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相对论密度泛函法对 CN^- 在铜和银 电极上振动频率的研究

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摘要 对 CN^- 在铜和银电极上的吸附性质进行了相对论密度泛函簇模型计算. 结果表明, 电场微扰方法可以描述 CN^- 在铜和银电极上吸附的表面现象. 电极势诱导的频率移动被理解为 Stark 效应所引起; 内振动模式 M-CN 和 C-N 的耦合对电位诱导的 C-N 振动频率变化的大小起重要作用. 计算所得的由 Stark 效应所引起 C-N 振动频率变化的斜率与实验结果相符.

关键词 电位诱导, 振动频率, 铜电极, 银电极, 相对论密度泛函计算

A Relativistic Density-Functional Investigation of Vibrational Frequencies of CN^- on Cu and Ag Electrodes ^①

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The vibrational frequencies of adsorbed species (ligand) on electrodes (metal) are shifted when an electric field is applied. Two mechanisms have been proposed to explain this behaviour^[1]. One explanation involves molecular orbital arguments (chemical mechanism). According to this mechanism, the charge-transfer and bonding between a metal and ligand is normally divided into σ -donation from the ligand to the metal and π -backdonation from the metal to the ligand. The vibrational frequency of an adsorbed species may either increase or decrease with respect to an unadsorbed (solution) species, depending on the relative contributions of σ - and π -bonding interaction. The other mechanism is based on the electric field effect (Stark effect—physical mechanism) which involves the coupling of highly polarizable electrons of the ligand with a strong electric field across the electrochemical double layer.

Quantum chemistry method has been used in order to understand molecular processes on electrode surfaces. The adsorptive properties of cyanide on a copper electrode (CN^-/Cu) have been extensively studied^[2] using *ab initio* Hartree-Fock (HF) method. The potential dependence of the vibrational frequencies was ascribed to a Stark effect. A theoretical study of the vibrational properties of the CN^-/Ag system was firstly carried out by Anderson et al.^[4]. Using a semiempirical ASED (atom superposition and electron delocalization) molecular orbital method, and the chemical bonding mechanism was found to be responsible for the frequency shifts. Lin et al.^[5] also reported a SCC-DV- X_α (self-consistent-charge discrete variational X_α) calculation. Because of rather high inaccuracy in 'total' energy evaluation, the old DV- X_α method is limited to analyzing problems based on orbital energies, population analysis, atomic charge distributions etc., and it therefore provided no quantitative results for some properties concerned. So far no more accurate calculations are available for the CN^-/Ag system. The previous conclusions^[4, 5] will still be questioned until they are checked against our accurate calculations.

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In present work, the adsorption systems CN^-/Cu and CN^-/Ag are studied with Amsterdam density-functional (ADF) method including relativistic effects^[10]. A $M(100)$ (the notation M represents the metals) plane was selected as the adsorption surface and was modeled by a $M_{10}(1, 4, 5)$ cluster which contains one M atom in the first layer, four in the second and five in the third. This cluster model is somewhat different from the model used in ref. ^[2], where the 5, 4 and 1 M atoms are in the first three layers. The adsorbed CN^- is placed at an on-top site directly above a M surface atom with its molecular axis perpendicular to the surface and carbon pointing towards the metal. The M - M distance is the bulk crystal distance.

Additionally, the electrode potential has to be also modeled in order to investigate the influence of the effects of electrode potential on the adsorption system. Several models^[3] have been used in quantum chemistry cluster calculations. As a crude approach, the electrode potential is described by charging the metal cluster. Different charging for the system represents a change in the electric field. In spite of its simplicity, such an approach has some shortcomings^[3]. Another approach to model the electrode potential is to consider the system in the presence of an external field F . Suppose F be the strength of the external field and normal to the surface. The total Hamiltonian $H(\vec{F})$ is now written as

$$H(\vec{F}) = H(\vec{F}=0) + \left(\sum_i \vec{r}_i - \sum_i Z_i \vec{R}_i \right) \cdot \vec{F} \quad (1)$$

where $H(\vec{F}=0)$ is the Hamiltonian for $\vec{F}=0$; \vec{r}_i and \vec{R}_i are the electron and nuclear coordinates, respectively; Z_i is the nuclear charge. The total energy E_{total} is then divided into two terms:

$$E_{\text{total}}(\rho) = E_{\text{DF}}(\rho) + \vec{\mu}(\rho) \cdot \vec{F} \quad (2)$$

The last term of Eq. 2 represents the interaction energy of the external field \vec{F} with the dipole moment μ of the system. The so-called Stark effect is given by the first-order perturbation energy $\vec{\mu}(\vec{F}=0, \rho^0) \cdot \vec{F}$, where ρ^0 is the electron density of the system calculated with $\vec{F}=0$. So the term $\vec{\mu} \cdot \vec{F}$ does not include any chemical changes caused by the field.

The second approach has been chosen for our modeling of the electrode potential. Within this scheme, the electrode surface remains essentially uncharged, and it may also lead to some errors involved in choosing the model. However, this approach presents an advantage that there is the possibility of dealing with a wide range of electric fields. According to calculations by Bagus et al.^[2]. For the system CN^-/Cu , the changes in the vibrational frequencies with potential depend mainly on the Stark effect. We now make an assumption that the Stark effect could account for the spectral shift in the system CN^-/Ag . As a matter of fact, this assumption has been shown to be consistent with the calculated evidence. In Eq. 2, we have chosen $F = \pm 0.01 \text{ a. u.} = \pm 5.2 \times 10^7 \text{ V/cm}$, as was the magnitude used by Bagus et al.^[2]. This electric field is comparable to the fields on the electrode surface of an electrochemical cell when a potential of 1 V is applied.

We now give a discussion for the results, which are shown in Tab. 1. Our present analysis focuses only on the following properties of the systems: M-CN and C-N vibrational frequencies, force constants and bond lengths. These properties were obtained from a two-dimensional complete fourth-order polynomial fit to the energy surface determined by a large number (~ 25) of calculated energy points about equilibrium. In this case, the obtained normal vibrational frequencies are a mixture of the internal C-N and M-CN modes.

At a same potential the calculated frequencies $\omega_{\text{C-N}}$ of the ligand differ slightly for both metals, whereas the calculated potential dependent shifts in $\omega_{\text{C-N}}$ are similar. These trends are in agreement with experiment^[2]. When compared with experimental data (e. g. $2\,094 \sim 2\,114\text{ cm}^{-1}$ for CN⁻/Ag in potential range $-1.4 \sim -0.7\text{ V}$ ^[6]), the calculated $\omega_{\text{C-N}}$ values are somewhat overestimated. However, it is not so easy to give a direct comparison between the calculation and experiment. The calculated frequency shift with potential is shown to be nearly linear. The change $\Delta\omega$ in $\omega_{\text{C-N}}$ is about $40 \sim 45\text{ cm}^{-1}/\text{V}$, which is close to the value $\sim 50\text{ cm}^{-1}/\text{V}$ measured (in potential range $-1.2 \sim -0.6\text{ V}$) by Philpott et al^[2]. Different experiments may give different slopes. For instance, a measurement of Kötzt and Yeager^[6] for CN⁻/Ag gave a change $\Delta\omega_{\text{C-N}}$ of about $26\text{ cm}^{-1}/\text{V}$.

Experimental metal-ligand frequency is only known for the CN⁻/Ag system. The calculated Ag-CN frequency is substantially too large compared with experimental value of $\sim 224\text{ cm}^{-1}$ ^[6]. Similar large values were also found in the semiempirical calculations of Anderson et al^[4] and in the ab initio HF calculations (on CN⁻/Cu) of Bagus et al^[2]. This is because all these calculations neglected 'environmental' effects, which have an influence on surface charge and potential. Since CN⁻ has a very strong adsorption on these metals, the coverage effect might contribute significantly to the reduction of the M-CN frequency. Calculations based on a high coverage model for which each CN⁻ is surrounded by four CN⁻ species on a same metal site are in progress. In contrast to the calculation on the ligand C-N frequency, the calculated M-CN frequencies for both systems are quite close. Also there is a rather large variation of $\omega_{\text{M-CN}}$ with potential. The calculated average slope is about $60\text{ cm}^{-1}/\text{V}$ for Cu-CN and $65\text{ cm}^{-1}/\text{V}$ for Ag-CN. These values are intermediate between experimental value ($26\text{ cm}^{-1}/\text{V}$ by Kötzt and Yeager for CN⁻/Ag^[6]) and the value from the ab initio HF calculations (average slope $\sim 95\text{ cm}^{-1}/\text{V}$)^[2].

The variation in the C-N force constants is seen to be inconsistent with the trend of the calculated C-N frequencies. The changes Δk in the C-N force constants with potential are relatively small, indicating that the coupling of the C-N and M-CN internal modes leads to a large shift in the C-N frequency. The C-N distance is very weakly dependent on potential. This can be expected from a triple bond of the CN species. The changes in the M-CN distance with potential are relatively large. The ab initio HF calculations^[2] found a strong dependence of the Cu-CN bond length on potential. This behaviour was attributed to an ionic bond between the metal and ligand^[2].

Tab. 1 Calculated results of the $M_{10}\text{-CN}^-$ ($M = \text{Cu}, \text{Ag}$) complexes in different uniform electric fields F (bond length R in \AA , force constant k in mdyne/\AA and normal vibrational frequencies ω in cm^{-1}). The values in brackets are the nonrelativistic results

	R_{M-CN}			R_{C-N}		
	$F=+0.01$	$F=0$	$F=-0.01$	$F=+0.01$	$F=0$	$F=-0.01$
$\text{Cu}_{10}\text{-CN}^-$	1.86	1.90 (1.92)	1.95	1.169	1.173 (1.173)	1.177
$\text{Ag}_{10}\text{-CN}^-$	2.00	2.05 (2.16)	2.12	1.168	1.172 (1.172)	1.176

	k_{M-CN}			k_{C-N}		
	$F=+0.01$	$F=0$	$F=-0.01$	$F=+0.01$	$F=0$	$F=-0.01$
$\text{Cu}_{10}\text{-CN}^-$	2.38	1.77 (1.67)	1.15	17.57	17.13 (17.09)	16.68
$\text{Ag}_{10}\text{-CN}^-$	2.58	1.81 (1.38)	1.13	17.88	17.38 (17.27)	16.89

	ω_{M-CN}			ω_{C-N}		
	$F=+0.01$	$F=0$	$F=-0.01$	$F=+0.01$	$F=0$	$F=-0.01$
$\text{Cu}_{10}\text{-CN}^-$	387	335 (326)	271	2182	2144 (2138)	2104
$\text{Ag}_{10}\text{-CN}^-$	402	339 (297)	270	2206	2162 (2144)	2116

^{a)} F is in a. u.

In conclusion, our relativistic density-functional calculations show that an electric field perturbation method furnishes an acceptable description of the surface phenomena of CN^- adsorbed on the Cu and Ag electrodes. The potential dependence of the vibrational frequencies can be accounted for in terms of a Stark effect. The coupling of the internal M-CN and C-N modes plays an important role for the magnitude of the potential-induced changes in the C-N frequency, thereby confirming the conclusion drawn by Philpott et al.^[2]. The obtained Stark slopes for the normal C-N frequencies are in good agreement with experiment.

Key words Potential Dependence, Vibrational Frequency, Copper-electrode, Silver-electrode, Relativistic density-functional calculation

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