



## Compton profile and charge transfer of $\text{CaCl}_2$

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### ABSTRACT

*The purpose of the present work study the experimental of electron momentum density for  $\text{CaCl}_2$  which is measured for the first time by employing 100mCi  $^{241}\text{Am}$  Compton spectrometer. To compare experimental momentum densities the Compton profiles has been studied using Hartree–Fock within linear combination of atomic orbitals(LCAO) and simple ionic model. The experimental isotropic profiles are found to be relatively in better agreement with the Hartree–Fock data. To evaluate the charge transfer the ionic model for number of configuration of  $(\text{Ca}^{+x})(\text{Cl}^{-x/2})_2$  has been used to estimate the charge transfer on compound formation. This model supports transfer of 0.5 electrons from 4S state of each Ca Atom to 3P State of  $\text{Cl}_2$ .*

**Keywords:**  $\text{CaCl}_2$ , LCAO method, Charge Transfer, Compton Profile, Ionic Model

## منحني كومبتون وانتقال الشحنة لكاربونات الكالسيوم

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### الملخص

الهدف من البحث هو دراسة كثافة الزخم الالكتروني لكاربونات الكالسيوم ( $\text{CaCl}_2$ ) تجريبيا باستخدام مطياف كومبتون  $100\text{mCi}^{241}\text{Am}$  لمقارنة كثافة الزخم التجريبي تم حساب منحني كومبتون باستعمال هاتري فوك (HF) ضمن الارتباط الخطي للمدارات الذرية (LCAO) ونموذج الأبوني البسيط. وجد ان هناك توافق نسبي جيد لمنحني كومبتون مع بيانات هاتري فوك (HF). ولتقدير انتقال الشحنة في المركب المشكل  $(\text{Ca}^{+x})(\text{Cl}^{-x/2})_2$  يستخدم النموذج الايوني لعدد من التشكيلات. وان هذا النموذج يدعم انتقال 0.5 من الكترونات من مستوي 4S لكل ذرة Ca الى المستوي 3P من  $\text{Cl}_2$

الكلمات الدالة :  $\text{CaCl}_2$ ، كثافة الزخم، انتقال الشحنة، منحني كومبتون، النموذج الايوني.

### 1.INTRODUCTION

Calcium chloride ( $\text{CaCl}_2$ ) a II-VII compound with orthorhombic wurtzite structure space group pnnm, No 58, having a large direct band gap (6.9 eV), many workers have reported theoretical and experimental work on the structural, electronic, elastic, vibrational and pressure-induced properties. For example , Jean-Miche et al.[1] has studied the phase transition sequence induced by high-pressure. *ab initio* prediction of the potential energy surface and vibration-rotating energy levels of calcium chloride has been reported by Jacek Koput[2], phase transition and optical properties of calcium chloride under high pressure have been calculated using *ab initio* pseudo potential plane-wave by Lin et al. [3], results show that the transition happens at about 2.9 GPa, which is agreement with experimental data and calculated structure parameters, charge transfers ,bond structure, density of state and optical properties .Valgoma et al.[4] studied the ferroelastic phase transition is  $\text{CaCl}_2$ . Monico et al. [5] has studied the geometry parameters, frequencies, heats of formation and

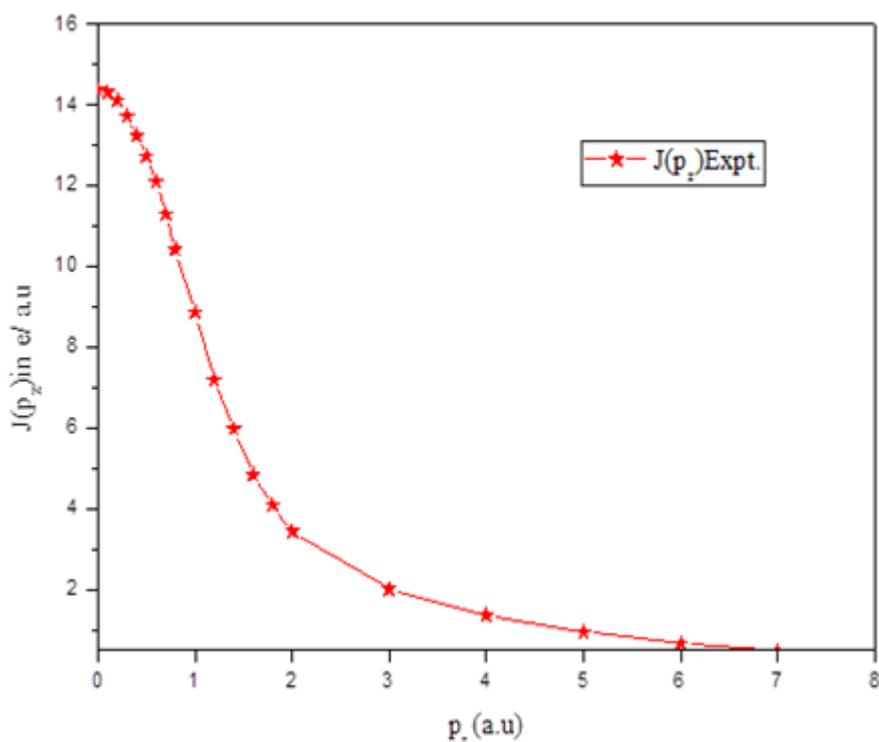
bond dissociation energy in  $\text{CaCl}_2$ . Beaden et al. [6] calculate the binding energy of the 3P electrons for  $\text{Ca}^{++}$  in the free atom and find its value is 25.5 eV. Also Sugiura et al. [7] has studied K-shell, x-ray spectra and electronic band structure of alkaline-earth chloride and calculated the band gap of calcium chloride. The common applications of calcium chloride include brine for refrigeration plants, ice dust control on roads and desiccation etc. because of its hygroscopic nature [8]. Due to its hygroscopic nature anhydrous calcium chloride must be kept in tightly sealed, air-tight containers.

The purpose of the present paper is many folds

- (a) To measure accurate Compton profile of  $\text{CaCl}_2$  at an intermediate resolution (0.55 a.u.).
- (b) To compute the Compton profile of  $\text{CaCl}_2$  using linear combination of atomic orbitals (LCAO) with Hartree–Fock theory (HF) and to compare with the experimentally measured momentum density.
- (c) To compute charge transfer using Ionic model

## 2. EXPERIMENTAL

For the measurement of Compton profile of  $\text{CaCl}_2$ , we have used 100mCi  $^{241}\text{Am}$  source. The details of the Compton spectrometer are described elsewhere [9], at an intermediate momentum resolution of 0.55 a.u. (Gaussian full-width at half-maximum). The high purity (99.99%) polycrystalline  $\text{CaCl}_2$  sample was in form of pellet (diameter 2.03cm and thickness 0.303cm). The incident beam of 661.65 keV was scattered through a mean angle of  $165 \pm 1.5^\circ$  from the high purity  $\text{CaCl}_2$  sample. The energy spectra of scattered radiations were measured with a HPGe solid state detector (Canberra, Model GL0510P) and associated electronics. The raw data have been measured 78 h, and the raw Compton data were corrected for several systematic corrections like background, instrumental resolution (limited to stripping off the low energy tail), sample absorption, detector efficiency, Compton scattering cross-section and multiple scattering, etc.[10-11]. Finally, the experimental profiles were normalized to have an area of 24.679 electrons which is equal to that of the free atom profile area in the momentum range 0 to +7 a.u.[12]. The shape of experimental profile after application of different corrections is shown in **Figure (1)** .



**Figure (1):** Experimental Compton profile of CaCl<sub>2</sub>. The profile is convoluted with the Gaussian of 0.6 a.u. FWHM.

### 3. THORITICAL CALCUATION

#### A. HF-LCAO Calculation

The Compton scattering is an inelastic scattering in which an energetic photon collides with an electron and transfers a part of its energy to the electron. This technique has been employed to probe the ground-state electron momentum densities of a variety of materials. Within impulse approximation (IA), the Compton profile is related to the Doppler broadening of scattered radiations by the motion of electrons in the target [13]. From such experiments, one measures the double differential cross section that is related to Compton profile  $J(pz)$  as shown in Eq.(1)[14].

$$\frac{d^2\sigma}{d\Omega d\omega^2} \propto J(\mathbf{p}_z) = \iint n(\mathbf{p}) dp_x dp_y \quad (1)$$

where  $n(\mathbf{p})$  is the ground-state electron momentum density. The momentum density, within an independent-particle model, is given by Eq.(2)

$$n(\mathbf{p}) = \frac{1}{(2\pi)^3} \sum |\psi(\mathbf{r}) \exp(i\mathbf{p} \cdot \mathbf{r}) \, d\mathbf{r}|^2 \quad (2)$$

where  $\psi(\mathbf{r})$  represents the electron wave function and the summation extends over all the occupied states. The units used for momentum densities are atomic units (a.u.). In this system  $e = m = \hbar = 1$  and  $c = 137.036$ . The SI equivalent of 1 a.u. of momentum is  $1.99 \times 10^{-24} \text{ kg ms}^{-1}$  [14].

To compute the theoretical Compton profile, the HF- LCAO method embodies in CRYSTAL code [15] of Torino group has been used. In this method each crystalline orbital  $\psi_i(\mathbf{r}, \mathbf{k})$  is a linear combination of Bloch functions  $\phi_\mu(\mathbf{r}, \mathbf{k})$  defined in terms of local function  $\phi_\mu(\mathbf{r})$  normally referred as atomic. The local functions are expressed as linear combination of certain number of individually normalized Gaussian type function. For Ca and  $\text{Cl}_2$  the local functions were constructed from the Gaussian type basis sets [16]. The HF operator Hamiltonian is defined as, [15].

$$\hat{H}_{\text{HF}} = \hat{T} + \hat{V} + \hat{C} + \hat{X}_{\text{HF}} \quad (3)$$

$\hat{T}$ ,  $\hat{V}$ ,  $\hat{C}$  and  $\hat{X}_{\text{HF}}$  are the kinetic, external potential, Coulomb and exchange operators, respectively.

## B. Ionic Model

The theoretical Compton profile of  $\text{CaCl}_2$  for different ionic configurations was calculated from the free atom profile of Ca and  $\text{Cl}_2$  as taken from Bigge et al. [16]. The valence profile for various  $(\text{Ca}^{+x})(\text{Cl}^{-x/2})_2$  ( $0.0 \leq x \leq 0.2$  in step of 0.5) configurations were calculated by transferring  $x$  electrons from the 4S shell of Ca to the 3P shell of Cl. All the profiles were then appropriately normalized area under curve which is represent within system number of electrons in comparison to compare other calculations and the measurement.

## 4.RESULTS AND DISCUSSION

In table 1, Compton profile from the HF-LCAO method and the ionic computed. The ionic profiles derived from the free-atom model, considering ionic arrangements  $(\text{Ca}^{+x})(\text{Cl}^{-x/2})_2$  ( $0.0 \leq x \leq 0.2$  in step of 0.5), along with experimental result, the experimental errors at selected points are also given in the table 1. For a quantitative comparison of all ionic profiles, difference profiles  $\Delta J = J^{\text{Teorey}}(p_z) - J^{\text{Exp.}}(p_z)$  have been deduced after convoluting all theoretical profile with a Gaussian function of 0.55 a.u. FWHM. All values are normalized to 26.679 electrons within 0 to +7a.u. The difference curves thus obtained from various ionic

arrangements are polluted in the **Figure (2)**. From the same figure , it can be seen that the effect of varying charge on Ca and Cl<sub>2</sub> is visible only up to 2.0 a.u. Beyond 2.0 a.u. all ionic configurations show identical behavior and overlapping with each other because the contribution in this momentum region is dominated by the inner electrons, which are unaffected in the charge transfer. To check the overall agreement of all ionic configurations with the experiment in the whole range i.e., 0 to +7 a.u., the  $\chi^2$  as given in Eq.(4)

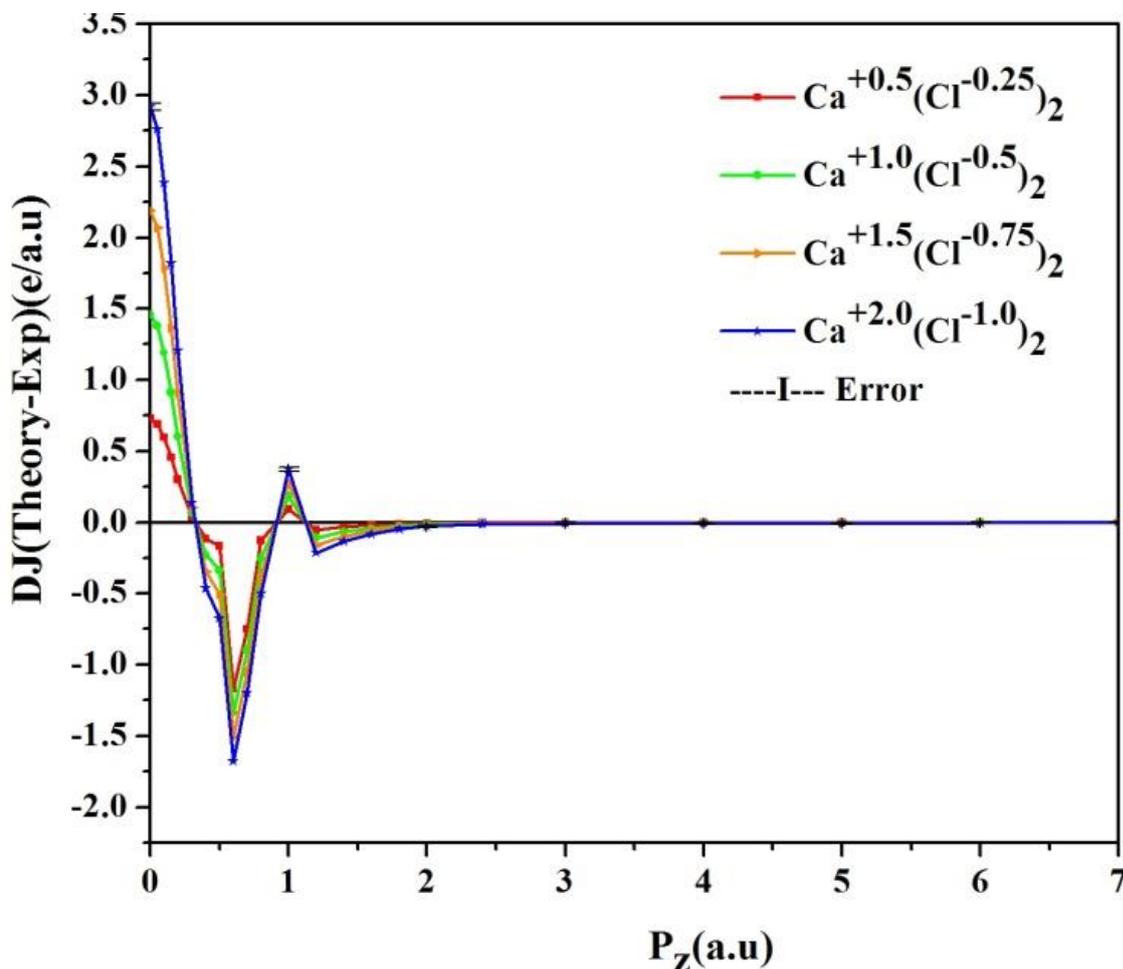
$$\chi^2 = \sum_{p_z}^{7.0} \left| \frac{\Delta J(p_z)}{\sigma(p_z)} \right|^2 \quad (4)$$

where  $\sigma(p_z)$  is the corresponding experimental error. On the basis of  $\chi^2$  test and **Figure (2)** also, it is obvious that configuration corresponding to Ca<sup>+0.5</sup>(Cl<sup>-0.25</sup>)<sub>2</sub> gives the best agreement with the experiment. Hence the ionic model suggests the transfer of 0.5 electrons from the valence 4s state of Ca atom the 3p state of Cl atoms. next, in **Figure (3)** , we present the difference profiles deduced from convoluted HF-LCAO and best agreed ionic arrangement Ca<sup>+0.5</sup>(Cl<sup>-0.25</sup>)<sub>2</sub> with the present experimental profile of CaCl<sub>2</sub>, the HF-LCAO covers the effects of periodicity following the first-principles for periodic system, the figure reveals that differences shown by the HF-LCAO method are smaller in comparison to the ionic profile indicating large improvement in computing the electron momentum density by the HF-LCAO method. The maximum difference shown by the HF-LCAO with experiment is about 7.8% of J(0). For  $p_z > 2.0$  a.u., the differences in both the schemes are beyond experimental errors.

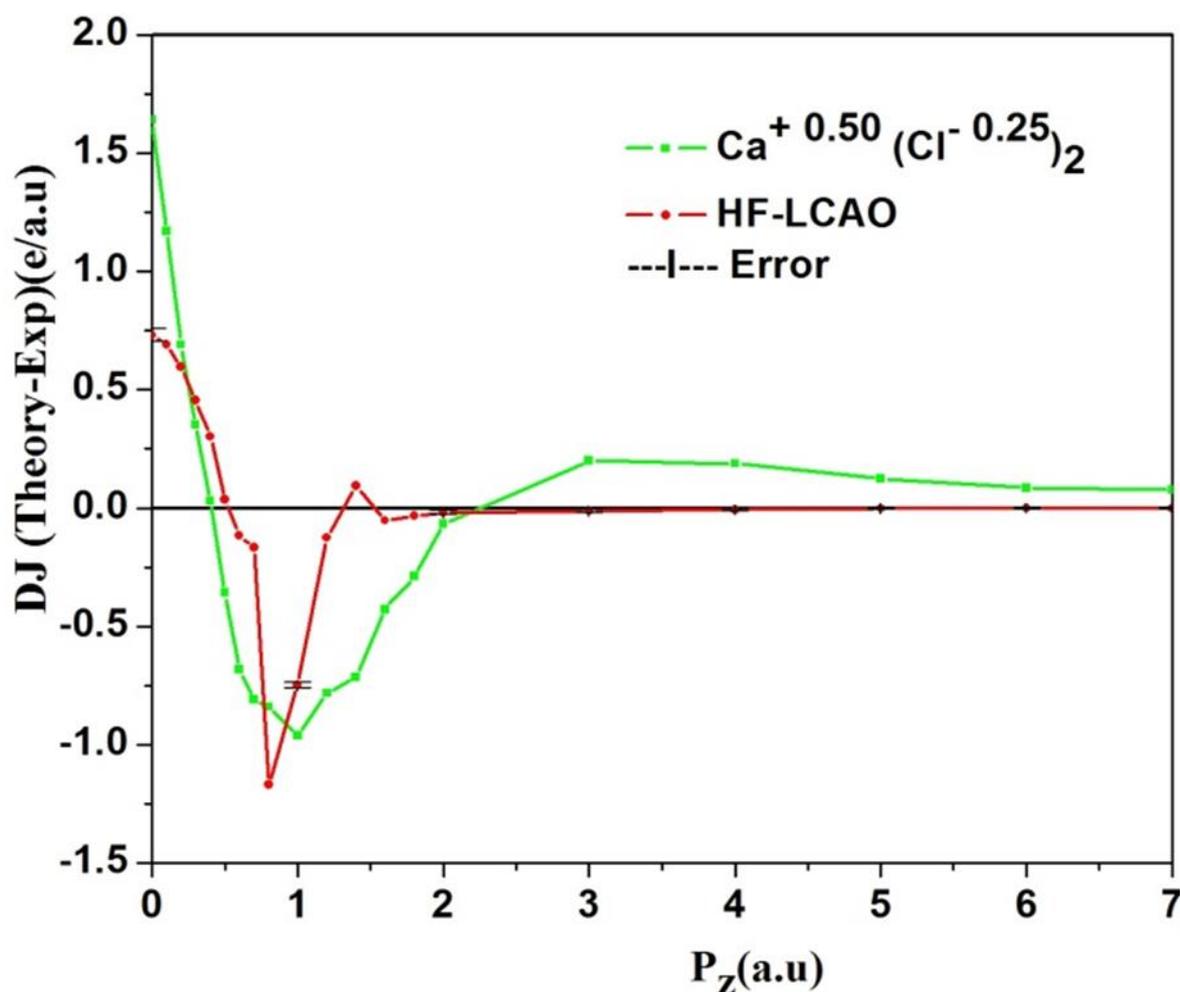
**Table (1):** Unconvoluted theoretical and the experimental Compton profile of CaCl<sub>2</sub>.

All profile are normalized to 26.679 electrons between 0 to +7 a.u. Statistical errors( $\pm\sigma$ ) are given at some points . All profiles are expressed in e/a.u.

P <sub>z</sub> (a.u)	Jp <sub>z</sub> (e/a.u)					
	HF-LCAO	Ionic Model				Experiment
		Ca <sup>+0.5</sup> (Cl <sup>-0.25</sup> ) <sub>2</sub>	Ca <sup>+1.0</sup> (Cl <sup>-0.5</sup> ) <sub>2</sub>	Ca <sup>+1.5</sup> (Cl <sup>-0.75</sup> ) <sub>2</sub>	Ca <sup>+2.0</sup> (Cl <sup>-1.0</sup> ) <sub>2</sub>	
0	16.005	17.300	16.570	15.840	15.110	18.030±0.0251
0.1	15.484	16.824	16.229	15.633	15.038	17.420
0.2	14.805	15.698	15.397	15.095	14.794	16.000
0.3	14.075	14.466	14.432	14.398	14.364	14.500
0.4	13.260	13.366	13.482	13.598	13.714	13.250
0.5	12.361	12.398	12.567	12.736	12.905	12.230
0.6	11.418	11.409	11.578	11.748	11.917	10.240
0.7	10.486	10.429	10.579	10.729	10.878	9.680
0.8	9.584	9.455	9.581	9.707	9.833	9.330
1	7.895	7.477	7.384	7.291	7.198	7.570±0.0132
1.2	6.419	6.213	6.267	6.321	6.375	6.160
1.4	5.257	5.113	5.147	5.180	5.214	5.080
1.6	4.413	4.320	4.341	4.361	4.381	4.300
1.8	3.812	3.752	3.764	3.776	3.788	3.740
2	3.369	3.327	3.334	3.341	3.348	3.320±0.0089
3	2.205	2.210	2.212	2.213	2.215	2.209±0.0076
4	1.544	1.544	1.546	1.547	1.549	1.543±0.0064
5	1.071	1.069	1.071	1.071	1.073	1.068±0.0053
6	0.747	0.745	0.745	0.746	0.747	0.744±0.0043
7	0.549	0.532	0.533	0.534	0.534	0.532±0.0036



**Figure (2):** The difference ( $\Delta J$ ) between convoluted ionic model and experimental Compton profiles of  $\text{CaCl}_2$ . Experimental error ( $\pm\sigma$ ) are also shown at points. All ionic profile are convoluted with Gaussian of 0.55 a.u.



**Figure (3):** Difference ( $\Delta J$ ) between convoluted theoretical Compton profile (HF-LCAO and best ionic) and experimental error ( $\pm\sigma$ ) are also shown at some points. Both profiles are convoluted with Gaussian of 0.55 a.u. FWHM.

## 5. CONCLUSIONS

In this paper, Compton profile measurement of polycrystalline  $\text{CaCl}_2$  is reported. The experimental data on polycrystalline sample has been compared with the HF-LCAO and simple ionic model calculations are in a good agreement with the measurement. The HF-LCAO based momentum density shows better agreement with the measurement, the ionic model suggests a transfer of 0.5 electrons from 4S state of each Ca atom to 3P state of  $\text{Cl}_2$ . Measurement on single crystalline samples with better resolution and high statistics will be very helpful to examine these finding rigorously.

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