92. An Ag-Atom in the 6-6 Subunit of a Zeolite: Model Calculations

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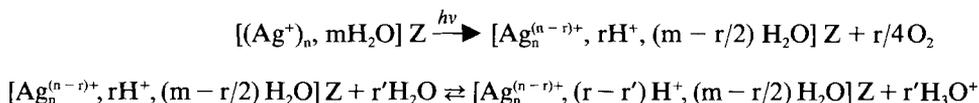
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Self-sensitisation of photo-oxygen evolution occurs in aqueous dispersions of silver zeolites. In presence of Cl^-, chlorine is the photoproduct in acidic medium, and the same type of self-sensitisation occurs. Self-sensitisation means that systems which are first insensitive to light of a certain wavelength become photo-active after they have been illuminated by light of higher energy. For a better understanding of silver zeolites, we have carried out EH-MO calculations on the 6-6 subunit (SBU) of a zeolite, on the 6-6 SBU with an Ag-atom in the center, on the 6-6 SBU with one Ag-atom in the center and one outside on top of the hexagon, and finally on another with one Ag-atom in the center and two Ag-atoms outside, each on top of a hexagon. The Ag^0 in the cage of the 6-6 SBU is significantly polarized by the 6-6 SBU environment. The energy barrier to escape the 6-6 SBU is 0.8 eV for Ag^0 and 0.5 eV for Ag^+. The HOMO of the Ag(6-6 SBU) is a totally symmetric 5s* orbital and the LUMO is a $5p_z^*$ type. $5p_z^* \leftarrow 5s^*$ electronic excitation reduces the energy barrier and allows an $(Ag^0)^*$ to exit the 6-6 SBU, provided the excited-state lifetime is long enough. The MO picture predicts low-energy charge-transfer transitions from the zeolite framework to the 5s* orbital. The highest occupied orbitals of the zeolite framework are localized on the O-atoms. Interactions between an Ag-atom in the 6-6 SBU and one or two external Ag-atoms are discussed.

1. Introduction. – Several, very interesting observations on Ag-containing zeolites have been made lately. 1971, it was observed that Ag^+ ions introduced into the lattice of synthetic *zeolite 13X* show luminescence in the visible when irradiated by UV light. The luminescence depends on the pretreatment of the sample [1]. In a study of the redox behaviour of transition metal ions in zeolites, it was found that the reduction of a silver-Y zeolite with H_2 and the reoxidation with O_2 is fully reversible [2]. Two publications on photochemical/thermal cleavage of water over silver zeolites have appeared in 1977 [3] [4]. Optical absorption spectra [5], colour centers created upon degassing [6], and ESR spectra of silver zeolites [7] became known later. These experimental results among others formed the starting point of our interest on silver zeolites. We developed sensitive techniques for the detection of H_2, O_2, and Cl_2 in photochemical experiments [8–10].

Thus, we detected self-sensitisation of photo-oxygen evolution in aqueous dispersions of silver-A zeolite [9]. By self-sensitisation, we mean that dispersions which are initially insensitive to light of a certain wavelength become photo-active, after they have been illuminated by light of higher energy. In a computer controlled experiment which allowed us to keep parameters constant, we proved that our interpretation was correct [10a]. From our present knowledge, the overall stoichiometry of this photo-oxygen generation can be described by the following scheme:

$$[(Ag^+)_n, mH_2O] Z \xrightarrow{hv} [Ag_n^{(n-r)+}, rH^+, (m-r/2) H_2O] Z + r/4 O_2$$

$$[Ag_n^{(n-r)+}, rH^+, (m-r/2) H_2O] Z + r'H_2O \rightleftarrows [Ag_n^{(n-r)+}, (r-r') H^+, (m-r/2) H_2O] Z + r'H_3O^+$$

where Z represents the negatively charged zeolite lattice. We have also observed that in the presence of Cl^-, Cl_2 is the photoproduct in acidic medium and that the same type of self-sensitisation occurs [10b]. By changing from acid to neutral or alkaline, we observe a jump from Cl_2 to O_2 evolution.

For a better understanding of these observations, it is necessary to develop an idea how the Ag^+, the Ag-atom, and finally the Ag clusters interact with the zeolite framework. Quantum-chemical studies on Ag species in a zeolite environment have been published recently. In one of these studies, $Si_2Al_4O_{12}H_6$ was used as a model to represent the zeolite unit as a ligand for Ag_3 and Ag_6 clusters [11]. In another one, calculations were made on $[Ag(OH_2)]^0$, $[Ag_2(OH_2)_6]^{0,+}$, $[Ag_3(OH_2)_6]^{0,+,2+}$, and $[(H_2O)_3Ag_3(OH_2)_3]^{0,+,2+}$. The influence of the zeolite framework was neglected [12]. Both studies describe certain aspects of Ag species in a zeolite environment. Some general theoretical treatments of zeolites should be mentioned [13]. Studying the relative shift of ligand vs. metal orbitals, we have identified the conditions where the crystal field as well as the angular overlap model break down, and we have applied these results on Ag^+, Cu^{2+}, Cu^+, Cu^0 in the 4-4 subunit of the zeolite framework [14].

No theoretical studies on Ag and Ag^+ in a 6-6 subunit (SBU) have appeared up to now. The 6-6 SBU is the smallest zeolite cage in which a Ag atom/ion has been identified [15]. In the present study, we try to obtain information about the following questions by applying the EH-MO model [16–18]. What is the charge distribution of the empty 6-6 SBU and the change of an $Ag^{+1,0}$ in the center of the 6-6 SBU. What happens if a second or a third Ag^+, Ag^0 is brought from the outside to the neighbourhood of the Ag sitting in the cage? What kind of electronic transitions are expected in the different situations? How large is the energy barrier for an Ag^+ or an Ag^0 to escape the 6-6 SBU cage in the electronic ground state and in electronically excited states?

2. Comments on the Method. – Direct comparison of the presented theoretical results with experimental data is not yet possible. Therefore, we first compare some observations on AgX molecules with the corresponding calculation. It is well known that bond distances of molecules like Ag_2 or AgH cannot be calculated by the EH-MO model, unless the core-core repulsion is included. It was shown by *Anderson* and *Hoffmann* how this can be done [19], and we apply his approach. *Anderson* and *Hoffmann* used the *Wolfsberg-Helmholz* formula [16] with K = 2.25 to calculate the non-diagonal elements. They also discussed some problems of his method and tried to improve it [23]. A more satisfactory possibility to calculate the resonance integrals is to apply the weighted *Wolfsberg-Helmholz* formula [20].

$$H_{ij} = k' \frac{S_{ij}}{2} (H_{ii} + H_{jj})$$

$$k' = K + \Delta^2 + \Delta^4(1 - K), K = 1.75$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}$$

In this formula k' is equal to K for homonuclear molecules, otherwise it is always larger than K, which is reasonable. We have found that this approach leads to a satisfactory prediction of bond lengths and reasonable dissociation energies, if charge iteration is applied. *Table 1* reports experimental and calculated data of 4 AgX species, which are

Table 1. *Comparison of the Experimental and Calculated Data of AgX Species*

	Bond length [Å]		Dissociation Energy D_0 [eV]		Electronic transition							
					Type	Energy [eV]		H_{ii} [eV]				
	Calc.	Exp.	Calc.	Exp.		Calc.	Exp.	5s	5p	4d	ns	np
Ag_2	2.9	2.47	3.0	1.66	$'\Sigma_g^+ - '\Sigma_u^+$	2.5	2.85	−7.56	−3.83	−11.58		
AgH	1.9	1.62	3.6	2.5	$'\Sigma^+ - '\Sigma^+$	3.1	3.707	−8.97	−7.05	−13.50	−9.69	
AgO	2.3	2.0	1.8	2.2	$^2\Pi - {}^2\Pi$	3.24	3.027	−10.16	−7.31	−14.61	−25.63	−10.42
AgCl	2.4	2.32	4.0	3.22	$'\Sigma^+ - '\Sigma^+$	3.69	3.91	−9.58	−6.60	−14.11	−22.21	−11.13

relevant to the context of this paper. To obtain a set of *Coulomb* parameters H_{ii} for Si, Al, and O, we have applied charge iteration to the 4-4 SBU. Test calculations on smaller units have shown that this is the only approach leading to satisfactory *Coulomb* integrals which can also be used for larger units as *e.g.* the β-cage. Charge iteration was carried out on all Si, Al centers and on the O-atoms between them. We have always set the H_{ii} of the terminal O-atoms equal to the values of those belonging to the bridging O-atoms. All T–O (T = Si, Al) distances were put at 1.63 Å. We have found that using unequal Al–O, Si–O bond lengths does not change the results reported, but a fully symmetric structure makes the interpretation easier. The H_{ii} for Ag have been obtained by charge iteration in the middle of the 6-6 SBU. All parameters are listed in *Table 2*.

Table 2. *EH-MO Parameters Used for the Zeolite Calculations*

Orbital		H_{ii} [eV]	Exponents	Orbital		H_{ii} [eV]	Exponents
O	2s	−21.99	2.275	Al	2s	−16.77	1.167
O	2p	−7.5	2.275	Al	2p	−10.38	1.167
Si	2s	−20.26	1.38	Ag	5s	−9.77	1.54
Si	2p	−12.26	1.38	Ag	5p	−8.54	0.92
				Ag	4d	−14.30	6.07 (0.5593)
							2.66 (0.6050)

Charge Iteration Parameters for Ag [eV] [22]

A	B	C	
0.545	8.394	7.575	$s(d^{10}s)$
0.372	8.877	8.803	$s(d^9s^2)$
0.310	9.708	10.229	$s(d^9sp)$
0.769	6.460	3.831	$p(d^{10}p)$
1.178	6.856	4.761	$p(d^9sp)$
1.178	6.856	8.121	$p(d^9p^2)$
3.899	25.597	0.000	$d(d^{10})$
0.459	12.659	12.771	$d(d^{10}s)$
0.806	11.667	14.494	$d(d^{10}p)$

For the main group elements, the exponents of the radial part of the atomic *Slater*-type orbitals, calculated by *Burns,* are taken [24], and for Ag, we rely on the orbitals published by *Basch* and *Gray* [25]. *Mulliken* population analysis was applied [26].

3. An Ag-Atom in the 6-6 SBU of a Zeolite. – We now describe some properties of Ag⁰ and Ag⁺ in the 6-6 SBU of a zeolite. The chosen coordinate system is shown in *Fig. 1* together with the charge distribution in the empty 6-6 SBU and in the Ag⁰ (6-6 SBU). In
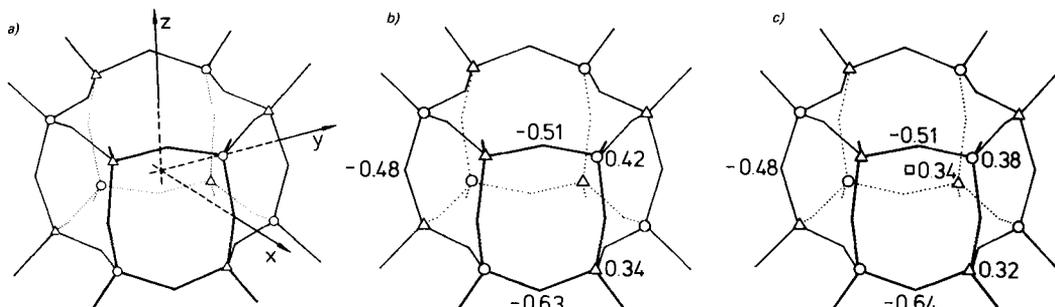
Fig. 1. a) *Coordinate system;* b) *EH-MO charge distribution in the empty 6-6 SBU;* c) *EH-MO charge distribution in the Ag^0(6-6 SBU).* ○ Al, △ Si, □ Ag.

the empty cage, Al turns out to be more positive than Si, and the three different O-atoms of the cage have slightly different negative charges. The Ag^0 is significantly polarized by the 6-6 SBU environment. Charge is transferred to the framework of the zeolite, mainly to the Si centers. In case of Ag^{+1}, the charge of Ag is 0.52.

We would like to know, whether an Ag^0 or an Ag^+ wobble in such a 6-6 SBU, and how much energy is needed for them to escape from the cage. The radii of the Ag species are $r(Ag^0) = 1.60$ Å and $r(Ag^+) = 1.26$ Å, and the radius of the cage in the 6-6 SBU is estimated as 1.56 Å. This means that Ag^+ is a little smaller than the hole and that Ag^0 fits perfectly into the cage. The hexagonal hole has a radius of 1.25 Å. From this, we expect a very low barrier for the escape of Ag^+ and a high one for the Ag^0.
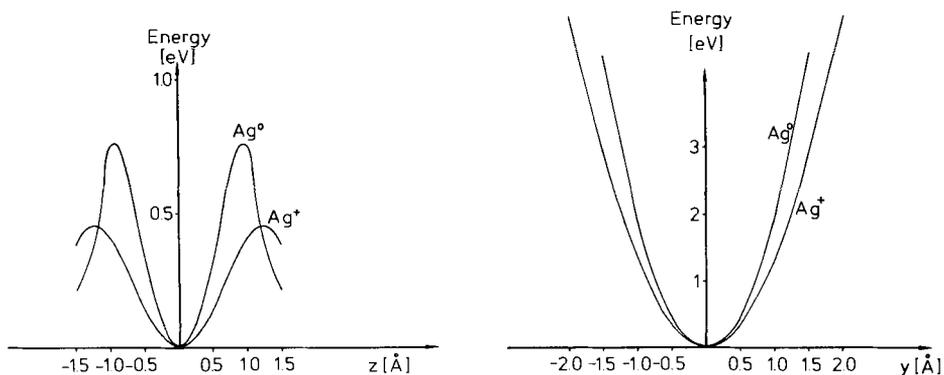

Fig. 2. *Energy barrier for a movement of Ag^0 and Ag^+ in the 6-6 SBU along the z-achses* (left) *and along the y-achses* (right), *resp.*

On the basis of the result of the EH-MO calculation shown in *Fig. 2*, we conclude that Ag^+ can easily and Ag^0 slowly escape along the z-axes from the 6-6 SBU at room temperature. How easily Ag^+ or Ag^0 can enter the cage depends on the environment. The very high energy barrier for a displacement perpendicular to the z-axis looks as expected. The higher barrier for a movement along the z-axes of the Ag^0 compared to the Ag^+ is mainly due to the antibonding interaction of the 5s Ag orbital with the totally symmetric
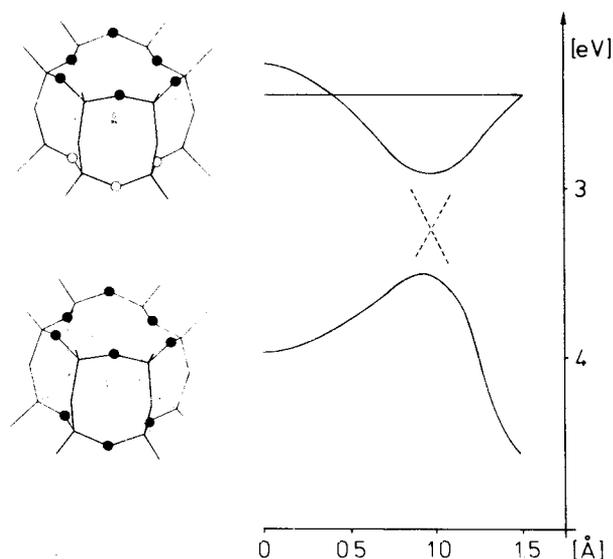
Fig. 3. *HOMO (5s*) and LUMO (5p*). Energy of these orbitals and the orbital above the LUMO for a movement of Ag" along the z-achses*

nonbonding zeolite orbitals, localized on the O-atoms as shown in *Fig. 3*. We call this orbital 5s*. It is the HOMO in case of Ag'' (6-6 SBU). The coefficient of the 5s Ag orbital in this MO is 0.8. Interestingly, the $5p_z^*$ orbital to which the $5p_z$ Ag orbital contributes with a coefficient of 0.67, is stabilized when Ag is moved along the z-axis because the antibonding interaction decreases. We conclude that electronic excitation $5p_z^* \leftarrow 5s^*$ significantly reduces the barrier for the $(Ag'')^*$ to exit the 6-6 SBU cage, provided the excited state life-time is long enough. The energy for the $5p^2P_{i_2} \leftarrow 5s^2S_{i_2}$ transition in the isolated Ag-atom is 3.664 eV. The energy for the $5p_z^*Ag \leftarrow 5s^*Ag$ transition is calculated to shift to a lower value, namely 1.7 eV. It might be worthwhile to mention, that in partially reduced silver zeolites X luminescence in this region can be observed, when excited in the near UV [1].

It is of great interest that the MO picture predicts charge-transfer transitions to occur from the zeolite framework to the 5s* orbital. The highest occupied orbitals in the zeolite framework are localized on the O-atoms *(Fig. 4)*. This means that such transitions correspond to an oxygen-to-silver charge transfer and take place in both the Ag^0 and the Ag^- case. They create a positively charged zeolite framework which probably acts as an oxidizing agent. Probably, they play a role in the self-sensitisation process of photo-oxygen evolution from H_2O we have detected [9] [10]. Due to our results, we disagree with the general statement that the interaction of $Ag^{0,-}$ with the zeolite framework is weak [11] [12]. Some aspects of the metal atom or ion are maintained while others are completely changed.

4. Interaction of an Ag-Atom in the 6-6 SBU with one or two External Ag-Atom. – Evidence was given in several studies for the existence of Ag clusters of limited size in zeolites of types A, X, and Y, rather than for the formation of metal particles. In faujasit-type zeolites, simultaneous occupancy of sites I and I' by Ag was described [27].
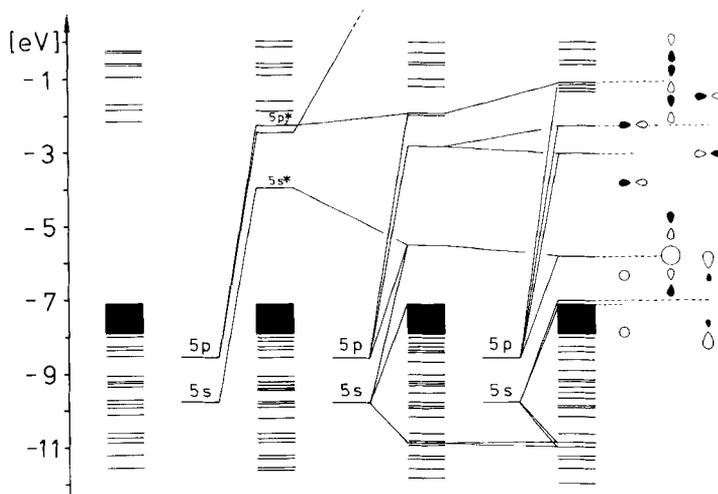
Fig. 4. *Correlation diagram of a 6-6 SBU, a 6-6 SBU with an Ag in the center, and the 6-6 SBU with one Ag-atom in the center and one outside on top of the hexagon* (d(Ag-Ag) = 3 Å) *and finally three Ag symmetrically along the Z-axis at Z = 3 Å, 0 Å, and −3 Å*

The sites I and I' correspond to the (x, y, z) coordinates $(0, 0, 0)$ and approximately $(0, 0, 3)$ in *Fig. 1*. By approaching an Ag^+ sitting in the 6-6 SBU cage with an Ag^0 along the z-axis, we do not observe bonding interaction. This result is expected from *Figs. 2* and *3*. The antibonding interaction with the zeolite orbitals dominates the bonding Ag-Ag interaction. The experimentally determined Ag-Ag distances in zeolites are in the range of 2.85 to 3.12 Å, depending on the framework [27], and they are similar to the bond length of the Ag_2 molecule *(Table 1)*. The reason for the stability of such an experimentally found structure is subject to further studies, where the whole β-cage will be added to the 6-6 SBU. In the following calculations, we have chosen Ag-Ag distances of 3 Å. At this distance, we expect a significant interaction. The same is true, if a third Ag-atom is added into $(x, y, z) = (0, 0, -3)$ position. In *Fig. 4*, a correlation diagram for the empty 6-6 SBU, the Ag(6-6 SBU), the Ag[Ag(6-6)SBU], and the Ag[Ag(6-6)SBU]Ag is shown. The (x, y, z) coordinates for the Ag are $(0, 0, 0)$, $(0, 0, 3)$ $[(0, 0, 0)]$ and $(0, 0, 3)$ $[(0, 0, 0)]$ $(0, 0, -3)$.

The highest occupied orbitals of the empty 6-6 SBU are localized on the O-atoms. The interaction between the O-atoms is very small so that no real band structure is formed. If we now go to the Ag(6-6 SBU) or the Ag^+(6-6 SBU), the properties of the zeolite change completely. As already discussed, charge transfer transitions to the 5s* orbital can occur. By adding a second silver (Ag^0 or Ag^+), a new dramatic change in the molecular orbital picture is observed. Depending on the temperature and the occupation either a singlet or triplet situation is realized in the case of Ag^0. The doublet situation for Ag^+ leads to two types of interesting possibilities for low-energy electronic transitions, namely charge transfer from the zeolite to the silver and a low energy silver-silver transition. Disturbed and broadened silver, silver transitions should occur in the visible. The charge distribution in case of the triplet, singlet and doublet configuration is shown in *Fig. 5*.

In every case, the Ag-atom in the cage is positively charged. This situation might change, depending on the ligands added to the external Ag-atom. The doublet case which has to be described as $Ag^{+1} - Ag$ or $[Ag-Ag]^{+1}$ from the point of view of oxidation
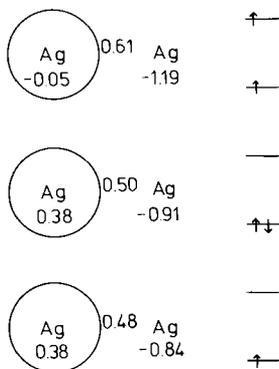
Fig. 5. *Charge distribution on the Ag-atom and overlap population on the Ag-atoms.* Ag⁺ = silver in the center of the 6-6 SBU, Ag = silver on the top of the hexagone, d(Ag-Ag) = 3 Å.

numbers, shows a very astonishing charge distribution. This charge distribution is an expression of the strong influence of the zeolite framework. It is due to the fact that the two orbitals indicated in *Fig.5* are distributed over the whole zeolite lattice and not localized on the Ag-atoms. Although these numbers might be too large to describe a real situation, they indicate that very new properties are to be expected with such a ligand system.

The orbital population shows that very strong interaction between the Ag-atoms occurs in either situation. It would be interesting to know more about magnetic properties in such cases [28]. If we finally add a third silver (Ag or Ag$^+$), the expected splitting of the already existing orbitals occurs. The charge distribution is similar to the Ag$_2$ case. The lowest Ag orbitals are admixtures of s and p type. Our drawing is simplified and describes mainly the symmetry of the situation. It might be of interest to mention that the Ag-Ag interaction of 6 Å distance is still relatively large, the 5s–5s′ overlap population is 0.16 and the 5p$_z$–5p$_z$′ is 0.38.

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