2.8	3.1

Note: X 1/2 is the ground state.

$$\langle \rho_B^{(0)1/3} \rangle = \int dr \rho_B^{(0)1/3}(r), \quad (4)$$

where X is the numerical coefficient (see [10] for a detailed derivation of (4)). The effect of skeleton polarization is allowed for in the Thomas-Fermi approximation. In this approximation, allowance is made for the polarization of all multipole orders. Needless to say, in each particular case, the rules of angular-symmetry selection leave out the contributions of a finite number of terms of multipole expansion. We also emphasize that the region of small r , where the use of the Dalgarno-type potentials, generally speaking, is not justified, is eliminated through a cutoff factor. Meanwhile this region is important for particles with orbitals that penetrate into the region of the polarized atom and is allowed for in (4). We note that the (4)-type expressions were successfully used by us in precision calculations of the energy levels, oscillator strengths in atoms and ions, and the potentials of other VDW systems (see [18-22, 25]). Except for using potential (4), our computational scheme corresponds to the standard scheme of the PP approach (see [8-12]).

Let us give the results of calculating the parameters of interatomic potentials for the Ne^+ , Ar^+ -A systems (A = Ne, Ar, Kr, Xe). We also note that matrix elements of the effective potential were calculated on wave functions for a one-quasi-particle Hamiltonian of the halogen-type atom. To obtain the contribution of W , we integrated expression (2) numerically. The calculated values of the basic parameters of the potentials (the equilibrium distance R , the potential-well depth E) of the systems sought are given in Table 1, in which, for comparison, the data recommended in [1] are presented. Analyzing the results obtained for a system of the form Ne^+ -Ne, Kr^+ -Kr, we can note a certain agreement with the reference data of [1]. For the remaining ions, there are no correct data on potential parameters in the literature. In conclusion, we note that although the correct procedure of allowing for polarization effects employed is the advantage of this work, the use of a rather limited basis in calculation, apparently, resulted in a certain error in the results. In this connection, a further, particularly experimental, study of the systems sought seems of importance, taking into account the important part that they play in such applications as plasma chemistry, laser physics, etc.

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