

## Variational Cellular Model of the Electronic Structure of the Rare Gas Halide Excimers NeF, NeCl, ArF and ArCl

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The Variational Cellular Method (VCM) was used to calculate the  $C^+$  potential energy curves of NeF, ArF, NeCR, ArCR, both in their ground states and ionic first-excited states. The excited states of these molecules are the first instance of application of the VCM to ionic bonding. Previous applications of the VCM were restricted to covalent diatomic molecular systems. The fact that the present results agree fairly well with experiment and *ab initio* calculations, shows that the VCM is a good technique to molecular calculations and can also be applied to describe the molecular excited states.

O método Celular Variacional (MCV) foi usado para calcular as curvas de potencial  $^2\Sigma^+$  do NeF, ArF, NeCR, ArCR, no estado fundamental e primeiros estados iônicos excitados. Os estados excitados destas moléculas representam o primeiro caso de aplicação do MCV para ligações iônicas. Aplicações anteriores do MCV foram restritas a moléculas diatômicas covalentes. O fato de que os resultados deste trabalho concordam bem com a experiência e com cálculos *ab initio*, mostra que o MCV é uma boa técnica em cálculos moleculares e pode também ser aplicado para descrever os estados moleculares excitados.

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## 1. INTRODUCTION

The rare gas monohalides ( $RgX$ ) constitute an important class of systems for laser applications<sup>1</sup>. The emission in the visible or ultraviolet regions is assumed as due to a charge-transfer transition from a strongly ionic bonding upper state to a repulsive or weakly bound covalent lower state<sup>2</sup>. The importance of the excimer lasers for applications in photochemistry, isotope separation, etc., has stimulated wide interest in the rare gas halides, both under a theoretical and practical point of view<sup>3,4</sup>. Preliminary theoretical studies of the rare gas halide molecules were done by analogies with alkali halide systems<sup>5</sup>. The efforts in the study of these molecules include applications of the electron-gas charge-density model<sup>6</sup>, and *ab initio* methods<sup>7-9</sup>. The long-range forms of the molecular potentials have been discussed by Krauss<sup>10</sup>. Recently Michels et al have successfully applied the Slater  $K\alpha$  density functional approximation<sup>11</sup> to perform calculations of the electronic structure and related properties of  $ArF$ <sup>12</sup> and noble gas dimer ions<sup>13</sup>. The  $K\alpha$  equations were solved within the framework of the self-consistent multiple scattering method (MS- $K\alpha$ ) developed by Johnson and co-workers<sup>14</sup>. In order to minimize the errors inherent to the muffin-tin model of the molecular potential, an improved overlapping sphere version<sup>15,16</sup> of the method was assumed.

In this paper, the recently proposed Variational Cellular Method (VCM)<sup>17,18</sup> is used to perform calculations on the potential energy curves, spectroscopic properties and emission characteristics of the rare gas halide excimers  $NeF$ ,  $NeCl$ ,  $ArF$  and  $ArCl$ . This work represents a continuation of our exploratory calculations using VCM. In the initial papers the electronic structure calculations of the ground states of  $H_2^+$ <sup>17,18</sup>,  $H_2$  and some first-row diatomic molecules<sup>19,20</sup> were successfully performed. The method was also applied to calculate the band structure of metallic sodium<sup>21</sup>. The rare gas monohalides chosen for this study are well suited as a new test of the method, due to the large number of orbitals involved in the calculations and to the interesting properties of the excimer excited states. Accurate *ab initio* configuration calculations for  $NeF$  and  $ArF$  have been reported<sup>1,9,12</sup>.

The VCM is a new approach for solving the self-consistent-

field (SCF) problem for molecules and crystals. It is based on the original Wigner-Seitz-Slater cellular method proposed in 1934<sup>22,23</sup>. The SCF problem for the molecules analysed here is solved within the framework of the  $X\alpha$  density functional approach. Since the major virtue of the cellular theory is the removal of the muffin-tin approximation to the molecular potential, it is interesting to compare the VCM- $X\alpha$  results for ArF with those reported by Michels *et al.*, obtained by implementing the optimized MS- $X\alpha$  method<sup>12</sup>. It has been pointed out that the choice of optimum overlap radii for the muffin-tin spheres is very important if reliable *total* energies are required<sup>13</sup>.

The rare gas halide excimer state was identified, since the early studies, as an ion pair state<sup>10</sup>. The ground and excited states of the molecule are formed from nearly closed-shell system interactions, with no significant charge sharing in the chemical bonds<sup>13</sup>. The spherical cellular potentials that we are assuming here are then a very good approximation to the true molecular potential. The energy potential curves for the ground and lowest excited states of the molecules considered are obtained by us with a good degree of accuracy. The VCM- $X\alpha$  method leads to calculate binding energy and bond length values for the excimer states in excellent agreement with *ab initio* calculations. It is worthwhile to observe that even for this especial class of molecules the standard muffin-tin potentials approximation is not reliable. According to the results reported by Michels *et al.*, a significant overlapping of the muffin-tin spheres is necessary in order to improve on the molecular *total* energy<sup>13</sup>.

## 2. THEORY

The theoretical framework of the VCM has been formulated by two of us (LGF and JRL) in previous works<sup>17-19</sup>. The basic equations of the method are established in Ref. 18. In Ref. 19 it is shown how self-consistency can be implemented in the method and how the potential for the Schrödinger equation and the molecular total energy can be properly defined. According to the cellular theory, the crystal or molecular space is divided into nonoverlapping space-filling cells, and the poten-

tial is made spherical within each cell. Within the cell  $i$ , the wavefunction  $\psi_i$  is expanded in spherical harmonics

$$\psi_i = \sum_{\lambda} A_{i\lambda} f_{i\lambda}(\vec{r}), \quad (1a)$$

where

$$f_{i\lambda}(\vec{r}) = R_{\ell}^{\epsilon_0}(r_i) Y_{\lambda}(\hat{r}_i) \quad (1b)$$

$R_{\ell}^{\epsilon_0}$  is a solution of the radial Schrödinger equation for the energy  $\epsilon_0$ , regular at the center of the cell  $i$ ;  $A$  denotes the spherical harmonic angular momentum pair  $(\ell, m)$ . A variational expression for the energy eigenvalue, (Eq. (2) of Ref.18), is used to determine the coefficients  $A_{i\lambda}$  through the secular equations

$$\sum_{i'\lambda'} \langle i\lambda | H | i'\lambda' \rangle A_{i'\lambda'} = 0 \quad (2)$$

$H$  is a Hermitean square matrix, dependent on the energy eigenvalue, written as

$$\begin{aligned} \langle i\lambda | H | i'\lambda' \rangle &= (1 - \delta_{ii'}) \int dS_{ii'} \\ &\times \left[ \partial_n f_{i\lambda}^* f_{i'\lambda'} + f_{i\lambda}^* \partial_n f_{i'\lambda'} \right] \end{aligned} \quad (3)$$

where the symbols are explained in Ref. 18.  $H$  is evaluated by performing integrations along the cell surfaces. The zeroes of the determinant associated to Eq. (2) are the eigenvalues of the VCM problem.

The partitioning of the molecular space for the RgX systems discussed in this paper is schematically shown in Fig. 1. The two atomic cells are two calottes centered at the same point and have a plane surface of contact. The dots are the nucleus sites. The outer cell extends from the atomic cells to infinity. We remind that an important asset of the VCM is the freedom one has in the cell construction. The cells in general can have arbitrary shapes. The partitioning sketched in Fig.1 was already used to perform our previous calculations<sup>19,20</sup> It has been shown<sup>20</sup> how to improve on the calculated values of the total energy of  $N_2$  by varying the cell parameter  $\rho$ . In the present work, however, we decided to adopt the partitioning that has been used in most

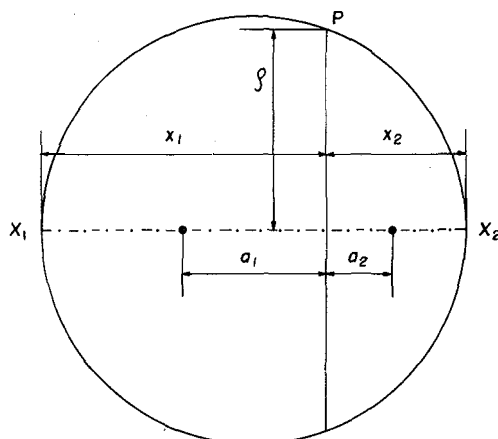


Fig.1 - Partitioning of the space for the rare gas monohalides. The dots are the nucleus sites. The cell surface are two calottes centered at the same point and have a plane surface of contact. The outer cell is bounded by one single spherical surface.

of our previous calculations, that is

$$x_1 = 2a_1$$

$$x_2 = 2a_2$$

$$\rho = 2\sqrt{a_1 a_2}$$

Therefore an outer cell bounded by one single spherical surface is chosen. The internuclear distance is

$$R = a_1 + a_2$$

The plane of contact between the atomic cells is located such that the internuclear distance is approximately divided in parts proportional to the ionic radii of the atoms<sup>24</sup>. For one fixed value of  $R$  the plane is placed at the same position for the ground and excited molecular states. As far as the exchange-correlation parameters are concerned, we assume the correspondent Hartree-Fock atomic values reported by Schwarz<sup>25</sup> in the atomic cells. A suitable average of the atomic values is supposed in the outer cell.

The potential energy curves for the RgX systems are determined by carrying out self-consistent calculations of the molecular total energy at a set of values of the internuclear distance  $R$ . The obtained

results are then adjusted, least squares, to the following expression for the molecular ground state and excited state energies<sup>26</sup>

$$E(R) = A + \frac{2}{B} \left[ \frac{B}{R} \right]^n \text{ in a.u. ,} \quad (4)$$

where  $A$ ,  $B$  and  $n$  are adjustable parameters. For the excited ionic state, the quantity  $-2/R$  is added to Eq. (4) in order to account for the long-range Coulombic attraction of the ion pair.

It is worth mentioning that the spin-orbit effects were neglected in these calculations. They have been included by simple semi-empirical models for NeF<sup>1,9</sup> and ArF<sup>9</sup>, and for other RgX containing elements as Kr<sup>7</sup> and Xe<sup>8</sup>. They were considered small for the purpose of the present work. The calculations reported here were performed within the framework of the SCF one-particle model, where the spin polarization effects are also neglected.

### 3. RESULTS AND DISCUSSION

#### A. Potential energy curves

The potential energy curves of the rare gas monohalides determined here correspond to the following molecular orbital configurations:  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 \pi^4 2\pi^4$  for the covalent lower state  $1^2\Sigma^+$ ;  $1\sigma^2 2\sigma^2 3\sigma^4 \sigma^2 1\pi^4 2\pi^4$  for the ionic upper state  $2^2\Sigma^+$ . Only the valence orbitals have been indicated. The core orbitals, fully occupied, were treated according to the frozen core approximation. Most of the calculation was performed assuming only one value of  $\lambda$  in the cellular expansion (Eq.1a). Therefore, the accuracy of our results are such that the  $^2\Sigma$  and  $^2\Pi$  potential energy curves are indistinguishable. The state which arises from the covalent limit  $\text{Rg}(p^6) + \text{X}(p^5)$  will be labelled as  $1^2\Sigma^+$ . That one which arises from the ionic limit  $\text{Rg}^+(p^5) + \text{X}^-(p^6)$  will be labelled as  $2^2\Sigma^+$ .

According to our calculations, the energy of the separated atom limit  $\text{Ne}(2p^6) + \text{Cl}^*(3s3p^6)$  lies below the minimum of the  $\text{Ne}^+\text{Cl}^-$  ionic potential energy curve. Thus, the efficiency for production of the

ionic state will be reduced as molecules are turned into the excited states  $\text{NeCl}^*$ . This mechanism should contribute to hinder emission in  $\text{NeCl}^3$ . The state which arises from the excited separated atom limit  $\text{Ne}(2p^6) + \text{Cl}^*(3s3p^6)$ , labelled as  $3^2\Sigma^+$ , corresponds to the MO configuration  $1\sigma^2 2\sigma 3\sigma^2 4\sigma^2 1\pi^4 2\pi^4$ . The core orbitals, whose notations are omitted here, were kept frozen in the calculations.

The ionic states of  $\text{Rg}^+\text{X}^-$  are separated from the covalent states of  $\text{RgX}$  at infinite internuclear distances by the quantity  $\Delta E$  which is

$$E_{\text{ion}}(R = \infty) - E_{\text{cov}}(H = \infty) = I.P.(\text{Rg}) - E.A.(\text{X}),$$

where  $I.P.$  means ionization potential and  $E.A.$  means electron affinity. Here we compare the VCM- $X\alpha$  calculated values of  $\Delta E$  with the experimental one. The latter were obtained from data quoted in Ref. 8 and 9 and considering the difference between the electron affinities of  $\text{Cl}$  and  $\text{F}$ <sup>27</sup>. It is found one deviation of about 2 eV between the calculated values of  $\Delta E$  and the experiment. These errors have most to do with the  $X\alpha$  approximation to the exchange-correlation energy and not with VCM itself. Within the context of the Slater  $X\alpha$  approximation, the value of  $\alpha$  which best reproduces Hartree-Fock energies varies with ionicity<sup>25</sup>. Different values of  $\alpha$  should be used then for the ions  $\text{Rg}^+$  and  $\text{X}^-$  in our calculations. The main conclusion is that the chosen exchange-correlation parameters are not accurately describing the electron affinities of the halogen atoms and the ionization potential of the rare gas atoms. We observe that the  $X\alpha$  description of the electron affinity of the fluorine atom is worse than that of the Chlorine atom.

The proper treatment of the exchange-correlation effect is important to determine the correct values of the ionization potentials and electron affinities<sup>13</sup>. These effects are roughly constant along the potential energy curve, and to the extent that they do not cancel, they can be removed by adjusting the potential curve to the correct separated atom limits. Such a procedure has been used by Winter *et al.*<sup>1</sup> in their *ab initio* calculations for  $\text{NeF}$ . *Ab initio* potential curves corrected for the errors in the separated atom energies have also been reported for rare gas monoxides<sup>2a</sup>. The same procedure was adopted to correct the VCM calculated potential energy curves.

Before we analyse the VCM potential energy curves, one more comment should be made. The many-electron effects that should split the energies in multiplet terms are not incorporated in the VCM calculations. The determined potential energy curves are not rigorously LS curves. The covalent and ionic states of RgX molecules analysed here correspond to open shell systems with *total* spin 1/2. In the present version of VCM this fact is not taken into account.

The determinant potential energy curves of NeF, NeCl, ArF and ArCl are plotted in Figs.2-5, respectively. The results show that the covalent  $1\ 2\Sigma^+$  state is repulsive for all molecules. The ionic  $2\ 2\Sigma^+$  state is found to be bound, a consequence of the long range Coulombic attraction of the ion pairs.

The *ab initio* methods have been the most common theoretical technique used to study the rare gas monohalides <sup>1-3,7-9,12</sup>. Besides the use of analogies with the alkali halide molecules <sup>3,5</sup>, only two attempts have been made to apply other less sophisticated techniques to the study of the RgX excimers. Calculations of the electronic states of some

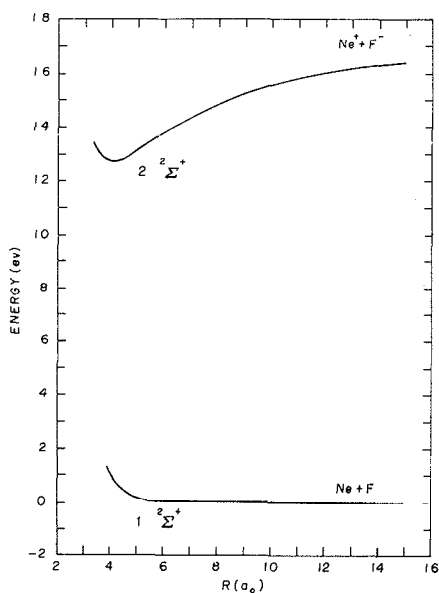


Fig.2 - Potential energy curves for the  $\Sigma^+$  electronic states of NeF as calculated by VCM. The separated atom limits correspond to the Ne( $2p^6$ ) + F( $2p^5$ ) ground state and Ne<sup>+</sup>( $2p^5$ ) + F<sup>-</sup>( $2p^6$ ) ionic state.



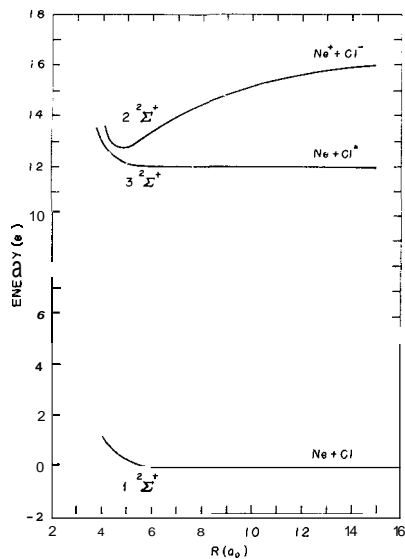


Fig.3 - Potential energy curves for the  $\Sigma^+$  electronic states of NeCl as calculated by VCM. The separated atom limits correspond to the Ne( $2p^6$ ) + Cl( $2p^5$ ) ground state, Ne<sup>+</sup>( $2p^5$ ) + Cl<sup>-</sup>( $3p^6$ ) ionic state and to the Ne( $2p^6$ ) + Cl<sup>+</sup>( $3s3p^6$ ) excited state.

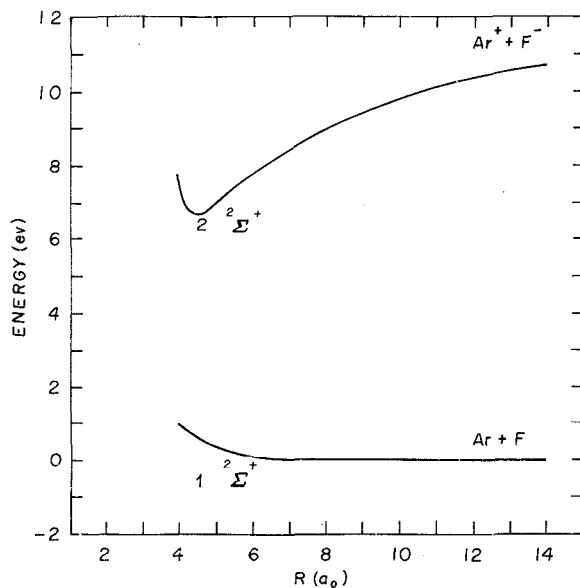


Fig.4 - Potential energy curves for the  $\Sigma^+$  electronic states of ArF as calculated by VCM. The separated atom limits correspond to the Ar( $3p^6$ ) + F( $2p^5$ ) ground state and Ar<sup>+</sup>( $3p^5$ ) + F<sup>-</sup>( $2p^6$ ) ionic state.

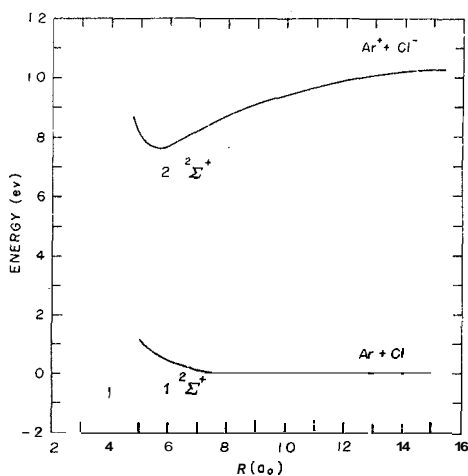


Fig. 5 - Potential energy curves for the  $\Sigma^+$  electronic states of ArCl as calculated by VCM. The separated atom limits correspond to the Ar( $3p^6$ ) + Cl( $3p^5$ ) ground state and Ar $^+$ ( $3p^5$ ) + Cl $^-$ ( $3p^6$ ) ionic state.

RgX have been reported by Clugston and Gordon, using the electron gas method<sup>6</sup> and for ArF by Michels *et al* using the MS- $X\alpha$  method<sup>1,2</sup>. The electron-gas potential energy curves have been reported only for KrF, and therefore are not directly comparable with the VCM curves. However, transition energies for NeF, ArF and ArCl have been published<sup>6</sup> and will be compared with the VCM results in the next section. The MS- $X\alpha$  method leads to potential energy curves for ArF in good agreement with the *ab initio* and VCM results<sup>1,2</sup>. Since Michels *et al* do not mention the values of the exchange parameters used in their work, we are not at a position to make a more detailed comparison between the MS- $X\alpha$  and VCM- $X\alpha$  calculations.

The potential energy curve for the  $3\ 2\Sigma^+$  state arising from the Ne( $2p^6$ ) + Cl\*( $3s\ 3p^6$ ) separated atom limit is shown in Fig. 3. It should be noted that the  $3\ 2\Sigma^+$  curve is essentially flat until  $6.0\ a_0$ . For shorter values of R it presents the expected repulsive behavior. We conclude that for NeCl the ionic state should be strongly predissociated.

It is shown in this section that VCM determines the potential energy curves for the covalent and ionic states of NeF and ArF with a reasonable degree of accuracy. The overall agreement between VCM and *ab*

*initio* methods is fairly good. VCM was then applied to determine the potential energy curves for the covalent and ionic states of NeCR and ArCR and for the excited state, NeCl\*. Potential energy curves for these molecules have not been reported yet.

## B. Spectroscopic constants and emission characteristics

Table I lists the spectroscopic constants  $R_e$  (bond length) and  $D_e$  (dissociation energy) of the  $2^2\Sigma^+$  ionic states of the rare gas monohalides. Besides the VCM results, values of  $R_e$  and  $D_e$  obtained by other authors are also listed for comparison. The internuclear equilibrium separations and dissociation energies were determined from Eq. (4) of section 2. The VCM calculations were performed at a set of  $R$  values surrounding the minima of the ionic curves. Molecular configurations correspondent to internuclear distances of  $10.0 a_0$  were also considered in order to determine the VCM energy of the separated atom limits, or the values of  $A$  in Eq. (4). The  $D_e$  values in Table I are relative to the ionic separated atom limit.

Table I. Calculated spectroscopic constants of the  $2^2\Sigma^+$  ionic states of the rare gas monohalides.

MOLECULE	$R_e$ (Å)		$D_e^a$ (eV)	
	VCM	Other Works	VCM	Other Words
NeF	2.12	2.01 <sup>b,c</sup>	5.54	6.38 <sup>b</sup> , 6.49 <sup>c</sup>
NeCR	2.49	2.5 <sup>d</sup>	5.14	—
ArF	2.41	2.40 <sup>b</sup>	5.64	5.52 <sup>b</sup>
ArCR	2.92	2.96 <sup>d</sup>	4.43	—

a) Relative to the ionic separated atom limit.

b) *ab initio* calculations (Reference 9).

c) *ab initio* calculations (Reference 1).

d) Estimated from data on the corresponding alkali halides, or taken from a private communication of N.W. Winter (Reference 3).

The *ab initio* and VOM spectroscopic constants listed in Table I are in good agreement. VOM reproduces the *ab initio* bond lengths for NeF and ArF within 5%. The estimated values of  $R_e$  for NeCl and ArCl reported in Ref. 3 and listed in Table I are surprisingly good. Previous estimations made by Ewing and Brau<sup>5</sup> based also on the alkali halide-rare gas halide analogy are 1.93 Å for NeF, 2.17 Å for ArF and 2.7 Å for ArCl. The results for ArF and ArCl seem to be unreliable. It is found from *ab initio* calculations that  $R_e$  increases in the sequence RgF with the increasing size of the Rg<sup>9</sup> and also increases in the sequence XeX with the increasing size of X<sup>8</sup>. If we add to these results those shown in Table I, we find the general trend in the spectroscopic constants  $R_e$ . They increase in the sequence RgX with the increasing size of Rg or with the increasing size of X. From the Xenon halides calculations it is verified that the difference between  $R_e(\text{XeF})$  and  $R_e(\text{XeCl})$  is 0.53 Å. This value is in good agreement with that found by us, 0.51 Å, for the difference between  $R_e(\text{ArCl})$  and  $R_e(\text{ArF})$ .

Based on *ab initio* calculations, Dunning and Hay show that the dissociation energies of the ionic states of the rare gas monofluorides fall in the narrow range  $5 \text{ eV} < D_e < 5 \frac{1}{2} \text{ eV}$ , with  $D_e$  decreasing with increasing size of the rare gas atom<sup>9</sup>. They pointed out that NeF is a notable exception, with a value of 6.38 eV for  $D_e$ . This result is confirmed by the *ab initio* calculations reported by Winter *et al* (6.49 eV)<sup>1</sup>. According to our calculations, the dissociation energy for NeF falls in the narrow range of energy mentioned above. In other words, our calculations do not confirm that NeF is an exception. From the *ab initio* calculations carried out for the Xenon halides<sup>8</sup> it is verified that  $D_e$  decreases with the increasing size of the halogens. Similar trend is observed in our calculations. Therefore we may conclude that the  $D_e$  values for RgX series decrease with the increasing size of X. From table I we note that  $D_e(\text{NeF}) < D_e(\text{ArF})$ .

We now compare the calculated VOM emission energies with the available experimental data and with the results of other calculations. This is done by evaluating the difference between the energy of the  $2^2\Sigma^+$  ionic state at its minimum ( $R_e$ ) and the energy of the  $1^2\Sigma^+$  covalent state at this same distance. These values (vertical emission energies) are then correlated with the wavelength (or photon energy) of maximum observed intensity. Here we assume that the  $2^2\Sigma^+ - 1^2\Sigma^+$  transition

should produce the strongest emission <sup>9</sup>. The assignment of a vertical transition to the emission of maximum intensity has to be made with some caution since such effects as emission from higher vibrational levels of the ionic states are not taken into account <sup>8</sup>.

Table II shows the emission characteristics of the  $2\ ^2\Sigma^+ - 1\ ^2C^+$  transition as calculated by VCM- $\chi\alpha$  ( $E_e$  = photon energy;  $\lambda_e$  = emission wave length). The results obtained from other calculations and experiments are also shown. Recently Rice, Hays, and Woodworth have attributed <sup>29</sup> to NeF an emission feature observed at 108 nm (11.46 eV) in e-beam excited Neon-Fluoride mixtures. According to Table II the VCM result agrees fairly well with the experimental value and with the *ab initio* results. Similar agreement is found between the calculations and the experiment for ArF. Hoffman, Hays, and Tisone <sup>30</sup> reported lasing in e-beam excited mixtures of Argon and Fluorine-containing compounds. The

Table II - Emission characteristics of the  $2\ ^2\Sigma^+ - 1\ ^2C^+$  transition in the rare gas monohalides. Units are as indicated.

MOLECULE	Photon energy, $E_e$ (eV)			Emission wave length, $\lambda_e$ (nm)		
	VCM	Other Works	EXP.	VCM	Other Works	EXP.
NeF	11.82	10.84 <sup>a</sup> , 11.58 <sup>b</sup>	11.46 <sup>e</sup>	105	114 <sup>a</sup> , 107 <sup>b</sup>	108 <sup>e</sup>
NeCl	12.45	-	-	100	-	-
ArF	6.24	6.49 <sup>a</sup> , 6.35 <sup>c</sup>	6.41 <sup>f</sup>	199	191 <sup>a</sup> , 196 <sup>c</sup>	193 <sup>f</sup>
ArCl	7.06	7.28 <sup>d</sup>	7.14 <sup>g</sup>	176	170 <sup>d</sup>	170 <sup>g</sup>

- a) *ab initio* calculations (Reference 9).
- b) *ab initio* calculations (Reference 11).
- c) *ab initio* calculations (Reference 12).
- d) Electron-gas model (Reference 6).
- e) Reference 29.
- f) References 30 and 31.
- g) References 32 and 33.

Table III - Calculated excitation energies,  $T_e$ , for the ionic states of the rare gas monohalides.  $T_e$ 's are the energies at the minima of the ionic  $2^2\Sigma^+$  curves, relative to Rg + X separated atom limits.  $\Delta E_e = T_e - E_e$  (see the text). All entries are in eV units.

MOLECULE	V C M		<i>ab initio</i> <sup>a</sup>	
	$T_e$ (eV)	$\Delta E_e$ (eV)	$T_e$ (eV)	$\Delta E_e$ (eV)
NeF	12.64	0.82	11.01	0.17
NeCl	12.82	0.37	-	-
ArF	6.76	0.52	6.59	0.10
ArCR	7.75	0.69	-	-

a) Reference 9

effect was also reported by Burnham and Djeu<sup>31</sup> from discharge experiments. The laser spectrum shows a peak at 193 nm (6.41 eV). According to Table II the VCM results for ArF is 6.24 eV. No emission has been observed for NeCl and also no theoretical studies have been reported. For ArCl the VCM result agrees fairly well with the experimental one<sup>32,33</sup> and with the electron-gas model estimate<sup>6</sup>.

The characterization of the lower state,  $1^2\Sigma^+$ , for the transition is made from the data shown in Table III. There we list the energy differences,  $T_e$ , between the minima in the  $2^2\Sigma^+$  ionic curve and the energies at the separated atom limits, Rg + X.  $\Delta E_e$  is the difference between  $T_e$  and the emission energy,  $E_e$ . Therefore  $\Delta E_e$  characterizes the repulsive region of the terminal state for the transition. According to *ab initio* results<sup>9</sup>, the transitions occur to the almost flat region of the potential energy curve of the covalent  $1^2\Sigma^+$  state. The electron transfer from the ionic to the covalent state takes place at a more repulsive region of the covalent curve, according to VCM calculations.

Among the RgX analysed here, ArF has been found to lase<sup>30,31</sup>. Waynant<sup>34</sup> has recently reported lasing in ArCR. NeF exhibits only fluorescence<sup>29</sup> and no emission is observed for NeCl<sup>3,6</sup>. These different

behaviors in the emission characteristics of the RgX excimers occur in spite of the similarities that exist among their potential energy curves. Previous analyses show that the production efficiency for the ionic state is closely related with the crossings of the potential energy curves for the excited states with the ionic curve<sup>3,6,9</sup>. Assuming that the potential curves for the excited states are flat and that the alkaline halide-rare gas halide analogy is valid, Ewing and Brau<sup>5</sup>, and Hay *et al*<sup>3</sup> estimate the values of the internuclear distances,  $R_c$ , where the crossings occur.

From Fig. 3 we observe that the potential energy curve for the  $3\ ^2\Sigma^+$  excited state arising from the  $\text{Ne}(2p^6) + \text{Cl}^*(3s3p^6)$  separated atom limit is essentially flat. For shorter values of  $R$ , it presents the expected repulsive behavior. The interesting conclusion is that the  $3\ ^2\Sigma^+$  curve lies below the ionic curve. Thus, no curve crossing occurs. This state, which has not been analysed in previous calculations, forms, with the lowest-lying excited state arising from the  $\text{Ne}(2p^6) + \text{Cl}^*(3p^44s)$  separated atom limit, the predissociation channels to the ionic states. Therefore, lasing or fluorescence are not expected for this material, in agreement with the experimental results<sup>3</sup>. The ground state potential energy curve arising from the  $\text{Ne}^*(2p^53s) + \text{Cl}(3p^5)$  separated atom limit<sup>3,5</sup> crosses the ionic curve at a very large internuclear distance.

The potential curves of the excited states arising from the  $\text{Ne}(2p^6) + \text{F}^*(2s2p^6)$ ,  $\text{Ar}(3p^6) + \text{F}^*(2s2p^6)$  and  $\text{Ar}(3p^6) + \text{Cl}^*(3s3p^6)$  lie above the correspondent ionic separated atom limit. Thus, no crossings occur. For NeF the potential energy curve arising from  $\text{Ne}(2p^6) + \text{F}^*(2p^43s)$  separated atom limit<sup>3,5</sup> crosses the ionic curve at  $R_c = 2.7\ \text{\AA}$ . This value agrees well with the estimate based on alkaline halide-rare gas halide analogy. Hay *et al*<sup>3</sup> report the value  $2.64\ \text{\AA}$  and Ewing and Brau<sup>5</sup> the value  $2.6\ \text{\AA}$  for  $R$ . According to our result, the energy at the crossing point relative to the energy at the minimum of the ionic curve,  $\Delta E_c$ , is 0.8 eV. The value reported by Hay *et al*<sup>3</sup> is 1.7 eV. For ArF crossing occurs at very large internuclear distance for the potential energy curve arising from the  $\text{Ar}^*(3p^54s) + \text{F}(2p^5)$  separated atom limit and no crossing occurs for the potential curve arising from the  $\text{Ar}(3p^6) + \text{F}^*(2p^43s)$  separated atom limit. These results are according to the estimates based on the alkaline halide analogies<sup>5</sup>. The potential energy

curve arising from the  $\text{Ar}^*(3p^54s) + \text{Cl}(3p^5)$  separated atom limit crosses the ionic curve at very large internuclear distance. The  $\text{Ar}(3p^6) + \text{Cl}^*(3p^44s)$  separated atom limit leads to a potential energy curve that crosses the ionic curve at  $R_e = 4.8 \text{ \AA}$ , according to the VCM calculations. This result agrees with the estimated value,  $4.47 \text{ \AA}$ , reported by Hay *et al.*<sup>3</sup>

In this section we show how the spectroscopic constants and emission characteristics of the ionic states of NeF, NeCl, ArF and ArCl molecules can be characterized on the basis of potential energy curves from VCM calculations. The results for NeF and ArF are in good agreement with available experimental data and with reported *ab initio* calculations. The results for NeCl and ArCl are consistent with experiment and with the estimates based on alkaline halide-rare gas halide analogy.

#### 4. CONCLUSION

From the results described in this work we conclude that the VCM is capable of yielding reasonably accurate spectroscopic constants and emission energies for the rare gas halide excimer states. As far as the computational effort required to implement the VCM is concerned, we verified that its speed is comparable to that of the standard MS-X $\alpha$  method. However, the VCM leads to more accurate values for the *total*, molecular energy. As we have said before, one virtue of the cellular theory is the removal of the muffin-tin approximation, inherent to the MS-X $\alpha$  method.

The results presented here could be still further improved by using the appropriate values of  $\alpha$  for the ions in the X $\alpha$  description of the electron interactions, or by assuming more elaborate functionals to approximate the exchange-correlation effects<sup>36,37</sup>.

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