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**Theoretical Study of Adsorption of Carbonyl
Compounds on Ionic Crystals: I. Formaldehyde, Glyoxal,
o- and *p*-Benzoquinone on the (100)
Face of Sodium Chloride**

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We have studied the adsorption of molecules such as formaldehyde, glyoxal, *o*- and *p*-benzoquinone on the (100) face of sodium chloride. The electronic adsorption energy is evaluated by means of an »ab-initio« SCF method and the dispersion energy by means of a semi-empirical Lennard-Jones pair potential. The total adsorption energies are equal to 2.3 kcal/mole for the formaldehyde along the {0,1,0} direction above Cl⁻, and to 4.6, 7.3 and 7.6 kcal/mole respectively for the glyoxal and the *p*- and *o*-benzoquinone along the {0,1,1} direction above an anion alignment. We also show the effect of the superficial defects as steps and kinks, in the adsorption phenomena. Various applications are envisaged.

INTRODUCTION

The phenomena of adsorption and deposit formation on crystals are, at the present time, certainly among the most studied problems, both experimentally and theoretically, owing to their many practical applications. Nevertheless, research is concerned chiefly with the fixation of atoms or small molecules on transition metals (owing to the application to catalysis), and the formation of metallic deposits on semiconductors (having in view the construction of photoelectric cells). The adsorption on ionic crystals is studied far less. Papers dealing with the adsorption of rare gas or small molecules on such crystals seem rather to belong to the outline of fundamental researches. Adsorption on ionic crystals certainly provides interesting applications.

It has been known for a long time (Romé de Lisle, in the 18th century) that the presence of organic substances (dyes in particular) can, under certain conditions, modify the facies of ionic crystals. Since then, many other examples have been found. Independently of the purely speculative interest in this phenomenon, it is possible to envisage practical applications, such as the modification of the facies of undesirable crystals which can take form in certain organs (kidney, articulations)

or the inhibition of their growth, the separation of isomers, the stereospecific orientation of some reactions, or the preparation of anisotropic films.

In a previous paper¹, one of us (A.J.) *et al* have studied the adsorption of linear paraffines on alkali halides. In this series of articles, we propose to study the fixation of molecules bearing one or many carbonyl groups by using the same method. At first we will consider plane molecules (formaldehyde, glyoxal, *o*- and *p*-benzoquinones) in order to show how interesting the phenomenon is and to point out general results concerning the conditions of adsorption.

PRINCIPLE OF THE METHOD

The direct treatment of the molecule + crystal system is, of course, impossible to perform. Approximations are necessary. Practically, we will utilize an adapted version of the *ab initio* self-consistent program, known as GAUSSIAN 70-STO6G,² which allows us to treat all the electrons of the molecule within the electrostatic field created by a finite number of point charges.

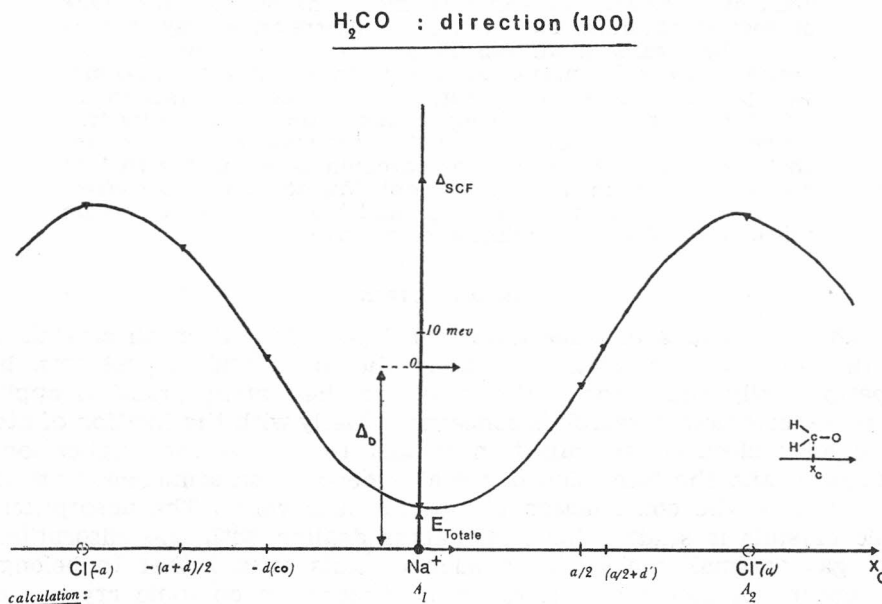


Figure 1. Variation of the Δ_{SCF} adsorption energy of H_2CO versus the position along the $\{0,1,0\}$ direction (A)

A previous study³ concerning the convergence of the electrostatic potential versus the number of the point charges, has shown that, practically, a few hundred charges located at the nodes of the lattice are sufficient to simulate the infinite crystal. Such a program allows us to

calculate the fixation energy of the molecules on a lattice of point charges. We will call this energy: Δ_{SCF} . In order to get the actual value of the adsorption energy on the crystal, Δ , it is necessary to add to Δ_{SCF} , the dispersion energy, Δ_D , arising from the fact that the lattice is built up on polarizable ions. For the dispersion energy, we will utilize a semi-empirical Lennard-Jones pair potential:

$$\Delta_D = \sum_{(MN)} \left(-\frac{A}{R^6} + \frac{B}{R^{12}} \right)_{MN} \quad (1)$$

where M is an atom of the adsorbed molecule, and N an ion of the lattice. Let us assume that R_o^{MN} is the minimal approach distance between M and N (assumed to be free). The contribution of the (MN) pair is reduced to:

$$\Delta_D^{MN} = -\frac{A^{MN}}{R^6} \left[1 - \frac{1}{2} \left(\frac{R_o^{MN}}{R} \right)^6 \right] \quad (2)$$

The A^{MN} coefficient will be taken equal to the asymptotical value given by London:⁴

$$A^{MN} = \frac{3}{2} \frac{I_M I_N}{I_M + I_N} \alpha_M \alpha_N \quad (3)$$

where I and α are respectively the ionization energies and the polarizabilities of the corresponding atoms.

Table I summarizes the terms necessary in calculating the various Δ_{MN} .

TABLE I

Ionization Energies,⁵ I ; Polarizabilities,⁶⁻⁷ α ; Ionic or Atomic Radii.⁶⁻⁸

	H	C	O	Na ⁺	Cl ⁻
$I(\text{eV})$	13.6	11.3	13.6	47	3.6
$\alpha(\text{\AA}^3)$	0.67	2.1	0.9	0.2	3.0
Radius (Å)	1.2	1.3	1.4	1.0	1.8

Moreover, the lattice of NaCl can be considered as built up on tangent spheres whose radii are respectively $R(\text{Cl}^-)$ and $R(\text{Na}^+)$ ($a_{\text{NaCl}} = 2.814 \text{ \AA}$). On a (1,0,0) face, it is assumed that the molecules are laid on the plane tangent to the spheres whose radius is the bigger, i.e. corresponding to Cl^- ions.

We will suppose that the adsorbed molecules keep the same geometry as in the isolated state. In support of this assumption, we can quote a very recent work,⁹ which shows that in order to obtain appreciable modifications in the geometry ($\sim 0.01 \text{ \AA}$) it is necessary to apply considerable electric fields ($\sim 10^{10} \text{ V/m}$).

APPLICATION TO FORMALDEHYDE

We have utilized the following geometry:¹⁰

$$d(\text{CH}) = 1.071 \text{ \AA}, \quad d(\text{CO}) = 1.225 \text{ \AA}, \quad \text{and } \widehat{\text{HCH}} = 123.5^\circ$$

On the basis of symmetry, we have considered only the three following orientations of the molecules which correspond to the extrema of Δ :

- A : {0,1,0} orientation
- B : {0,1,1} orientation above a cation alignment
- C : {0,1,1} orientation above an anion alignment.

The obtained values show a practically sinusoidal variation of Δ_{SCF} along each direction (Figures 1—2). In Table II, we have listed the values corresponding to the extremal values.

TABLE II

Extrema of SCF-Adsorption Energies of H₂CO for Various Orientations. Positive Values Correspond to Adsorption. (See Figure 1 and Figure 2).

Position	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂
Δ_{SCF} (meV)	— 40	46	— 35	29	41	— 25

In order to evaluate the Δ_{D} contribution, we first calculated the energies corresponding to C, O and H isolated atoms for various positions above the crystal face. In a previous work,¹ one of us (A.J.) has found that the dispersion energy corresponding to a given atom, located at a given height above the lattice, is practically independent of the site under consideration. As Table III shows, the same phenomenon arises here, so that the total dispersion energy is practically the same for all the positions : 52.6 ± 1.0 meV, i.e. 1.2 kcal/mole.

TABLE III

Dispersion Energy (in meV) for C, O and H in Different Positions Above the NaCl Lattice

Position	above Na ⁺	above Cl ⁻	above the center of Na ₂ Cl ₂ square	at equal distance between Na ⁺ and Cl ⁻	Average value
Atome : C	23.6	22.7	23.6	24.0	23.4 ± 0.6
O	10.9	10.4	10.7	11.1	10.8 ± 0.3
H	9.2	9.1	9.2	9.3	9.2 ± 0.1

The maximal adsorption energy $\Delta_{\text{SCF}} + \Delta_{\text{D}}$ is equal to 2.3 kcal/mole. This value is practically obtained when the carbon is above Cl⁻ (A₂).

We have stated above why the geometry of the molecule is not affected. Nevertheless, we can ask whether the vibration frequencies are modified in an appreciable manner. If so, the modification in frequency could be used to detect the adsorption and to determine the coverage of the surface. Unfortunately, it is well known that the correct calculation of the vibration frequencies requires a very elaborate calculation with a very extended configuration interaction,¹¹ that is impossible to perform in the present case. Nevertheless, in order to obtain an order of magnitude of the phenomenon, we have determined by means of our program the vibration frequency of C atom outside the plane of the molecule. For the free molecule, we have obtained 814 cm^{-1} and for the adsorbed molecules, 844 cm^{-1} . The experimental value for the isolated molecule¹² is 1170 cm^{-1} .

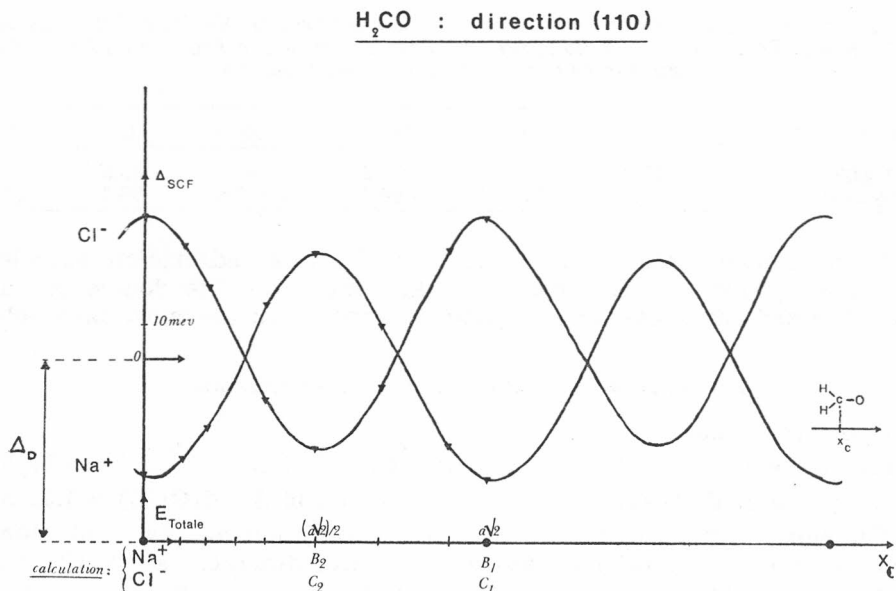


Figure 2. Variation of the Δ_{SCF} adsorption energy of H_2CO versus the position along the $\{0,1,1\}$ directions: B, above Na^+ ; C, above Cl^-

Though the difference is great, the increase in frequency (30 cm^{-1}) may be considered as being significant enough to be detected experimentally. Let us remember that a similar phenomenon is observed on metals.¹³

ADSORPTION OF CIS- AND TRANS-GLYOXAL

The molecule of glyoxal ($HCO-COH$) can present, as butadiene, two forms: *s-cis*, and *s-trans*. The *trans*-form is largely preponderant. For both of these molecules, we have utilized the following geometrical data:¹⁰

$$d(CC) = 1.48 \text{ \AA}; \quad d(CO) = 1.22 \text{ \AA}; \quad d(CH) = 1.08 \text{ \AA} \quad \widehat{OCH} = 122^\circ$$

The total energies of the two forms are obtained respectively equal to: -225.7445 u.a. for the *trans*-form, and to -225.7420 for the *cis*-form, i.e. with a difference of 1.6 kcal/mole, the *trans*-form being the more stable. Results concerning the adsorption are listed in Table IV. The C—C bond is oriented along the direction A, B or C. For each direction, we have selected the following positions corresponding to the extrema of the energy: A_1 and B_1 : the middle point of C—C located above a cation; A_2 and C_1 : above an anion; B_2 and C_2 : at equal distance between two ions (respectively Na^+ and Cl^-).

According to Table III, the dispersion energy is practically the same for both of the forms, and is independent of the position: 86.8 ± 2.0 meV,

TABLE IV

Adsorption Energy Δ_{SCF} (meV) of *trans*- and *cis*-glyoxal in Various Positions on NaCl Lattice. The B_2 and C_2 Values for the *trans*-form are Practically the Same Than for the *cis*-form (see Discussion)

Position	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂
<i>trans</i> -glyoxal	— 57.2	64.3	— 71.2	—	80.9	—
<i>cis</i> -glyoxal	— 55.6	62.7	— 68.4	— 18.4	79.7	27.0

i.e. 2.0 kcal/mole. Consequently, the maximal total adsorption energies are the same for the two forms: 4.6 kcal/mole, i.e. the double of the value obtained for H₂CO. The C₁ position appears as the most favorable.

ADSORPTION OF ORTHO- AND PARA-BENZOQUINONE

Geometrical data:¹⁰

p-benzoquinone: $d(\text{C—O}) = 1.23 \text{ \AA}$; $d(\text{C—C}) = 1.47 \text{ \AA}$; $d(\text{C=C}) = 1.34 \text{ \AA}$
o-benzoquinone: $d(\text{C—O}) = 1.22 \text{ \AA}$; $d(\text{C—C}) = 1.48 \text{ \AA}$; $d(\text{C=C}) = 1.34 \text{ \AA}$

For the *p*-benzoquinone the maximal adsorption energy is obtained when the molecule is oriented along the {0,1,1} direction, above Cl⁻, the center of the molecule being located at equal distance between two Cl⁻. The corresponding energy is equal to 7.3 kcal/mole.

The *o*-benzoquinone can be regarded as a substituted *cis*-glyoxal, so that we can think that the most favorable position is the one which gives the maximal energy for the *cis*-glyoxal. We have studied three positions of the molecule oriented along the {0,1,1} direction above Cl⁻, and the results are in accordance with our previous results. The obtained value is equal to 7.6 kcal/mole.

DISCUSSION

The examples studied in the present paper show clearly that the adsorption is essentially conditioned by electrostatic effects. For instance, we show (Figures 1 and 2) that the positions which correspond for H₂CO to opposite fields give Δ_{SCF} roughly opposite values. Nevertheless, the differences observed for the absolute values show that the molecular polarization is not negligible (the polarization energy is proportional to the square of the electric field), so that it is impossible to reach the correct Δ_{SCF} energy from a purely electrostatic calculation, in which we could replace the molecule by point charges. We have directly verified this conclusion; the obtained energies are very far from the exact values.

Moreover, the quasi-equality between the Δ_{SCF} values for the two glyoxals located at given sites (Table III) shows an additivity for the contributions of the polar groups (the positions of the CO groups are the same with regard to the ions of the lattice). Therefore, we have not computed the values corresponding to B₂ and C₂ positions for the *trans*-glyoxal (Table IV). The equality of the adsorption energies for both of the forms forbids any separation of the isomers by selective adsorption on NaCl and probably also on any lattice of this kind (if the C₁ position remains preferential, as we can assume).

In compensation, owing to the fact that glyoxal exists practically only in the *trans*-form, its adsorption can have interesting applications in stereochemistry. For example, addition of HCN, followed by hydrolysis must give only the *d*- and *l*-tartaric acids: $\text{HCO}_2\text{---}^*\text{CHOH---}^*\text{CHOH---CO}_2\text{H}$, whereas the reaction in homogeneous phase produces also the inactive mesotartaric acid.

The difference of adsorption energy between both of the isomers of quinone is weak, only 0.3 kcal/mole. This value seems to allow us to separate these isomers by chromatography, over a long enough column of NaCl, as far as Gibbs energy changes are negligible.

REMARK ABOUT THE EFFECT OF SURFACE IRREGULARITIES

It is well known that crystal faces are far from being ideal. The faces are constituted by plane domains which form steps. In the vicinity of the defects, the electric field is modified so that we must expect that the adsorption energies are different from those corresponding to the (1,0,0) ideal face. In order to perceive on the phenomenon, we have studied the two following cases: the molecule located close to a double step (1,0,0)₂ or to a kink (1,1,1). Table V gives the corresponding total energies.

TABLE V

Total Adsorption Energy (kcal/Mole) Close to Crystal Defects

	(100) ₂ step	(111)
Formaldehyde	2.7	8.7
<i>trans</i> -glyoxal	3.6	6.7

The results show a large increase of the adsorption energies in the vicinity of the defects. This fact incites us to think that such preferential adsorptions can block up the normal growth of the equilibrium crystal face, and so can provoke modifications of the facies. Nevertheless, owing to the complexity of the crystal growth phenomena, a more elaborate study is necessary. A work about the effect of glycine and formamide on the growth facies is in progress.

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SAŽETAK

**Teorijska studija adsorpcije karbonilnih spojeva na ionskim kristalima:
I. Formaldehid, gliksal, o- i p-benzokinon na (100) plohi natrij-klorida**

A. Julg i B. Deprick

Adsorpcija molekula, kao što su formaldehid, gliksal, o- i p-benzokinon, promatrana je na (100) plohi natrij-klorida. Elektronska adsorpcijska energija procijenjena je uz pomoć »ab-initio« SCF postupka, a disperzijska energija s pomoću semiempirijskog Lennard-Jonesova potencijala parova. Ukupna adsorpcijska energija za formaldehid uzduž { 0,1,0 } smjera iznad Cl⁻-iona iznosi 2,3 kcal/mol, a za gliksal, p- i o-benzokinon uzduž { 0,1,1 } smjera iznad anionskog niza, 4,6 7,3 i 7,6 kcal/mol. Pokazan je također utjecaj površinskih defekata, kao što su stepenice i petlje, na adsorpcijske pojave. Predviđene su razne primjene.