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A FLOATING FUNCTION, AB INITIO STUDY OF MOLECULAR AND ELECTRICAL PROPERTIES OF FIELD-PERTURBED NaCl AND KCl ION-PAIRS.

S. Simon, M. Duran and J. Miró.

Departament de Química, Institut de Química Computacional, Universitat de Girona, C/Albereda 5, 17071 Girona.

RESUM

Per tal d'estudiar quin és l'efecte de l'entorn sobre els parells iònics, s'ha fet un estudi amb mètodes *ab initio*. Els parells iònics que s'han estudiat han estat els parells diatòmics formats per un halogen i un alcalí, NaCl i KCl, en estat gasós. Per tal de simular l'entorn s'han utilitzat dos efectes. El primer és l'aplicació d'un camp elèctric uniforme sobre el parell iònic, i l'altre seria la utilització de funcions flotants, les quals actuen com a funcions de polarització. Hem estudiat diferents paràmetres, tant moleculars com elèctrics, i quina és la seva variació amb l'entorn.

RESUMEN

Con el fin de estudiar cuál es el efecto del medio sobre los pares iónicos, se ha llevado a cabo un estudio con métodos *ab initio*. Los pares iónicos que se han estudiado han sido los pares diatómicos formados por um halógeno y un metal alcalino, NaCl y KCl, en estado gaseoso. Para simular el entorno se han utilizado dos efectos. El primero corresponde a la aplicación de un campo eléctrico uniforme sobre el par iónico; el otro efecto correspondería a la utilización de funciones flotantes, que actúan como funciones de polarización. Para establecer dichos efectos, se han estudiado varios parámetros, ya sean moleculares o eléctricos, así como cuál es su variación con el entorno.

ABSTRACT

Ab Initio calculations have been employed to investigate the environment effects on ion-pair systems, namely diatomic alkali halides, NaCl and KCl. Static uniform electric fields of different strengths have been applied to simulate the environment. Floating functions are used in this paper, since they work as polarization functions, so, these calculations are another way to improve the environment effect. Different parameters have been studied, e.g. molecular parameters (distances, dissociation energy, etc.) and electrical properties (dipole moment and polarizabilities). This paper shows how these properties change when an electric field is applied, and how different floating schemes improve the results.

Keywords: Ion-Pairs; Floating functions; Electric field; *Ab initio* methods;

INTRODUCTION

The study of ion-pair associations in solution has been quite important in the recent years. Although ion-pair formation between an alkali cation and a halide ion has been studied by many workers through molecular dynamics and Monte-Carlo simulations (1-2-3), only few studies have employed molecular orbital *ab initio* calculations to describe that kind of systems. The main interest in ion-pair systems is the way they behave when they are in solution, thus there are so many works using molecular dynamics techniques. A recent paper from Waizumi et al. (4) studied the formation of two different ion-pair in aqueous solution by density functional calculations. Geometry optimizations become a big problem when solvating water molecules are added, so *ab initio* calculations turn out to be too expensive. Nevertheless, a good understanding of these solvated ion-pairs systems is obtained by applying a static, time-independent, uniform electric field to the gas-phase systems.

These perturbations caused by the application of the field, change the ion-pair potential energy profiles, thus equilibrium parameters also change (i.e. distances, energy, ...). The main purpose of this paper is to analyze the changes produced by electric fields of variable strengths on dissociation energy, equilibrium distances, dipole moments, polarizabilities, rotational constants and vibrational frequencies.

A way to improve the study about the environment effect, is using polarization functions. However, the increase of the number of functions implies a higher computational cost. An alternative way, is the use of floating functions, which are those whose coordinates are optimized independently from the nuclear coordinates. As shown in previous papers (5-6-7-8), floating functions have two very important advantages: first, they satisfy the Hellmann-Feynman theorem, (i.e. the Hellmann-Feynman force becomes zero at optimized geometries), and, second, they behave like polarization functions. This second advantage is used to save computational cost, since the number of functions does not increase. It is possible to build different floating schemes, so in this paper we are going to show how this floating schemes influence the ion-pair description. The methed can help us to get information about the two competitive effects in the ion-pair formation: the electrostatic attraction and the energy required to displace the solvent molecules.

METHODOLOGY

Almost all *ab initio* calculations were carried out by the GAUSSIAN 92 program (9), using the 3-21G basis set. Floating functions calculations have been performed by the GAUSSIAN 92 program using the massage option, by changing the nuclear charge of the centers which contain the basis functions to zero (i.e. they become goths atoms). The function and nuclear coordinates have been optimized independently using two different floating schemes.

To compute vibrational frequencies with floating functions, program written in our laboratory was used. In this program a numerical second derivative matrix is built using finite differences of the gradient. When nuclear coordinates are displaced (and their functions) from the equilibrium coordinates to compute second derivatives as finite differences of analytic first derivatives, the floating functions coordinates are allowed to relax in order to fulfill the Hellmann-Feynman theorem again.

RESULTS AND DISCUSSION

This section presents in the first place the results found for the two ion-pairs studied, NaCl, KCl, when a static, uniform, electric field is applied and, second, the results for floating functions with two different floating schemes.

A. Electric field

In Table I we summarize total energies, equilibrium distances and atomic charges for both ion-pairs studied. One must notice first that, the behavior of both ion-pairs is similar in every way. When a uniform electric field is applied to stabilize the ion-pair system, it is found that electric field increases the distances between the two ions, and that the net atomic charges increase. This charge increase will go on until an heterolytic breaking occurs, which happens when stronger electric fields (0.03 u.a. and stronger) are applied. At such strength, the ion-pair does not exist anymore, because it is split into separated ions, Na^+,K^+ and Cl^-. We have also studied what happens when a wrong direction electric field is applied, such as to destabilize the ion-pair association. In this case, the equilibrium distances and the atomic charge separation decrease, so these systems, tend to an homolytic breaking.

Further insight into the effect that a uniform electric field has on ion-pair associations is shown in Figure I and II for NaCl and KCl respectively. In these two figures we have depicted the potential energy profiles for field-free ion-pair system, two stabilizing electric fields (0.01 and 0.02 a.u.) and two destabilizing electric fields (-0.01 and -0.02 a.u.). When a stabilizing electric field is applied, a maximum appears in the potential energy profiles. This fact is due to two different effects taking place: the change of coulombic energy (E_e) and the change of field interaction energy (E_f):

$$E_e = -\frac{Z_i Z_j}{r}$$

$$E_f = -Fr$$

where Z_i and Z_j stand for the atomic charge of each ion, r is the distance between the ions, and F is the electric field strength. When the distance increases, E_e becomes higher but the electric field stabilizes the system, thus E_f becomes more negative. There is a certain distance where E_f will be more negative than E_e, so the total energy will decrease . When a strong electric field is applied the well depth of the energy minimum is decreased, until there is no minimum at all in the potential energy surface, the ion-pair is being broken.

In Table II and III we collect dissociation energies, geometrical parameters, dipole moments, polarizabilities, vibrational frequencies and rotational constants for each ion-pair studied, NaCl and KCl respectively. Paying attention to dissociation energy, one can see that stabilizing fields give higher values, so it seems to be more difficult to dissociate the ion-pair. As mention above, these electric fields tend to dissociate the ion-pair, yet the dissociation energy is higher. This fact is due to the dissociation energy not taking into account E_f, which is the most important component when strong electric fields are applied. A stabilizing electric field implies a large charge separation that translates into a large dipole moment, which is especially large when the strongest electric field is applied. Polarizabilities decrease with the field because of the charge separation, the system being more stable so the molecule is less polarizable. In figures I and II one can see how the vibrational frequencies change with different electric field strength. The more stabilizing the electric field, the smaller the curvature minimum profile at that energy, so, the vibrational frequency becomes smaller.

The relative behavior between both ion-pair systems when different uniform electric field strengths are applied, does not change too much. The KCl ion-pair has equilibrium distances longer than NaCl, so dipole moments and vibrational frequencies are larger, and polarizabilities and rotational constants become smaller. Experimentally, the association constant of KCl is higher than the association constant of NaCl. The model must to be inproved.

B. Floating functions

The second, more methodology-oriented goal of the present paper is to study how floating functions influence ion-pair association. As mention above, it is possible to build different floating schemes. As matter of fact two schemes have been tested: first the simplest one can think about, by keeping together all functions belonging to the same nuclei, in this case, one has twice the coordinates to optimize than as compared to fixed-functions. A second scheme is similar to a core-valence splitting: for both Na and Cl atoms, *1s,2sp* functions are placed in the same center, whereas *3sp,4sp* functions are put in another center, (for K *1s,2sp* and *3sp,4sp,5sp*, are grouped, respectively).

In the first case, when all functions grouped together, the ion-pair behavior is the same as fixed-functions calculations. Not only the geometric parameters do not change, but also the total and dissociation energies are the same. The reason is that basis functions for Na, Cl and K are not very diffuse, so they are not free enough to move. More freedom is given to the basis functions when we let them move independently one from each other. The most diffuse function set, (Na valence functions), tend to move towards Cl, so, the bond description is improved. This better description translates into a stabilization of the ion-pair as well as into an increase of the total and dissociation energies. Equilibrium distances also decrease because of the displacement of the basis functions of one nucleus with respect to the other nucleus. When these functions are displaced along the bond, the charge is distributed in a way different to that of fixed-functions calculations, because they are closer to each other, so dipole moments decrease, as do polarizabilities. Furthermore, vibrational frequencies and rotational constants increase, the reason being found in the bond length being smaller. Vibrational frequencies, as widely known, depend inversely on the distances.

Other floating schemes have been tested, (i.e. each shell in a different center), but, since the Cl atom is much more electronegative than Na and K, Na functions move towards the Cl center. Based in our previous experience (10), when functions move very far from the their original nucleus, it is very difficult to locate an energetic minimum. In these systems, Na functions will be place onto the Cl nucleus, so the system will be described ackwardly.

CONCLUSIONS

The results reported in this study show how ion-pair association behaves when uniform electric fields are applied, and, also provide a hint on the usefulness of floating functions. When different positive electric field are applied, not only they change the dissociation reaction profile, but also they break the ion-pair system, helping in the electron transfer. Floating functions tend to move towards the most electronegative nucleus, so they stabilize ion-pairs and reduce bond lengths. The results obtained with floating functions are very different thus, deserve further research, which will be reported in future papers.

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Bibliography

1. LAWRENCE, R., PRATT, HUMMER, G., and GARCÍA, A.E., Biophysical Chemistry, *1994*, 51, 147.
2. FOIS, E.S., and GAMBA, A., J. Chem. Phys., *1994*, 100, 9044.
3. SMITH, D.E., and LIEM X. Dang, J. Chem. Phys., *1994*, 100, 3757.
4. WAIZUMI, K., MASUDA, H., and Fukushima, N., Chem. Phys. Let., *1993*, 205, 317.
5. HURLEY, A.C., J. Comput. Chem., *1988*, 9, 75.
6. HIRAO, K., and MOGI, K., J. Comput. Chem. *1992*, 13, 457.
7. HELGAKER, T., and ALMLÖF, J., J. Chem. Phys. *1988*, 89, 4889.
8. DURAN, M., and SIMON, S., Sci. Ger., *1994*, 20, 95.
9. Gaussian 92, FRISCH, M.J., TRUCKS, G. W., HEAD-GORDON, M., GILL, P. M. W., WONG, M. W. J., FORESMAN, B., JOHNSON, R.G., SCHELEGEL, H. B., ROBB, M. A., REPLOGLE, E. S., GOMPERTS, R., ANDRÉS, J. L., RAGHAVACHARI, K., BINKLEY, J. S., GONZALEZ, C., MARTIN, R. L., FOX, D. J., DEFREES, D. J., BAKER, J., STEWART, J. J. P., and POPLE, J. A., "Gaussian", Inc. Pittsburgh PA, 1992.
10. SIMON, S., and DURAN, M., to be published.

Table I - Field strengths (a.u.), energies (a.u.), distances (Å) and atomic charges for both field-free ion-pair systems, NaCl and KCl, and under different uniform electric field strengths.

	F	E	r_e	Q_{Cl}	Q_A
	0.02	-618.329446	2.6380	-0.8629	0.8629
	0.01	-618.284664	2.5007	-0.8253	0.8253
NaCl	0.0	-618.243152	2.4210	-0.7991	0.7991
	-0.01	-618.204742	2.3660	-0.7191	0.7191
	-0.02	-618.169988	2.3278	-0.6370	0.6370
	0.02	-1043.649276	3.3214	-0.9157	0.9157
	0.01	-1053.593073	2.9592	-0.8932	0.8932
KCl	0.0	-1053.541604	2.8292	-0.8644	0.8644
	-0.01	-1053.493661	2.7477	-0.8185	0.8185
	-0.02	-1053.450364	2.6938	-0.7274	0.7274

Table II - Field strengths (a.u.), total energies (a.u.), dissociation energies (kcal/mol), equilibrium distances (Å), vibrational frequencies (cm^{-1}), dipole moments (a.u.), polarizabilities (u.a.) and rotational constants (a.u.) for NaCl. Italic number for floating functions in two different schemes.

F	E	D_e	r_e	ν_e	μ	_	B_e
0.02	-618.329446	-189.49	2.6380	216.98	4.677	12.90	5.24
	-618.329448	*-189.25*	*2.6366*	*217.05*	*4.675*	*12.90*	*5.24*
	-618.333968	*-192.42*	*2.5850*	*220.77*	*4.576*	*11.78*	*5.45*
0.01	-618.284664	-161.40	2.5007	294.20	4.305	16.01	5.83
	-618.284669	*-160.74*	*2.5007*	*294.27*	*4.305*	*16.01*	*5.83*
	-618.290553	*-164.89*	*2.4465*	*316.69*	*4.141*	*12.79*	*6.09*
0.00	-618.243152	-135.43	2.4210	346.85	3.999	20.98	6.22
	-618.243160	*-135.43*	*2.4210*	*346.94*	*3.999*	*20.98*	*6.22*
	-618.250798	*-140.23*	*2.3706*	*381.28*	*3.817*	*15.18*	*6.48*
-0.01	-618.204742	-111.24	2.3660	386.38	3.674	29.66	6.51
	-618.204754	*-111.25*	*2.3660*	*386.48*	*3.674*	*29.65*	*6.51*
	-618.214282	*-117.03*	*2.3180*	*427.39*	*3.503*	*20.15*	*6.78*
-0.02	-618.169988	-89.19	2.3278	413.88	3.247	50.92	6.72
	-618.170004	*-89.22*	*2.3277*	*414.00*	*3.247*	*50.89*	*6.72*
	-618.180956	*-95.26*	*2.2787*	*460.97*	*3.121*	*33.05*	*7.02*

Table III - Field strengths (a.u.), total energies (a.u.), dissociation energies (kcal/mol), equilibrium distances (Å), vibrational frequencies (cm^{-1}), dipole moments (a.u.), polaritzabilities (u.a.) and rotational constants (a.u.) for KCl. Italic numbers for floating functions in two different schemes.

F	E	D_e	r_e	v_e	μ	–	B_e
0.02	-1053.649276	-181.04	3.3214	80.48	6.091	10.51	2.49
	-1053.649276	*-181.03*	*3.3214*	*80.52*	*6.091*	*10.51*	*2.49*
	-1053.649360	*-179.95*	*3.2904*	*83.76*	*5.995*	*10.37*	*2.53*
0.01	-1053.593073	-146.05	2.9592	196.46	5.336	12.88	3.13
	-1053.593074	*-146.03*	*2.9592*	*196.51*	*5.336*	*12.88*	*3.13*
	-1053.594875	*-150.29*	*2.9269*	*204.15*	*5.100*	*12.19*	*3.20*
0.00	-1053.541604	-113.85	2.8292	252.21	4.971	18.47	3.43
	-1053.541607	*-113.85*	*2.8291*	*252.27*	*4.970*	*18.47*	*3.43*
	-1053.546282	*-116.78*	*2.7944*	*263.34*	*4.636*	*16.60*	*3.51*
-0.01	-1053.493661	-83.67	2.7477	292.79	4.605	32.68	3.63
	-1053.493665	*-83.67*	*2.7477*	*292.86*	*4.605*	*32.68*	*3.63*
	-1053.502040	*-87.50*	*2.7116*	*306.87*	*4.208*	*27.01*	*3.73*
-0.02	-1053.450364	-56.47	2.6938	319.25	3.930	125.05	3.78
	-1053.450371	*-56.22*	*2.6938*	*319.33*	*3.930*	*125.00*	*3.78*
	-1053.462574	*-63.87*	*2.6550*	*337.72*	*3.620*	*80.05*	*3.89*

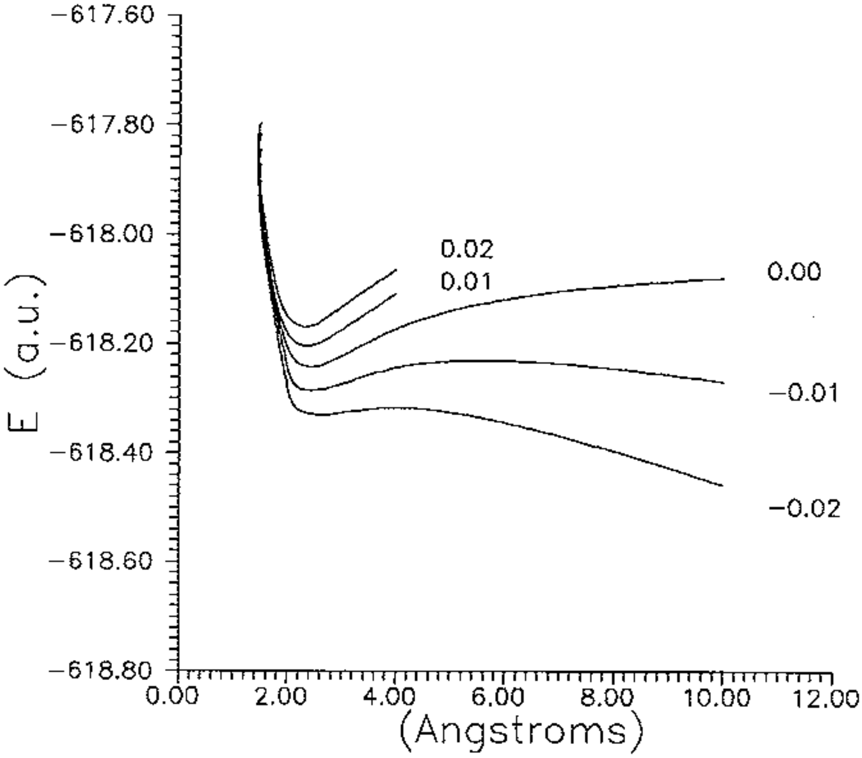

Figure I - Potential energy profiles for NaCl under different uniform electric fields. Field strength in atomic units.

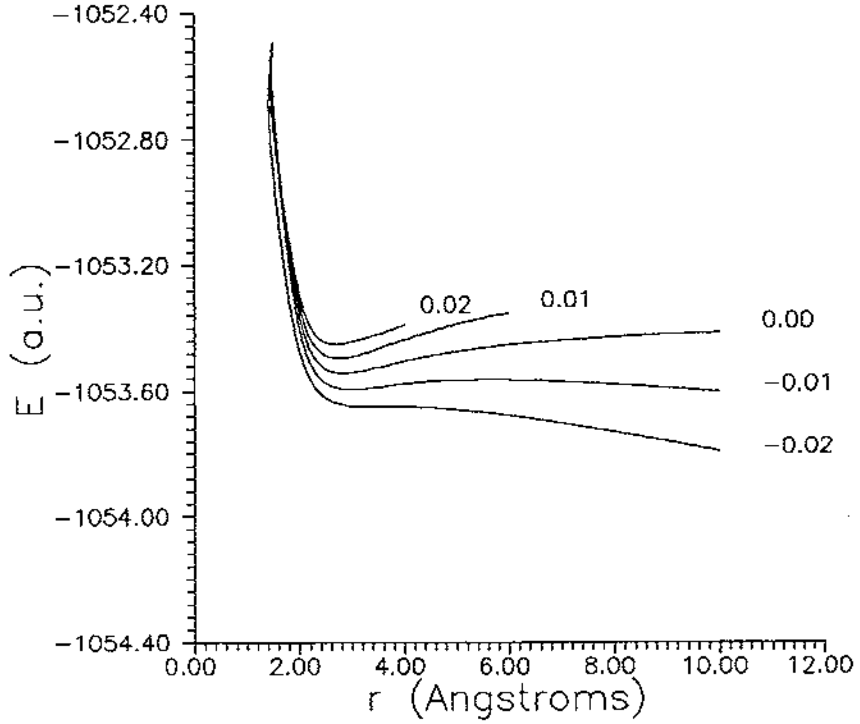

Figure II - Potential energy profiles for KCl under different uniform electric fields. Field strength in atomic units.