CHIMIA *42* (1988) Nr. 3 (März)

Interaction of Carbon Dioxide with Silver Zeolites**

Jürg Baumann, Robert Beer, and Gion Calzaferri*

Abstract: Photooxidation of water to O_2 and of $Cl^\ominus$ to Cl_2 by $Ag^\oplus$-exchanged zeolite A is briefly reviewed. Thermodynamic considerations concerning the free energy storage during these reactions are given. Interaction of CO_2 with $Ag^\oplus$-exchanged zeolite A of various $Ag^\oplus$ content, in the original and partially reduced state, is probed by in situ FTIR transmission spectroscopy. Chemisorbed, carbonate-like species are found in samples of low silver content. The CO_2 physisorption capacity is lowest for highly $Ag^\oplus$-exchanged samples. After removing the physisorbed CO_2 by evacuation, a small amount of weakly bound CO_2 remains in the zeolite. Its ν_3 (asymmetric stretching) frequency is cation dependent, reflecting some specific interaction with the cations. On chemical reduction of the $Ag^\oplus$, the amount of weakly bound CO_2 markedly increases, accompanied by spectral changes of the ν_3 band of CO_2.

1. Photochemical Reduction of Silver Zeolites

Zeolites have become a widely used class of materials for diverse applications as heterogeneous catalysis, selective gas adsorption, ion exchange, and others. Their properties are related to two facts: (*i*) The zeolite structure determines the size and connectivity of the internal cavities and acts as an effective size selector for molecules to be adsorbed. (*ii*) The nature of the cations, which balance the negative charge of the zeolite framework, determines electronic properties of the system and the occurence of specific interactions with adsorbates. It has been known for some time that silver-exchanged zeolites are light sensitive and turn grey or black after prolonged irradiation. Qualitative and later quantitative photochemical experiments[1,2] have clearly shown that on illumination of silver zeolites in aqueous dispersion the $Ag^\oplus$ ions are reduced to Ag^0 and molecular oxygen is evolved according to

$$[(Ag^\oplus)_n, mH_2O]Z \xrightarrow{h\nu} [Ag_n^{(n-r)\oplus}, rH^\oplus, (m-r/2)H_2O]Z + r/4\,O_2 \qquad (1)$$

followed by partial transfer of the zeolitic protons to the solution, which results in a measurable decrease of pH.

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

(Z represents the negatively charged zeolite lattice).

This photoreaction is an interesting candidate for photochemical conversion of solar energy because any of the three following energy storage reactions involves the oxidation of water to molecular oxygen:

$$H_2O \rightarrow H_2 + 1/2\,O_2 \qquad (3)$$

$$CO_2 + 2\,H_2O \rightarrow CH_3OH + 3/2\,O_2 \qquad (4)$$

$$1/2\,N_2 + 3/2\,H_2O \rightarrow NH_3 + 3/4\,O_2 \qquad (5)$$

To produce O_2, 4 redox equivalents per molecule have to be transferred, a requirement which necessitates the existence of some kind of charge storage device. The zeolite matrix appears to efficiently mediate this multiple charge transfer.

After establishing the products of reaction (1), a detailed quantitative investigation of the spectral sensitivity was undertaken[2] with the surprising result that a self-sensitization takes place: the further the reaction proceeds, the more the sensitivity shifts from initially UV to visible wavelengths out into the red range. This brings up the question about the fate of Ag^0 in the zeolite. As clearly demonstrated by the self-sensitization, new chromophores are produced with bathochromically shifted absorption in the process of the photoreaction. They are themselves able to drive the photoreaction if they get excited. Quantumchemical calculations at the Extended Hückel level of silver ions in zeolitic environments have provided the necessary theoretical background to understand the nature of the electronic transitions[3]. It was found that the lowest energy transition is of charge transfer type, exciting an electron from orbitals mainly localized on zeolite oxygen atoms to the silver ion which is coordinated to the zeolite. In addition, bathochromic shifts are predicted by these calculations if interaction among silver atoms within the zeolite is taken into account. The self-sensitization phenomenon can therefore be rationalized by the photoinduced formation of partly reduced silver clusters which absorb at longer wavelengths. Formation of silver clusters in zeolites under thermal treatment, under dehydration, and chemical reduction is known from ESR spectroscopy[4], from single crystal X-ray structure analysis[5], and has been inferred from far infrared spectroscopic results[6].

In a later study it was observed that silver zeolites are also capable of photoproducing Cl_2 if dispersed in a 0.2 M

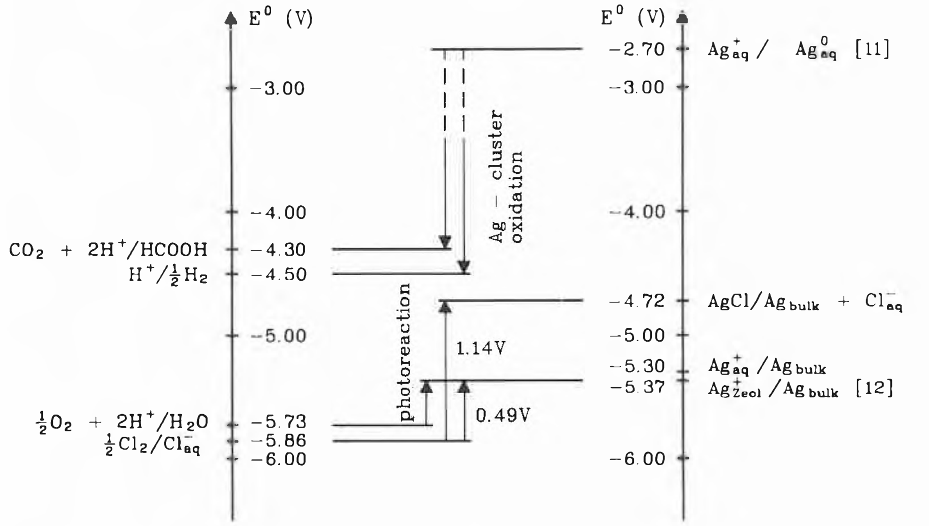


Fig. 1. Standard redox potentials[8] of some redox couples, referenced against the free electron in vacuum.

---

* *Correspondence:* Prof. Dr. G. Calzaferri
Institut für Anorganische, Analytische und
Physikalische Chemie
Universität Bern
Freiestrasse 3, CH-3012 Bern

** This article is based on a paper presented at the Workshop «Photochemical Transformation and Storage of Solar Energy; Conversion of CO_2 and Fuel Cells» in Kulturzentrum Appenberg in Zäziwil, November 9/10, 1987, organized by Prof. G. Calzaferri (Universität Bern), sponsored by the Bundesamt für Energiewirtschaft. – The work described therein is part of grant NEFF 329, financed by the Schweizerischer Nationaler Energieforschungsfonds. Beate Waldeck is gratefully acknowledged for some of the measurements.

aqueous KCl solution of low pH[7]. Similarly as in the water oxidation (1), self-sensitization occurs. The reaction can be formulated as

$$[Ag^{\oplus})_n]Z(mCl^{\ominus})_{ads} \xrightarrow{h\nu} [Ag_n^{(n-r)\oplus}]Z(m-r)Cl^{\ominus}{}_{ads} + r/2\ Cl_2 \qquad (6)$$

An important question always to be asked in solar energy conversion systems is whether thermodynamically energy storage is achieved in a given photoreaction. In case of the $Cl^{\ominus}$ oxidation, this question has an unambiguous positive answer. In Fig. 1 there is a collection of some standard redox potentials, either experimentally known[8] or estimated, which are pertinent to this work. These data are referenced to the electron in vacuum, thus the normal hydrogen electrode has a potential of −4.5 V[9]. In estimating the free energy of reaction (6) two assumptions are introduced. As far as the state of reduced Ag^0 is concerned, we take the most pessimistic case that the bulk state is reached. The state of the educt $Cl^{\ominus}$ is expected to be intermediate between $Cl^{\ominus}_{aq}$ and AgCl. It has been pointed out[7] that $Cl^{\ominus}$ can, for electrostatic reasons, hardly enter the zeolite cavities where it could form AgCl aggregates. $Cl^{\ominus}$ will therefore be adsorbed at the external surface where also the electron transfer takes place, forming an adsorbate of stability between $Cl^{\ominus}_{aq}$ and AgCl. Taken these considerations one obtains a potential difference corresponding to the stored free energy of 5.86 − 5.37 V = 0.49 V for the hydrated $Cl^{\ominus}$ as educt, and 5.86 − 4.72 V = 1.14 V for AgCl as educt. Energy storage is thus accomplished even under the worst case approximations. The feasibility of an unsupported AgCl layer to photochemically produce Cl_2 has recently been demonstrated[10] and photopotentials between the illuminated AgCl electrode and a Pt or graphite counterelectrode exceeding 1 V in open circuit have been measured. With such a high driving force it is very noticeable that reoxidation of the photochemically produced Ag^0 is kinetically strongly hindered. In contrast to chlorine production, the energetics of water oxidation (1) is pH dependent and endergonic only at low pH, if again bulk silver is the reaction product. Energy storage in this reaction does therefore highly depend on the actual form of the reduced silver species. The redox potential of finely dispersed silver atoms and clusters in the zeolite is now of interest. Since coordination of $Ag^{\oplus}$ in the zeolite is partly by water molecules, partly by framework oxygen, the solvation energies may be approximated by those in water. The standard redox potential of $Ag^{\oplus}/Ag^0$ in water has been estimated to be −2.7 V[11], the Ag^0 atom in water thus being an extremely strong reductant. With increasing cluster size a gradual decrease of the standard potential is expected until the value −5.3 V for $Ag^{\oplus}/Ag_{bulk}$ is reached.

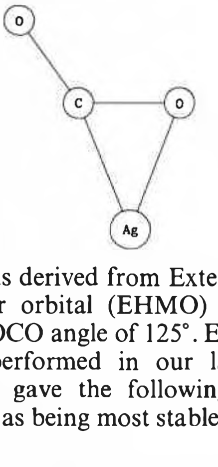
2. *Interaction of CO_2 with Ag^0*

The silver zeolite systems described in Section 1 provide the difficult step of photoinduced water oxidation. However, in order to make them usable solar energy conversion devices, the reduced silver needs to be reoxidized. From a thermodynamic point of view, finely dispersed, reduced silver clusters should be able to reduce $H^{\oplus}$ or CO_2 (Fig. 1). $H^{\oplus}$-reduction has been achieved at temperatures above 600 °C whereby H_2 was evolved so that the splitting of water into O_2 and H_2 could be completed[1]. We are currently studying other ways to reoxidize Ag^0 species either thermally or photochemically with the aim to produce in this step a fuel of high energy content. More specifically, we have concentrated on the interaction of CO_2 with silver zeolites of different reduction degrees. Several experimental results have led to this choice.

CO_2, although an apolar molecule as a whole, possesses a remarkable bond dipole moment of 1.33 debye[13] which makes the carbon atom a strong Lewis acid. An interesting experiment[14] showed that CO_2 can react with a silver surface at room temperature to silver carbonate and CO if the silver is mechanically activated by continuous grinding:

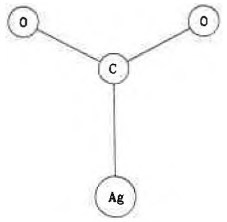
$$2\,Ag + 2\,CO_2 \rightarrow Ag_2CO_3 + CO \qquad (7)$$

The free enthalpy ΔG of this reaction is 212 kJ/mol and thus comparable with the 228 kJ/mol required for water photolysis. It can be speculated that the microscopic basis of this reaction are small silver particles formed on the surface by the mechanical treatment which have a lower work function than the bulk silver . This would correspond to the situation of the redox couple $Ag_n^{m\oplus}/nAg^{\oplus}$ (m < n) in water or zeolitic environment where we have presented evidence that silver clusters of low nuclearity are expected to be strongly reducing. The third piece of information are matrix isolation studies by *Ozin* et al.[15]. They found, using UV/VIS, Raman, and IR spectroscopy that codeposition of CO_2 and Ag atoms or the mixture $Ar/CO_2/Ag$ at low temperature results in formation of a single, weakly bound $Ag(CO_2)$ molecule which has four new absorptions in the UV and blue region. The geometry of the $Ag(CO_2)$ molecule is given[15] by the structure



(8)

which was derived from Extended Hückel molecular orbital (EHMO) calculations, with an OCO angle of 125°. EHMO calculations performed in our laboratory[16], however, gave the following symmetric structure as being most stable:



(9)

The OCO angle is also 125° and structure (9) is by 0.1 eV more stable than (8). The orbital stabilization energy of (9) is 1.95 eV so that this molecule can be regarded as fairly stable.

3. *FTIR Characterization of CO_2 Adsorbed on Zeolite A*

It has been realized some time ago that CO_2 adsorption on alkali and alkaline earth cation exchanged zeolites A and X can lead to both physisorbed and chemisorbed species[17,18]. The latter are stable at temperatures exceeding 200 °C. IR spectroscopy has proven invaluable in discriminating between the two types of adsorbates: physisorbed, weakly interacting CO_2 is best identified through its strong asymmetric stretching vibration ν_3 in the range 2340–2360 cm^{-1} while new bands appear between 1200 and 1700 cm^{-1} for the chemisorbed species. Several structural propositions have been given for this chemisorbed CO_2; at the current state of knowledge we prefer the term «carbonate-like species».

A recent study of CO_2 adsorption on completely dehydrated $Na_{12}A$ zeolite[19] has provided adsorption isotherms at low coverage and initial heats of adsorption for the physisorption only. However, no data for CO_2 adsorption on $Ag^{\oplus}$-exchanged zeolites could be found in the literature.

We therefore extended CO_2 adsorption studies to pure $Ag^{\oplus}$- and mixed $Ag^{\oplus}/Na^{\oplus}$-zeolites A, using FTIR transmission measurements to monitor adsorbed species. The sample preparation as well as the transmission spectrum of room temperature dehydrated $Na_{12}A$ and $Ag_{11.8}Na_{0.2}A$ from 20 to 13 800 cm^{-1} have been discussed elsewhere[20]. Briefly, self-supporting, undiluted zeolite disks of about 20 µm thickness are prepared. A high vacuum cell attached to a BOMEM DA3 FTIR spectrometer has been constructed which allows in situ evacuation, heating, cooling, gas loading, and illumination with visible or UV light. All spectra presented here have been recorded with a resolution of 2 cm^{-1}. They are unsmoothed spectra which have, for ease of comparison, been numerically scaled to a constant sample thickness of 20 µm. Intensities between different samples are therefore comparable within the accuracy of the thickness determination which is estimated to be ±20%. We have made no attempt to completely dehydrate our samples; after several hours evacuation at 10^{-6} torr and room temperature some residual water remains in the zeolite (it has been shown by X-ray crystallography that even on evacuation at 350°C at least 3 water molecules could be located in the β-cage of fully silver-exchanged zeolite A[21]). Our results are therefore coadsorption studies of CO_2 with H_2O. The silver A zeolites have been prepared from commercial Linde 4A by ion exchange with $AgNO_3$ solution in the dark. An excess of 0.23 M $AgNO_3$ solution was used for the preparation of the fully exchanged sample $Ag_{11.8}Na_{0.2}A$, and stoichiometric amounts of 53, 31, 6 mM concentration for the partially exchanged samples $Ag_{7.5}Na_{4.5}A$, $Ag_{4.3}Na_{7.7}A$, and $Ag_{0.9}Na_{11.1}A$, respectively. $Na_{12}A$ was obtained by washing Linde 4A in a 0.26 M $NaNO_3$ solution. All consecutive sample treatments, except for reduction with H_2, have been carried out at room temperature.

In Fig. 2A the formation of chemisorbed species is examined for three unreduced samples with different silver content. The lower curve of each pair corresponds to the unreacted zeolite, evacuated at 10^{-6} torr for one hour. The upper trace is the spectrum after one hour reaction with 15 torr CO_2 followed by one hour evacuation. The intensities of the thus observed bands are the same as when measured in the 15 torr CO_2 atmosphere. The species which are responsible for these bands desorb only to a negligible amount on evacuation so that the term chemisorption is justified. Absorption frequencies of these samples together with $Ag_{0.9}Na_{11.1}A$ and $Ag_{7.5}Na_{4.5}A$ are summarized in Table 1. It is clearly seen that the strong new bands attributable to chemisorbed CO_2 appear most pronounced with $Na_{12}A$ while fully silver-exchanged zeolite A chemisorbs almost no CO_2. There is a gradual transition in this behaviour with increasing silver content. It can be seen that already the exchange of the first 4 $Na^{\oplus}$ by $Ag^{\oplus}$ (curve 2 in Fig. 2A) strongly diminishes the chemisorption capacity. Since it is known from single crystal X-ray crystallography[22] that the first few $Ag^{\oplus}$ ions replace $Na^{\oplus}$ in oxygen 6-ring sites, it can be concluded that chemisorption requires $Na^{\oplus}$ ions at these sites. It is also interesting to note that together with CO_2 chemisorption a redistribution of structural hydroxy groups occurs (curve 1, Fig. 2B). The initially strong band at 3713 cm^{-1} is reduced in favour of a new band at 3662 cm^{-1}. It is seen by comparison with curve 2 that this is also the OH-band of partially $Ag^{\oplus}$-exchanged zeolite. Chemisorption of CO_2 has therefore the same effect on the distribution of structural OH groups as has the replacement of the first few $Na^{\oplus}$ by $Ag^{\oplus}$. Note that in fully $Ag^{\oplus}$-exchanged zeolite A (curve 3) the OH-band has moved to 3610 cm^{-1}. In both fully and partially exchanged $Ag^{\oplus}$-zeolite A the OH frequencies are unaltered on exposure to CO_2.

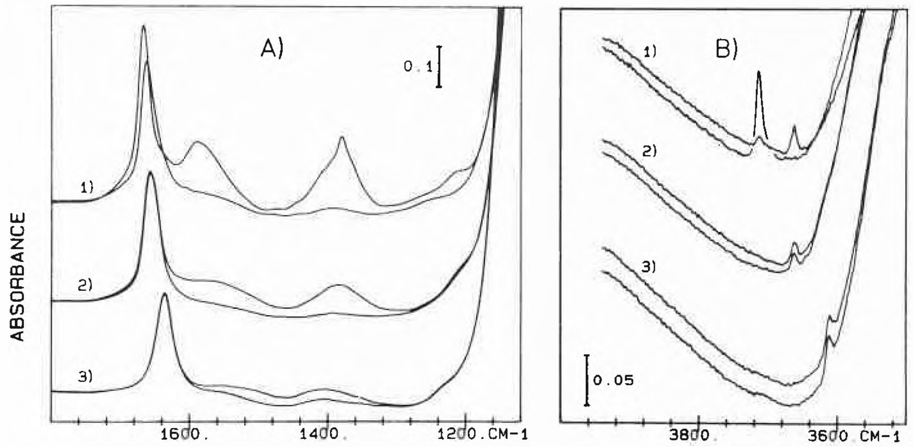


Fig. 2. Chemisorption of CO_2 on 1) $Na_{12}A$, 2) $Ag_{4.3}Na_{7.7}A$, 3) $Ag_{11.8}Na_{0.2}A$. Lower trace of each pair: 1 h evacuation. Upper trace of each pair: 1 h adsorption of 15 torr CO_2 followed by 1 h evacuation. – A) frequency range of carbonate-like species. – B) frequency range of structural hydroxy groups.

Table 1. Chemisorption of CO_2 on variously silver-exchanged zeolites A. Absorption frequencies [cm^{-1}] after one hour reaction with 15 torr CO_2 followed by one hour evacuation (see Fig. 2).

	H_2O bend	chemisorbed CO_2					OH stretch		
$Na_{12}A$	1667	1742[a)]	1655[a)]	1589	1380	1207	3713	3662	
$Ag_{0.9}Na_{11.1}A$	1665		1656[a)]	1588	1381	1207	3713	3662	
$Ag_{4.3}Na_{7.7}A$	1658				1383			3661	
$Ag_{7.5}Na_{4.5}A$	1651							3660	3609
$Ag_{11.8}Na_{0.2}A$	1637								3610

a) These values are taken from an experiment with deuterated samples to avoid interference with the H_2O bending mode.

Table 2. Physisorption of CO_2 on variously silver-exchanged zeolites A. Absorption frequencies [cm^{-1}] of physisorbed CO_2 (Fig. 3A). 15 torr CO_2 are adsorbed for one hour. The measurements are done in this CO_2 atmosphere.

	ν_2	$\nu_3(^{12}CO_2)$	$\nu_3(^{13}CO_2)$	$\frac{\nu_3(^{12}CO_2)}{\nu_3(^{13}CO_2)}$	$\nu_3+\nu_1$ $\nu_3+2\nu_2$	
gas phase[24]	667.38	2349.14	2283.49	1.0287	3612.84	3714.78
$Na_{12}A$		2352	2285	1.029		3712
$Ag_{0.9}Na_{11.1}A$		2352	2285	1.029	3599	3713
$Ag_{4.3}Na_{7.7}A$	656	2351	2284	1.029	3599	3713
$Ag_{7.5}Na_{4.5}A$	656	2348	2283	1.028	3595	3709
$Ag_{11.8}Na_{0.2}A$	656	2338	2273	1.029		

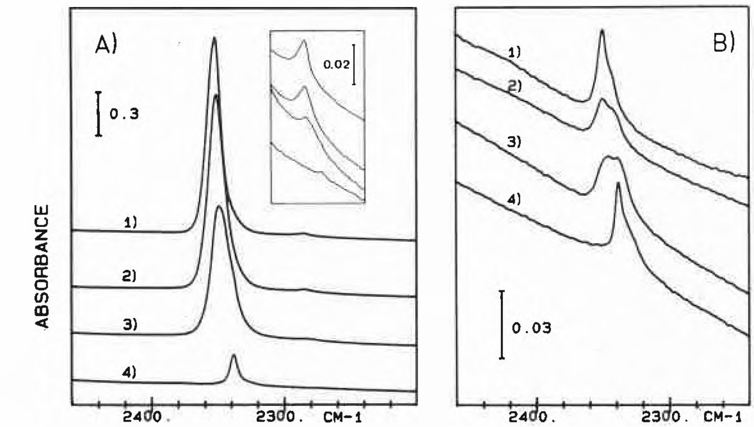


Fig. 3. Physisorbed (A) and weakly bound (B) CO_2 on unreduced silver zeolites A, ν_3 band of CO_2. 1) $Na_{12}A$, 2) $Ag_{4.3}Na_{7.7}A$, 3) $Ag_{7.5}Na_{4.5}A$, 4) $Ag_{11.8}Na_{0.2}A$. – A) 1 h adsorption of 15 torr CO_2, measured in this CO_2 atmosphere; absorptions due to gas phase CO_2 are completely compensated for. – B) 1 h evacuation after A).

Physisorption of CO_2 is presented in Fig. 3 and Table 2. The CO_2 bending mode ν_2, which is not shown in the figure, is weak and not suited for quantitative studies since there is a framework absorption in its vicinity. The frequency of the ν_2 vibration is 656 cm^{-1} irrespective of the silver content. The weak combination bands $\nu_3 + \nu_1$, $\nu_3 + 2\nu_2$ at 3712 and 3600 cm^{-1} which are in Fermi resonance, can be observed, the lower frequency band only visible in deuterated samples where the broad overlapping water stretching band is reduced. The strong asymmetric stretching band ν_3 of CO_2 on $Na_{12}A$ has been analyzed in detail

Table 3. Effect of chemical reduction of variously silver-exchanged zeolites A on CO_2 adsorption. ν_3 frequency [cm^{-1}] and peak integrals [arbitrary units] of weakly bound $^{12}CO_2$ remaining on the zeolite after one hour evacuation in the unreduced and reduced state. For details of the reduction procedure see text.

	Unreduced samples (Fig. 3B) absorption frequency			integrated intensity	Reduced samples (Fig. 4) absorption frequency			integrated intensity
$Na_{12}A$	2350	2343 (sh)						
$Ag_{0.9}Na_{11.1}A$	2350	2343 (sh)						
$Ag_{4.3}Na_{7.7}A$	2350	2342 (sh)		0.8	2349	2341		4.3
$Ag_{7.5}Na_{4.5}A$	2345	2338		1.0	2346 (sh)	2337		4.4
$Ag_{11.8}Na_{0.2}A$		2337	2328 (sh)	1.1		2336	2326	1.5

earlier[23]. It was shown in this work that this band is composed of 3 subbands centered around 2362, 2352, and 2344 cm^{-1} at room temperature. Their weight was found to depend on temperature and degree of hydration. Our data for the partially hydrated sample are in good agreement with these findings: the observed frequency is 2352 cm^{-1} which corresponds to band II of[23]. With increasing silver content the ν_3 frequency of CO_2 shifts to lower wavenumbers. This is also found for the H_2O bending frequency (Fig. 2A, Table 1). The inset of Fig. 3A shows an enlarged section containing the natural abundance $^{13}CO_2$ band. It undergoes the same shift as the main peak. The frequency ratio of the two isotopic CO_2 molecules is 1.029, the same value as in the gas phase. The adsorption capacity is strongly reduced in the fully silver-exchanged sample. On evacuation after CO_2 loading most of the CO_2 desorbs. What remains after one hour of pumping is shown in Fig. 3B and Table 3. This residual CO_2, which we will call «weakly bound CO_2», must experience an interaction of medium strength with the zeolite: weaker than the carbonate-like species because it is slowly removed on prolonged evacuation, but stronger than the bulk of physisorbed CO_2 which desorbs much faster. It possesses an asymmetric stretching band ν_3 which is not much displaced from the frequency in the gas phase. This ν_3 band of weakly bound CO_2 as shown in Fig. 3B for both the pure $Na^{\oplus}$- (curve 1) and pure $Ag^{\oplus}$-zeolite (curve 4) is made up of two components, a main peak and a low frequency shoulder, the whole pattern being displaced in going from $Na^{\oplus}$ to $Ag^{\oplus}$. This profile possibly reflects the heterogeneity of adsorption sites. Visual inspection shows that the mixed $Na^{\oplus}/Ag^{\oplus}$ samples (curves 2, 3) contain both profiles of the ionically pure samples (curves 1, 4) at different ratio.

Without going into a more quantitative analysis we draw the conclusion that CO_2 adsorption at $Na^{\oplus}$ or $Ag^{\oplus}$ sites is independent of the presence of the other cation, at least at these low coverages. Comparison of the intensities of these bands should be done with precaution since especially the thickness of sample 1) is uncertain. Nevertheless it is obvious that all four samples have a comparable capacity to weakly bind CO_2 although the total amount of physisorbed CO_2 before evacuation was very different (Fig. 3A).

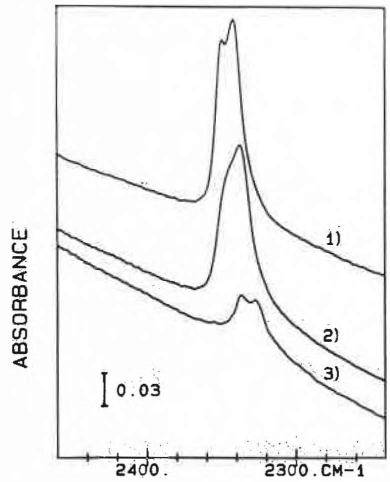


Fig. 4. Weakly bound CO_2 on partially reduced silver zeolites A, ν_3 band of CO_2. 1) $Ag_{4.3}Na_{7.7}A$, 2) $Ag_{7.5}Na_{4.5}A$, 3) $Ag_{11.8}Na_{0.2}A$. 1 h adsorption of 15 torr CO_2 followed by 1 h evacuation. For reduction conditions see text.

Up to now the $Ag^{\oplus}$ ions have not yet been reduced to Ag^0. Reduction can be done by reacting the zeolite with molecular hydrogen at or above room temperature. In the experiment presented here reduction was carried out with 200 torr H_2 at 100 °C for five minutes. This leads to a partially reduced sample whose reduction degree has not been determined analytically. Prior to and after reduction, 15 torr CO_2 were adsorbed for one hour and evacuated again for one hour. The ν_3 band of the weakly bound CO_2 in the reduced state of the zeolites is shown in Fig. 4 and Table 3. Some integrals of this peak for the reduced and unreduced state, derived from the same samples, are also given in Table 3. Reduction of the $Ag^{\oplus}$ ions has two effects on the interaction of CO_2 with the zeolite. First, the amount of weakly bound CO_2 after one hour evacuation is up to 5 times higher than in the unreduced state. For the fully silver-exchanged zeolite this increase is much less pronounced. Second, the two-component contour of the band in the unreduced state (Fig. 3B) is basically maintained, however, the low frequency component is much enhanced in intensity relative to the high frequency component. It is too early to relate this result to a detailed microscopic picture. Nevertheless it is remarkable that the interaction of CO_2 with partially reduced silver zeolites is stronger than with the unreduced samples.

4. Conclusions

FTIR spectroscopy is found to be a very useful tool for the understanding of the adsorbate – zeolite interaction. Band frequencies, line widths (not exploited in this work), and relative or even absolute intensities provide a broad set of detailed information. If combined with conventional quantitative adsorption/desorption techniques, a refined picture of the state of the adsorbate in the zeolite can be expected.

It has been shown in this work that the interaction of CO_2 with silver zeolite A depends on the $Ag^{\oplus}/Na^{\oplus}$ ratio. In addition, partially reduced samples show an enhanced capability to retain CO_2. We have not succeeded in finding an IR absorption band attributable to the intermolecular $CO_2 \cdots Ag^{\oplus}$ and $Ag \cdots CO_2$ vibration. Such a band will be located in the far IR. If it could be found this would constitute the most direct information on the interaction between the molecule and the zeolite.

Received: December 15, 1987 [FC 129]

---

[1] S. Leutwyler, E. Schumacher, *Chimia 31* (1977) 475; P. A. Jacobs, J. B. Uytterhoeven, K. J. Beyer, *J. Chem. Soc. Chem. Commun.* (1977) 128.
[2] G. Calzaferri, S. Hug, T. Hugentobler, B. Sulzberger, *J. Photochem. 26* (1984) 109.
[3] G. Calzaferri, L. Forss, *Helv. Chim. Acta 69* (1986) 873; *70* (1987) 465.
[4] J. R. Morton, K. F. Preston, *J. Magn. Reson. 68* (1986) 121; P. J. Grobet, R. A. Schoonheydt, *Surf. Sci. 156* (1985) 893.
[5] Y. Kim, K. Seff, *J. Am. Chem. Soc. 100* (1978) 6989; *J. Phys. Chem. 82* (1978) 921; *91* (1987) 668.
[6] M. D. Baker, G. A. Ozin, J. Godber, *Catal. Rev. Sci. Eng. 27* (1985) 591, and references cited therein.
[7] G. Calzaferri, W. Spahni, *J. Photochem. 32* (1986) 151; *Chimia 40* (1986) 435.
[8] *CRC Handbook of Chemistry and Physics*, 55th Ed., CRC Press, Boca Raton, FL (1974).
[9] F. Lohmann, *Z. Naturforsch. A22* (1967) 813.
[10] G. Calzaferri, W. Spahni, *Chimia 41* (1987) 200; R. Beer, G. Calzaferri, W. Spahni, *ibid;* in press.
[11] A. Henglein, *Ber. Bunsenges. Phys. Chem. 81* (1977) 556; J. Belloni, personal communication.
[12] B. Sulzberger, Ph. D. Thesis, Universität Bern (1983).
[13] W. J. Orville-Thomas, S. Suzuki, G Riley, in A. J. Barnes, W. J. Orville-Thomas (Ed.): *Vibrational Spectroscopy – Modern Trends*, Elsevier, Amsterdam (1977), p. 167.
[14] H. Jost, J. Jedamzik, K.-O. Backhaus, R. Langenstrassen, *Z. Anorg. Allg. Chem. 497* (1983) 224.
[15] G. A. Ozin, H. Huber, D. McIntosh, *Inorg. Chem. 17* (1978) 1472.
[16] L. Forss, Ph. D. Thesis, Universität Bern (1987); G. Calzaferri, *Chimiu 40* (1986) 74.
[17] P. A. Jacobs, F. H. van Cauwelaert, E. F. Vansant, *J. Chem. Soc. Faraday Trans. I 69* (1973) 2130.
[18] T. Masuda, K. Tsutsumi, H. Takahashi, *J. Colloid Interf. Sci. 77* (1980) 232.
[19] Y. Delaval, R. Seloudoux, E. Cohen de Lara, *J. Chem. Soc. Faraday Trans. I 82* (1986) 365.
[20] J. Baumann, R. Beer, G. Calzaferri, *Microchim. Acta*, in press.
[21] Y. Kim, K. Seff, *J. Phys. Chem. 82* (1978) 1071.
[22] Y. Kim, K. Seff, *J. Phys. Chem. 91* (1987) 671.
[23] Y. Delaval, E. Cohen de Lara, *J. Chem. Soc. Faraday Trans. I 77* (1981) 869.
[24] L. S. Rothman, L. D. G. Young, *J. Quant. Spectrosc. Radiat. Transfer 25* (1981) 505.