PHYSICAL REVIEW VOLUME 180, NUMBER 1 5 APRIL 1969

Interatomic Potential Model for Ion-Atom Systems Including a Charge-Exchange Contribution*

M. G. Menendez
Martin Marietta Corporation, Orlando, Florida 32805 *and Rollins College, Winter Park, Florida*
and
M. J. Redmon[†]
Valdosta State College, Valdosta, Georgia
and
J. F. Aebischer
Martin Marietta Corporation, Orlando, Florida 32805

(Received 18 November 1968; revised manuscript received 9 January 1969)

A model for the interatomic potential between alkali ions and rare-gas atoms accounting for repulsive and attractive exchange forces has been calculated. The attractive exchange contribution is estimated using Mulliken's charge-transfer theory. The repulsive potential is calculated using Firsov's theory of interacting Thomas-Fermi-Dirac atoms. Two models, $\phi(R)=A/R^n-B/R^4-C/R^6$ (12-4-6 model), and $\phi(R)=A/R^n-B/R^4-C/R^6+\Delta E^{\mathrm{CT}}$ (exchange model), were used to calculate the interatomic potential for all the alkali-ion–rare-gas-atom combinations. A comparison shows that the charge-exchange contribution

$$\Delta E^{\mathrm{CT}}\approx-[2S^2/(1+S^2)]\,(E_{A^+})^2/(I_B+B/R^4+C/R^6-E_{A^+}),$$

where E_{A^+} is the electron affinity of the ion, I_B is the ionization potential of the atom, B and C are the coefficients of the polarization interaction terms, and S is the two-center overlap integral between the outer orbitals, enhances the long-range attraction and increases the well depth by about a factor of 5 over the 12-4-6 model. The predictions of the classical rainbow scattering angle for the Cs$^+$/Ar case are compared for the two models. The difference in the two calculated rainbow angles strongly suggests that low-energy elastic-scattering angular distributions would be a valid test of the assumptions used in the charge-exchange model.

INTRODUCTION

A detailed knowledge of atomic-collision phenomena is essential to several areas of current scientific endeavor, for example, the many-body problem of plasma physics, stellar structure, upper atmospheric phenomena, molecular structure, and molecular biology. The details of collisional phenomena are embedded in the potential energy of interaction and become calculationally manifest by the application of an appropriate scattering theory.

In this paper we develop a model for the interaction potential between an ion and an atom which includes an estimate of attractive and repulsive charge-exchange forces. The rainbow scattering phenomenon is calculated for this model and compared to the more conventional 12-4-6 model.[1]

I. THE PHYSICAL FORCES IN ION-ATOM SYSTEMS

The expressions for the fundamental electrostatic forces between two charge distributions, derivable from classical electrodynamics,[2] are applicable to atomic interactions provided account is taken of the quantum nature of the atom. It is in accounting for the quantum properties that uncertainty is introduced into the classical expressions, nevertheless, they are usually adequate for a first approximation. Of the many electrostatic interactions that compose the total interaction only a few are sufficiently large to merit inclusion in an approximate expression for the potential energy of interaction. The important interactions between an ion and an atom are conveniently expressed in terms of the potential energy of interaction; they are

(1) the charge-induced dipole (cid) interaction

$$\Phi_{\mathrm{cid}}=-\alpha_2{}^2e/2R^4\,, \tag{1}$$

(2) the charge-induced quadrupole (ciq) interaction

$$\Phi_{\text{ciq}} = -\tfrac{3}{4}\alpha_2{}^2 I_2/f_2 R^6 , \tag{2}$$

(3) the induced dipole-induced dipole interaction or dispersion (dis) interaction

$$\Phi_{\text{dis}} = -\tfrac{3}{2}[I_1 I_2/(I_1+I_2)]\alpha_1\alpha_2/R^6 , \tag{3}$$

where α is the static polarizability, I is the ionization potential, f is the oscillator strength, R is the internuclear separation, and 1 and 2 refer to the ion and atom, respectively. The expression for the dispersion interaction[3] is the least exact, since it is a second-order perturbation term involving averages over all of the magnetic quantum numbers for the two atoms. The fact that static polarizabilities are used in all the above expressions leads to inaccuracies, since dynamical distortion effects are neglected. There are other higher-multipole terms which are orders of magnitude smaller, and we shall neglect them. The uncertainties in the above expressions are minimized when applied to the case where both atomic centers are in singlet states. We will have frequent occasion to utilize the closed-shell configuration condition to advantage.

In order to complete the expression for the interatomic potential, we must allow for the repulsion of the overlapping electron cloud. It has been customary to follow the lead of earlier workers and to choose a repulsive term having the form

$$\Phi_{\text{rep}} = A/R^n . \tag{4}$$

We shall content ourselves here with the above empirical form for the repulsive potential, deferring further analysis until later.

The total potential energy of interaction is given by

$$\begin{aligned}\Phi(R) &= \Phi_{\text{rep}} + \Phi_{\text{cid}} + \Phi_{\text{ciq}} + \Phi_{\text{dis}} \\ &= A/R^n - B/R^4 - C/R^6 ,\end{aligned} \tag{5}$$

where B and C are the coefficients of the attractive terms. Let us consider this form of the interatomic potential as a model and, since n is usually taken to be 12, we call it the 12-4-6 model. For all practical purposes it accounts for what may be called the "normal physical forces," albeit some quantum-mechanical effects are included in the dispersion term.

This model has been used by Mason and Vanderslice to analyze the scattering of slow ions in gases and to calculate ionic mobilities.[1] Mason and Vanderslice recast this model into the parametric form

$$\begin{aligned}\Phi(R) = \tfrac{1}{2}\delta[&(1+\gamma)(R_m/R)^{12} - 4\gamma(R_m/R)^6 \\ &- 3(1-\gamma)(R_m/R)^4] ,\end{aligned} \tag{6}$$

where δ is the value of $\Phi(R)$ at the equilibrium internuclear separation, R_m and γ measures the relative strength of the R^{-6} attractive term. By comparing calculated ionic mobilities with experimental results Mason was able to determine the parameters of the 12-4-6 model.

A problem that often arises in the use of parametric models is that parameters obtained from one type of experiment do not consistently predict the results of other types of experiments. Menendez and Datz[4] found that the 12-4-6 model did not satisfactorily predict the angular distribution of elastically scattered Cs^+ from Ar and Kr at low energies, where the scattering is dominated by the attractive portion of $\Phi(R)$. The minimum values of $\Phi(R)$, the binding energy of the corresponding molecular ions, predicted by the 12-4-6 model are typically on the order of a few tenths of an eV. One would not expect that this binding energy is sufficient to produce "stable" molecular ions; that is, with a long enough lifetime to be observable under typical experimental conditions. Herman and Cermak[5] have observed $CsAr^+$ and $CsKr^+$ formed by Penning ionization in a mass spectrometer. This observation indicates that the binding energy may be greater than that predicted by the 12-4-6 model. One is tempted to conjecture, and we do so here, that the 12-4-6 model is perhaps incomplete in that it does not include a consideration of charge-exchange forces which could be of importance in ion-atom systems. In the next section we present a method for treating charge-exchange forces.

II. AN APPROXIMATE TREATMENT OF CHARGE-EXCHANGE PHENOMENON

It is reasonable to expect that long-range exchange forces are important in the interaction between a heavy ion and an atom. The effect of exchange forces can be estimated by utilizing the concept of charge transfer. We follow, and outline below, R. S. Mulliken's quantum-mechanical formulation of a charge-transfer theory.[6] This theory has been used to explain the formation of relatively stable charge-transfer complexes among large molecules.[7]

Consider an ion and an atom each in a singlet ground state separated by an internuclear distance R. In particular, we wish to confine our attention to any alkali-ion–rare-gas-atom pair. The ground-state wave function for the two-particle system, Ψ_N, can be represented as a linear combination of two wave functions each representing a "limiting" configuration of the system:

$$\Psi_N = a_1\Psi_1(A^+,B) + a_2\Psi_2(A,B^+) , \qquad (7)$$

where

$$\Psi_1(A^+,B) = \mathcal{A}\Psi_A + \Psi_B + \text{small modifying effects}, \qquad (8)$$

and

$$\Psi_2(A,B^+) = \mathcal{A}\Psi_A\Psi_B + \text{small modifying effects}, \qquad (9)$$

and $\mathcal{A}$ is an operator that properly symmetizes the product wave function in accordance with the necessary symmetry requirements.[6] When both particles are in singlet states they possess the proper symmetry. Clearly, the difference between Ψ_1 and Ψ_2 is the transfer of an electron.

In the interaction between A^+ and B we seek the stabilization energy due to the mixing of the two states Ψ_1 and Ψ_2. This is accomplished by the methods of second-order perturbation theory. The eigenvalue equation is

$$H\Psi_N = E\Psi_N , \qquad (10)$$

where H is the exact Hamiltonian for the entire system. Applying the method of linear variation function to the eigenvalue equation, we obtain the secular equation

$$\begin{vmatrix} H_{11} - S_{11}E & H_{12} - S_{12}E \\ H_{21} - S_{21}E & H_{22} - S_{22}E \end{vmatrix} = 0 . \qquad (11)$$

The second-order energy correction is obtained by letting $E = H_{11}$ in every term except the first, and since $S_{11} = S_{22} = 1$, $H_{12} = H_{21}$, and $S_{12} = S_{21}$, we obtain from Eq. (11)

$$E \simeq H_{11} - (H_{12} - S_{12}H_{11})^2/(H_{22} - H_{11}) . \qquad (12)$$

Equation (12) can be recast in a more useable form by employing the following approximations based on the one-electron approximation[8] and use of the Mulliken magic formula;[9] they are

$$H_{12} \simeq S_{12}(H_{11} + H_{22}) , \qquad (13)$$

$$S_{12}{}^2 \simeq 2S^2/(1+S^2) , \qquad (14)$$

where S is now the two-center overlap integral between the two outer atomic orbitals only. Using (13) and (14) in (12) and defining $\Delta E \equiv (H_{11} - E)$ as the stabilization energy due to charge transfer leads to

$$\Delta E^{\mathrm{CT}} = -[2S^2/(1+S^2)]H_{22}{}^2/(H_{11} - H_{22}) . \qquad (15)$$

We can easily approximate the matrix elements H_{11} and H_{22} at $R = \infty$ by choosing the zero of energy to be the configuration where the two ions and the electron are infinitely separated. Then,

$$H_{22}(R = \infty) = E_{A^+} , \qquad (16)$$

$$H_{11}(R = \infty) = I_B , \qquad (17)$$

where E_{A^+} is the electron affinity of the ion A^+ (the ionization potential of A) and I_B is the ionization potential of B. The difference in energy between states $\Psi_1(A^+, B)$ and $\Psi_2(A, B^+)$ becomes

$$(H_{11} - H_{22}) \approx I_B + B/R^4 + C/R^6 - E_{A^+} , \qquad (18)$$

where we account for the R-dependence of H_{11} by

$$H_{11}(R) \approx I_B + B/R^4 + C/R^6 , \qquad (19)$$

but neglect the R-dependent polarization interaction of the state $\Psi_2(A,B^+)$ saying that

$$H_{22}(R) \approx E_{A^+} . \qquad (20)$$

This results in a conservative estimate of the stabilization energy due to the mixing of the two states which is approximately given by

$$\Delta E^{\mathrm{CT}} \approx -\frac{2S^2}{1+S^2}\,\frac{(E_{A^+})^2}{(I_B + B/R^4 + C/R^6 - E_{A^+})} . \qquad (21)$$

In a sense, ΔE is a measure of the tendency for the system to share an electron, i.e., form a one-electron bond.

A model for the interaction potential accounting for exchange forces between an ion and an atom, both in singlet states, may be written as

$$\Phi(R) = A/R^n - B/R^4 - C/R^6 + \Delta E^{\mathrm{CT}} . \qquad (22)$$

A few comments regarding the two-center overlap integral S are in order. The overlap, in the case of an alkali-ion–rare-gas-atom pair, is between a p orbital of the atom and the unfilled s orbital of the ion. The greater the overlap, at large distances between these two orbitals, the greater is the tendency of forming a one-electron bond. For heavy ions Slater atomic orbitals are not suitable wave functions. A program developed at the Oak Ridge National Laboratory[10] was used to calculate the two-center overlap integral using Herman-Skillman wave functions.

III. THE REPULSIVE POTENTIAL

The use of the repulsive term given by Eq. (4) introduces the two parameters A and n. It is desirable, in the interest of developing a model based as much as possible on physical principles, to eliminate the use of this parametric term.

The repulsive potential between two interacting atoms can be calculated by the application of a variational minimization and maximization principle[11] to the Fermi-Thomas-Dirac (FTD) statistical model of the atom.[12] We briefly present the final theoretical expressions as developed by Abrahamson[13] for the repulsive potential. This theory is most suitable for interacting atoms of closed-shell configurations and was used by Abrahamson to calculate the repulsive potential between rare-gas atoms.

The interaction potential (at close distances) of two ground-state atoms is approximately given by[13]

$$U_{\mathrm{FTD}}(R)=\tfrac{1}{2}(Z_1Z_2e^2/R)[\chi(Z_1^{1/3}R/a)+\chi(Z_2^{1/3}R/a)]+\bar{\Lambda}\ , \tag{23}$$

where e is the magnitude of the electronic charge; Z_1, Z_2 are the respective atomic numbers of the interacting atoms; χ is the (FTD) screening function[12]; $a=0.8853a_0$; and

$$\bar{\Lambda}=\tfrac{1}{6}\int_{D_{12}}\{K_k[(\rho_{01}+\rho_{02})^{5/3}-(\rho_{01}^{5/3}+\rho_{02}^{5/3})]-2K_a[(\rho_{01}+\rho_{02})^{4/3}-(\rho_{01}^{4/3}+\rho_{02}^{4/3})]\}dv\ . \tag{24}$$

Here $K_k=2.871e^2/a_0$, $K_a=0.7386e^2$, $\rho_{0i}(r_i)$ is the exact undistorted FTD electron density distribution due to the ith atom as a function of the radial distance r_i of the volume element dv from the center of the ith atom; D_{12} denotes the overlap region shared by the two electron clouds. This equation, developed for interacting neutral atoms, is appropriate in its present form to an interacting ion-atom pair provided one uses the screening function and electron density of the ion.

This interaction potential accounts for exchange effects but correlation, inhomogenieties, nonvanishing absolute temperatures, and relativity are neglected. Expression (23) was found to yield repulsive potentials for rare-gas atom interactions which are in good agreement with experimental results as well as other approximate theories at close distances.

We choose, then, to use expression (23) to calculate the repulsive potential of interacting ion-atom systems. However, a word of caution: $U_{\mathrm{FTD}}(R)$ does not directly replace A/R^n; instead

$$\lim_{R\to 0}\Phi(R)=U_{\mathrm{FTD}}(R)\ , \tag{25}$$

because in models of the type we are considering A/R^n accounts for not only $U_{\mathrm{FTD}}(R)$ but must be large enough to cancel the attractive terms at close distances as well. We will return to this limit condition in the next section.

We have calculated by machine computation the repulsive potential for all alkali-ion–rare-gas-atom combinations using the screening functions and electron densities given by Thomas.[14] Representative values of the repulsive potentials are shown in Table I. Since $\log U_{\mathrm{FTD}}(R)$ versus R is practically linear over a considerable range of R, values of $U_{\mathrm{FTD}}(R)$ to about twice the largest R in Table I can be found by extrapolation.[13]

IV. DESCRIPTION OF THE CHARGE-EXCHANGE MODEL

In the interest of keeping the parameters of the charge-exchange model Eq. (22) at a minimum, we utilize the calculated repulsive potentials and the limit condition Eq. (25) to arrive at a parametric procedure which is equivalent to finding a suitable A and n. The development of the parametric procedure can be appreciated by first considering the alternative of finding a suitable A and n. Assume that $n=12$ is a suitable choice for the repulsive exponent, the parameter A must now be adjusted to give a desired equilibrium internuclear distance. If the equilibrium separation is known this procedure does not lead to any difficulty. The difficulty is that for the systems of interest here, and for most systems where the use of a model is indicated, the equilibrium separation is unknown.

In order to arrive at the parametric procedure we rely principally on physical intuition and the limit condition. Consider the ion and the atom separated by a distance R larger than the sum of their FTD radii; clearly, the dominant forces are attractive. As R decreases to less than the sum of the FTD radii, the electron-cloud repulsion comes into effect and begins to dominate the interaction. Since the equilibrium separation is unknown it is not possible to exactly determine the excursion of $\Phi(R)$ through its minimum. The calculated values of $U_{\mathrm{FTD}}(R)$ show that this term is small until R is about equal to the radius of the largest atom, R_{b2}. On the other hand, at small internuclear distances $U_{\mathrm{FTD}}(R)$ is large and the attractive forces, as we use them, are no longer effective nor correct. The procedure that suggests itself is to carry the attractive forces down to the largest FTD radius, hold it constant for smaller R, and add them to $U_{\mathrm{FTD}}(R)$. Since $U_{\mathrm{FTD}}(R)$ increases quite rapidly with decreasing R, it soon takes over completely and insures the limit condition. One is at liberty to choose the cutoff of the attractive portion of the potential and the slope ascribed to it for smaller R in order to produce a particular excursion of $\Phi(R)$ through the minimum. In spite of the apparent generous latitude of the parametric procedure, a moments reflection indicates that, in fact, the opposite is

TABLE I. Repulsive potential $U_{\mathrm{FTD}}(R)$ (in e^2/a_0) for pairs consisting of an alkali ion and a rare-gas atom as a function of R in a.u.

Ion	R	He	Ne	Ar	Kr	Xe	Rn
Li^+	0.03	187.5	923.6	1648.8	3258.1	4846.7	7628.1
	0.10	49.1	235.6	415.1	805.4	1183.6	1836.1
	0.60	3.74	16.3	27.6	50.9	72.5	109.1
	1.20	0.76	3.17	5.24	9.34	13.1	19.4
	1.40	0.45	1.87	3.01	5.28	7.38	10.8
	1.60	0.25	0.98	1.58	2.66	3.58	5.08
Na^+	0.10	173.9	833.8	1468.7	2847.5	4182.5	6482.2
	0.60	12.5	54.2	91.1	166.4	235.8	352.1
	1.50	1.43	5.9	9.65	16.9	23.6	34.6
	2.20	0.32	1.43	2.27	3.96	5.50	7.99
	2.40	0.21	0.92	1.49	2.52	3.41	4.84
	2.60	0.11	0.52	0.85	1.46	1.93	2.66
K^+	0.10	294.0	1410.0	2483.5	4814.7	7070.4	10 953.
	0.60	20.4	88.1	147.5	267.6	377.6	560.9
	1.50	2.3	9.4	15.2	26.4	36.4	53.0
	2.00	0.83	3.48	5.71	9.95	13.7	19.7
	2.50	0.29	1.30	2.16	3.70	5.02	7.1
	3.00	0.08	0.38	0.62	0.99	1.29	1.7
Rb^+	0.10	555.6	2666.8	4697.7	9106.4	13 370.	20 705.
	0.60	37.1	157.2	261.7	471.0	661.1	975.1
	2.00	1.5	6.1	9.9	17.2	23.4	33.2
	2.50	0.54	2.4	4.0	6.8	9.2	13.0
	3.00	0.19	0.88	1.5	2.4	3.3	4.6
	3.30	0.09	0.40	0.65	1.1	1.5	1.8
Cs^+	0.10	810.0	3886.6	6846.5	13 273.0	19 486.6	30 171.0
	0.60	52.7	221.1	365.6	653.9	914.1	1341.7
	2.00	2.1	8.5	13.7	23.4	31.6	44.4
	2.50	0.75	3.37	5.6	9.4	12.6	17.6
	3.00	0.28	1.28	2.1	3.5	4.7	6.6
	3.30	0.15	0.64	1.0	1.9	2.6	3.4

true if we are to be consistent with our previously stated intuitive ideas. For example, if large modifications of the above procedure are required in order to bring the model into agreement with experiment then this strongly implies that the model is not correct. Here, then, lies its main advantage: since the parameter adjustment range is limited, the model and consequently the charge-exchange contribution is amenable to experimental verification for a class of interactions. For the present, in lieu of experimental confirmation, we can only expect that the initial predictions of the model be reasonable.

A figure of merit for the parametric procedure can be that

$$\Phi(R_{b1})/U_{\mathrm{FTD}}(R_{b1}) \simeq 1.0 , \tag{26}$$

where R_{b1} is the radius of the smallest atomic center. We have found that this procedure leads to figures of merit for all alkali-ion–rare-gas-

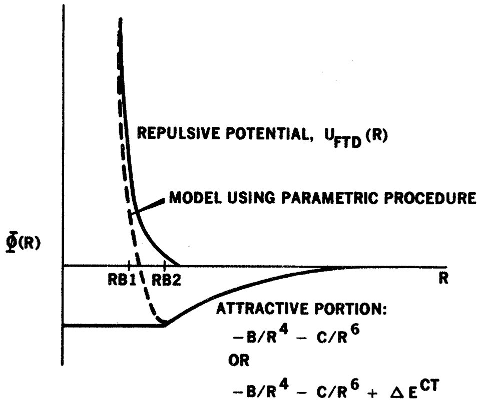

FIG. 1. The graph indicates the parametric procedure used in lieu of the two constants A and n. The attractive portion of the interatomic potential is calculated down to R_{b2} and taken to be constant for smaller R. The procedure permits the adjustment of the attractive cutoff (show above as R_{b2}) and the slope for smaller R (shown above as zero) within a narrow range of values for each.

atom systems from 0.8 to 0.95 while making the excursion through the minimum smoothly. The procedure is shown schematically in Fig. 1.

The interatomic potentials have been calculated for all the alkali-ion–rare-gas-atom pairs using the charge-exchange model and the 12-4-6 model. The potentials were calculated from 0.25 to 12.00 a.u. every 0.25 a.u. A comparison of the two models is summarized in Table II by $\Phi(R_{eq})$ and $\Delta E^{CT}(R_{eq})$. Table III lists the values of the atomic quantities used in the calculations.

The equilibrium separations seem small but reasonable. For a given alkali ion the minimum values of $\Phi(R)$ increase from He to Xe owing mainly to the increase in the atom polarizability. For a given rare-gas atom the binding energy decreases from Li^+ to Cs^+. For the 12-4-6 model this trend is explained by a greater increase of the repulsive potential over the attractive portion due to the increasing size of the ion. For the charge-transfer model the same considerations apply along with the added feature that the charge-transfer contribution decreases in going from Li^+ to Cs^+ owing to the decrease in electron affinity of the ion. The charge-transfer contribution augments the long-range attraction and leads to stronger binding energies.

Except for the alkali ions on Ne cases the charge-transfer contribution increases the binding energy over the 12-4-6 model by an average factor of about 5. For the Ne cases this factor ranges from 7 to 44. This increase seems unduly large but in part is explainable by the behavior of the two-center overlap integral which is greatest for any alkali ion with Ne. Nevertheless, the values of ΔE^{CT} for the Ne cases seem reasonable in

TABLE II. Comparison of the total potentials at the equilibrium separation for the 12-4-6 and charge-exchange models with R_{eq} in a.u., and ΔE^{CT} and Φ in eV.

Ion	Model	Quantity	He	Ne	Ar	Kr	Xe
Li^+	12-4-6	R_{eq}	3.25	4.00	4.25	4.50	4.50
		Φ	−0.18	−0.16	−0.53	−0.65	−0.85
	charge exchange	R_{eq}	3.25	4.00	4.25	4.50	4.50
		S	0.28	0.47	0.49	0.47	0.42
		ΔE^{CT}	−0.24	−0.93	−1.26	−1.49	−1.78
		Φ	−0.42	−1.09	−1.79	−2.14	−2.62
Na^+	12-4-6	R_{eq}	4.75	5.75	4.75	4.75	4.75
		Φ	−0.03	−0.02	−0.19	−0.33	−0.64
	charge exchange	R_{eq}	4.25	4.75	4.25	4.50	4.75
		S	0.21	0.53	0.51	0.49	0.45
		ΔE^{CT}	−0.12	−0.70	−1.18	−1.41	−1.69
		Φ	−0.12	−0.68	−1.27	−1.71	−2.33
K^+	12-4-6	R_{eq}	5.25	6.00	5.25	5.50	5.00
		Φ	−0.03	−0.03	−0.15	−0.22	−0.43
	charge exchange	R_{eq}	5.00	5.25	5.00	5.00	4.75
		S	0.18	0.55	0.52	0.52	0.49
		ΔE^{CT}	−0.06	−0.50	−0.76	−0.97	−1.36
		Φ	−0.07	−0.50	−0.90	−1.15	−1.73
Rb^+	12-4-6	R_{eq}	4.25	6.50	6.00	6.00	5.75
		Φ	−0.05	−0.01	−0.10	−0.15	−0.26
	charge exchange	R_{eq}	4.00	5.75	5.50	5.50	5.50
		S	0.21	0.53	0.51	0.52	0.49
		ΔE^{CT}	−0.06	−0.45	−0.68	−0.86	−1.07
		Φ	−0.12	−0.43	−0.75	−0.96	−1.30
Cs^+	12-4-6	R_{eq}	4.75	7.00	6.25	6.25	6.00
		Φ	−0.04	−0.02	−0.09	−0.14	−0.26
	charge exchange	R_{eq}	4.75	6.00	6.00	6.00	5.75
		S	0.17	0.54	0.51	0.52	0.50
		ΔE^{CT}	−0.04	−0.40	−0.57	−0.71	−0.93
		Φ	−0.08	−0.39	−0.65	−0.83	−1.17

TABLE III. Atomic quantities used in the calculations.

	Polarizability (10^{-25} cm^3)	Ionization potential (eV)	Electron affinity (eV)	Oscillator strength
He	2.16	24.6		1.1
Ne	3.98	21.6		2.4
Ar	16.30	15.8		4.6
Kr	24.80	14.0		4.9
Xe	40.10	12.1		5.6
Li^+	0.80		5.4	
Na^+	1.96		5.1	
K^+	9.0		4.3	
Rb^+	13.0		4.2	
Cs^+	24.0		3.9	

comparison with the other cases and follow the trends. Therefore it seems that the increase factor is unduly large because the minimum values of the 12-4-6 model are too small and not because the values of ΔE^{CT} are too large.

The results indicate that the charge-transfer contribution to the interatomic potential is reasonably large and can be used to explain the binding of some molecular ions that otherwise one would not expect on the basis of a 12-4-6 model.

V. CLASSICAL-MECHANICS DESCRIPTION OF RAINBOW SCATTERING

The advantages of the exchange model are that (i) the number of parameters are minimized, (ii) it estimates charge-exchange forces, (iii) its validity for a class of interactions can be tested experimentally.

We have concentrated on the latter virtue and in the interest of providing a basis for detailed experimental verification have computed the classical rainbow angle for Cs^+/Ar at a relative energy of 7.0 eV for the exchange model and compared it to the predictions of the 12-4-6 model.

We briefly present a description of elastic scattering which is useful for the analysis of low-energy collision experiments.[15] Since we are primarily interested in comparing the rainbow scattering for two interatomic potential models and since the essential features of classical and semiclassical theory as applied to low-energy collisions are similar, we can fruitfully utilize the simpler classical approach for our initial comparison.

The classical description of scattering at low-energies centers around the classical deflection function which is given by

$$\chi(b) = \pi - 2b\int_{R_c}^{\infty} \frac{dR}{R^2}\left(1 - \frac{b^2}{R^2} - \frac{\Phi(R)}{E_r}\right)^{-1/2}, \qquad (27)$$

where b is the impact parameter, R_c is the distance of closest approach, and $\Phi(R)$ is an interatomic potential model. The cross section at a given center of mass angle is given by

$$\sigma_{cl}(\chi) = (b/\sin\chi)\,|d\chi(b)/db|^{-1}\,. \qquad (28)$$

Even though we apply classical theory in our initial analysis it is worthwhile to indicate the development of the semiclassical expression since this, in turn, lends justification for the use of the classical approach. The quantum cross section is given by

$$\sigma = |f(\chi)|^2\,, \qquad (29)$$

where scattering amplitude $f(\chi)$ is

$$f(\chi) = \left(\frac{ƛ}{2i}\right)\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l} - 1)P_l(\cos\theta)\,, \qquad (30)$$

where l is the angular momentum and η_l is the phase shift. We can arrive at the semiclassical expression by making the following approximations in the quantum expression[15]:

(1) replace η_l by its JWKB approximate value – this requires that the potential vary smoothly,

(2) replace the Legendre polynomial by its asymptotic value for large l,

(3) replace $\sum_l$ by $\int dl$ – this and (2) require that many partial waves contribute to the scattering at a given angle.

The above approximations and evaluation of the resultant integral by the method of stationary phase leads to the semiclassical cross section[16]

$$\sigma_{sc} = [ƛ^2(l+\tfrac{1}{2})/\sin\chi]\,|d\chi(l)/dl|\,, \qquad (31)$$

which is found to be equal to the classical expression upon setting $b = ƛ(l+\frac{1}{2})$. Although these conditions are not always satisfied by the systems of interest here, it is nevertheless, legitimate to use the classical description for an initial comparison of two interatomic potential models.

The interaction of two particles via an interatomic potential possessing attractive and repulsive branches leads to a nonmonotic classical deflection function which possesses a minimum. Since the classical cross section contains the term $|d\chi/db|^{-1}$, it will have a singularity where $d\chi/db$ vanishes at some angle χ_r. On either side of χ_r there is a buildup of the cross section due to contributions from both branches at some angle near χ_r. We refer to χ_r as the rainbow angle and to scattering in the neighborhood of χ_r as rainbow scattering because of its analogy to optics.[17] At low energies the scattering is dominated by the attractive portion of the potential and, in particular, rainbow scattering is extremely sensitive to the shape of the attractive portion near the minimum.[18]

The semiclassical treatment is not very different from the classical one even when the above conditions are not met. In the semiclassical treatment the rainbow angle is shifted to slightly smaller angles and for low angular resolution there is a broad peak in $\sigma(\chi)\sin\chi$ versus χ instead of the classical sharp rise to infinity.

The rainbow angles were calculated using a computer program written by two of us (M. G. M. and J. F. A.) that determines, (1) the repulsive potential $U_{\mathrm{FTD}}(R)$; (2) the charge-exchange contribution ΔE^{CT}; (3) the classical deflection function $\chi(b)$; (4) the rainbow angle χ_r; (5) the supernumerary spacing; and (6) the phase shift η_l; for a given interatomic model containing up to four terms, for a given system at a relative energy of collision E_r.

The interatomic potential models for Cs$^+$/Ar are shown in Fig. 2. The results of the classical rainbow scattering calculation at $E_r = 7.0$ eV for the two models are

$$\chi_r = 1.4^\circ \quad \text{(12-4-6 model)},$$

$$\chi_r = 7.9^\circ \quad \text{(exchange model)}$$

in the center-of-mass system. It is clear that measurements of low-energy elastic scattering should provide a valid test of the exchange model. The predictions of the exchange model have been compared to rainbow scattering measurements of Cs$^+$/Ar [4] and were found to be in good agreement.

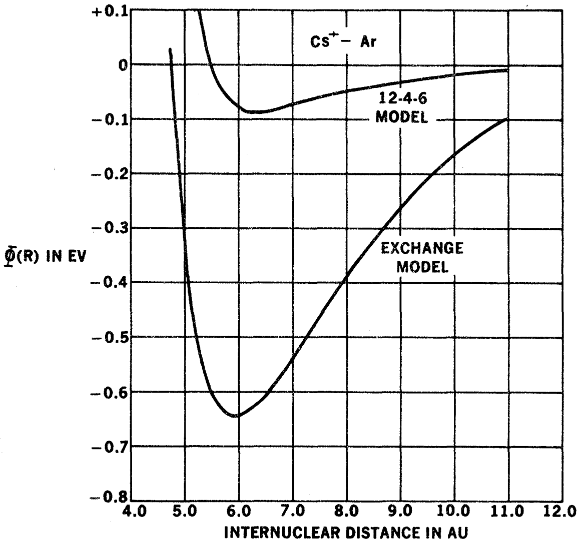

FIG. 2. A comparison of the attractive portion of the interatomic potential for Cs$^+$/Ar using the 12-4-6 model and the exchange model.

However, in view of an uncertainty in the scattering volume of this experiment the agreement can only be taken as an indication that the exchange model is more appropriate than the 12-4-6 model.

VI. SUMMARY

A charge-exchange model for the interatomic potential has been developed and applied to alkali-ion-rare-gas-atom interactions. As expected, the charge-exchange stabilization energy leads to stronger long-range attraction and greater binding energies. Its main advantage is that since it contains only one parameter (the parametric procedure) adjustable only within a narrow range it allows for detailed experimental verification of the physical assumptions. The predictions for rainbow scattering of the charge-exchange model and 12-4-6 model were compared, and it was found that they are sufficiently different to provide a suitable experimental verification of the exchange model, and consequently the charge-exchange contribution.

---

*A portion of this paper was submitted by M. J. Redmon to the Physics Department, Rollins College in partial fulfillment of the requirements for the MS degree in physics.

†Present address: Physics Department, University of Florida, Gainesville, Florida.

[1] E. A. Mason and T. A. Vanderslice, J. Chem. Phys. 31, 594 (1959); E. A. Mason and H. W. Schamp, Ann. Phys. (N. Y.) 4, 233 (1958).

[2] J. D. Jackson, Classical Electrodynamics (John

Wiley & Sons, Inc., New York, 1962).

[3] H. Margenau, Phil. Sci. 8, 603 (1941).

[4] M. G. Menendez and S. Datz, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965 (Science Bookcrafters, Inc., Hastings-on-Hudson, New York, 1965).

[5] Z. Herman and V. Cermak, Nature 199, 588 (1963).

[6] R. S. Mulliken, J. Am. Chem. Soc. 74, 811 (1952).

[7] J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, Chem. Rev. 65, 199 (1965).

[8] J. N. Murrell, J. Am. Chem. Soc. 81, 5037 (1959).

[9] R. S. Mulliken, J. Phys. Chem. 56, 295 (1952).

[10] E. Lee, private communication.

[11] O. B. Firsov, Zh. Eksperim. i Teor. Fiz. 32, 1464 (1957) [English transl.: Soviet Phys. – JETP, 5, 1192 (1957)].

[12] P. Gombas, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1956), Vol. 36.

[13] A. A. Abrahamson, Phys. Rev. 133, A990 (1964).

[14] L. H. Thomas, J. Chem. Phys. 22, 1758 (1954).

[15] K. W. Ford and J. A. Wheeler, Ann. Phys. (N. Y.), 7, 259, 287 (1959).

[16] N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Clarendon Press, Oxford, 1965) 3rd ed.

[17] H. C. Van der Hulst, Scattering of Light by Small Particles (John Wiley & Sons, Inc., New York, 1957).

[18] E. A. Mason, R. J. Munn, and F. J. Smith, National Aeronautics and Space Administration Report No. IMP-NASA-50. 1965.

PHYSICAL REVIEW VOLUME 180, NUMBER 1 5 APRIL 1969

Absorption Spectrum of Sr I in the Region of Autoionization from 1646 to 2028 Å

Robert D. Hudson and Virginia L. Carter
Space Physics Laboratory, The Aerospace Corporation, El Segundo, California

and

Paul A. Young*
TRW *Systems, One Space Park, Redondo Beach, California*

(Received 23 December 1968)

The atomic absorption cross section of strontium has been measured at an instrumental bandwidth of 0.07 Å in the autoionizing wavelength interval from 1646 to 2028 Å. Corrections have been applied to eliminate the bandwidth dependence of the results. Figures summarizing our best estimate of cross section versus wavelength are presented. The observed structure is grouped into series, and the measured wavelengths and oscillator strengths for the members of each series are tabulated.

I. INTRODUCTION

The absorption spectrum of strontium vapor at wavelengths shorter than its principal series limit at 2177.13 Å was first recorded photographically by Garton, Pery, and Codling in 1959.[1] Absolute absorption cross sections in this autoionizing region were first obtained by two of us (Hudson and Young) in 1963 at an instrumental bandwidth of 1 Å. Shortly thereafter Hudson, Carter, and Stein, using an improved apparatus, were able to obtain absorption spectra of hot gases at an instrumental bandwidth of 0.075 Å.[2] As this approaches the bandwidth used by Garton, Pery, and Codling (0.027 Å), we decided therefore not to publish the 1 Å data, but to wait until high-resolution spectra could be obtained. This paper is an account of these high-resolution spectra.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

Details regarding the basic theory and experimental arrangement have been discussed previously.[3,4] Figure 1 shows the configuration of the apparatus. It consists essentially of a 2.2-m normal incidence scanning monochromator, behind the exit slit of which is a temperature-regulated furnace that serves as an absorption chamber. Light was generated in a hydrogen Hanovia lamp operated at approximately 1000 W. A 1200 lines/mm Bausch and Lomb replica grating was used, which combined with 20-μ entrance