We note that the amount of strongly sorbed molecules is only about 7% of the molecules needed to completely fill the microporous voids. Further experiments revealed that by purging the water-loaded crystals in He at 20 °C, a stable oscillation frequency of the QCM could be obtained in 5–10 min. This pretreatment leaves most of the void volume (93% ± 1%) accessible to ethanol and further reduces the water sorption capacity by ca. 50%, as a result of saturating the reactive sites.

The selectivity of this preloaded QCM toward ethanol was studied in the presence of competing molecules (Figure 4). The response to pure ethanol is similar to that of a QCM completely degassed at elevated temperature. A high sorption capacity for ethanol (0.017 vs 0.024 $\mu g/\mu g$ in the degassed film, at 50.4 ppm vapor concentration) could still be observed. Sorption of a 75.0% isooctane/25.0% ethanol mixture, at alcohol concentrations of 50.4 and 722 ppm, resulted in weight changes of 0.017 and 0.066 $\mu g/\mu g$. These responses to the vapor mixture are almost the same as those to pure ethanol. Measurements of 18 sorption–desorption points for ethanol concentrations in the range 0–722 ppm in isooctane show a standard deviation of only 0.4 $ng/\mu g$ compared to pure ethanol responses. Sorption of a 33.1% water/50.1% isooctane/16.8% ethanol vapor mixture in the same alcohol concentration range only shows 1 $ng/\mu g$ deviation. The results demonstrate that *ethanol is* preferentially *adsorbed in competition with water or isooctane.*

The nature of the hydrophobic sensing layer and the preferential adsorption of ethanol over water on the preloaded QCM can be understood by evaluating the isosteric heats of adsorption.[12] Water sorption on a polar surface is through specific interactions with cations or hydroxyls. When such energetic sites (cations) are "blocked" by molecules presorbed in the sensing layer, the isosteric heat of adsorption of water over the range 8–14 $ng/\mu g$ in the sensing layer is about 6.6 kcal mol^{-1}, substantially below that of the heat of liquefaction of water (10.5 kcal mol^{-1} at 25 °C) and similar to that reported for pure silicalite.[13] Thus it is energetically unfavorable for water to condense into such a system. In contrast, for ethanol an isosteric heat of 11 kcal mol^{-1} is obtained over a wide sorption range of 20–80 $ng/\mu g$.[10] This value is *greater* than the heat of liquefaction of ethanol (10.1 kcal mol^{-1} at 25 °C). The favorable sorption of ethanol vs water also illustrates that pronounced micropore filling by ethanol can occur at low concentrations. Finally, the chemical stability of the coated QCM devices was tested by exposing them to the vapors above 1 M HCl for 12 h. The sorption behavior remained virtually unchanged after this treatment.

The microsensor design discussed in this communication shows that highly selective responses can be achieved when microporous adsorption is combined with tailored surface interactions in composite films. The only molecules that are expected to compete with ethanol adsorption are those small enough to enter the silicalite pores and with similar affinity to the intrazeolite surface, such as methanol. Ethanol sensing in applications such as fermentation would probably not be affected by such interferences. Further exploration of other selective interactions in microporous glass composites is in progress.

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Registry No. Ethanol, 64-17-5; 2,2,3-trimethylpentane, 7732-18-5; water, 564-02-3.

Supplementary Material Available: Figure showing dynamic sorption kinetics of ethanol during sorption and desorption (1 page). Ordering information is given on any current masthead page.

Microwave Frequency Behavior of the EPR Copper(II) Ion Pairs Spectrum Formed in CuCe Oxide

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In previous work,[1-3] it has been shown, mainly by EPR, that copper–cerium oxides (Cu/Ce = 0.01) contain Cu^{2+} ion pairs. Well-resolved EPR spectra of copper(II) ion pairs have been evidenced at either X-band (9.3 GHz) or Q-band (35 GHz) frequencies. The hyperfine structure of the half-field signal ($\Delta m_s = 2$) and the parallel and the perpendicular components of the normal-field signal ($\Delta m_s = 1$) have been observed. Since the EPR spectra of dimers have been seldom studied at Q-band frequency, the purpose of this work is to show some anomalous behavior of a copper(II) ion pairs spectrum with the variation of the microwave frequency of the spectrometer.

The CuCe Oxide sample with an atomic ratio Cu/Ce = 0.01 was prepared by calcination of the coprecipitated hydroxides of cerium and copper at 1173 K for 3 h under a flow of dry air.

The EPR spectra were obtained with a Varian (V-4502) spectrometer using the X and Q bands as microwave frequencies. The spectra were recorded at 77 and 293 K. The g values were measured in comparison with DPPH ($g = 2.0036$) or directly by measuring the magnetic field H and the microwave frequency ν.

The EPR spectra of CuCe oxide (Cu/Ce = 0.01) recorded at X- and Q-band frequencies are shown in Figure 1. As it was indicated elsewhere,[1-3] these well-resolved spectra clearly demonstrate the existence of three signals:

One signal, K, corresponds to copper(II) ion pairs. In fact, the seven components with relative intensities 1:2:3:4:3:2:1 of the hyperfine splitting with two identical nuclei Cu^{2+} of spin $^3/_2$ observed for $g_\parallel$ and $g_\perp$ and the weak

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(12) The isosteric heats were obtained from the sorption isotherms in the range 0–40 °C by the relation $Q_{st} = RT_1T_2 \ln (P_1/P_2)_a/(T_1 - T_2)$, where P_1 and P_2 are the equilibrium concentrations for the same sorption amount in the sensing layer, a, at the temperatures T_1 and T_2, respectively.

(13) An isosteric heat of 6 kcal mol^{-1} for water sorption was reported by Flanigen et al. in ref 6, and an isosteric heat of 12–14 kcal mol^{-1} for ethanol was reported by Dubinin in ref 10.

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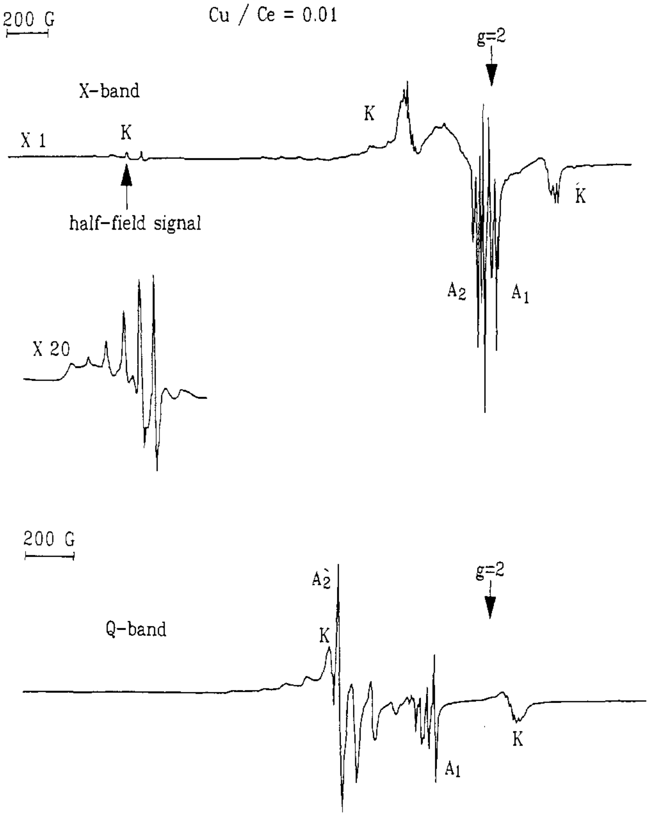

Figure 1. X- and Q-band EPR spectra of CuCe oxide (Cu/Ce = 0.01) recorded at 77 K.

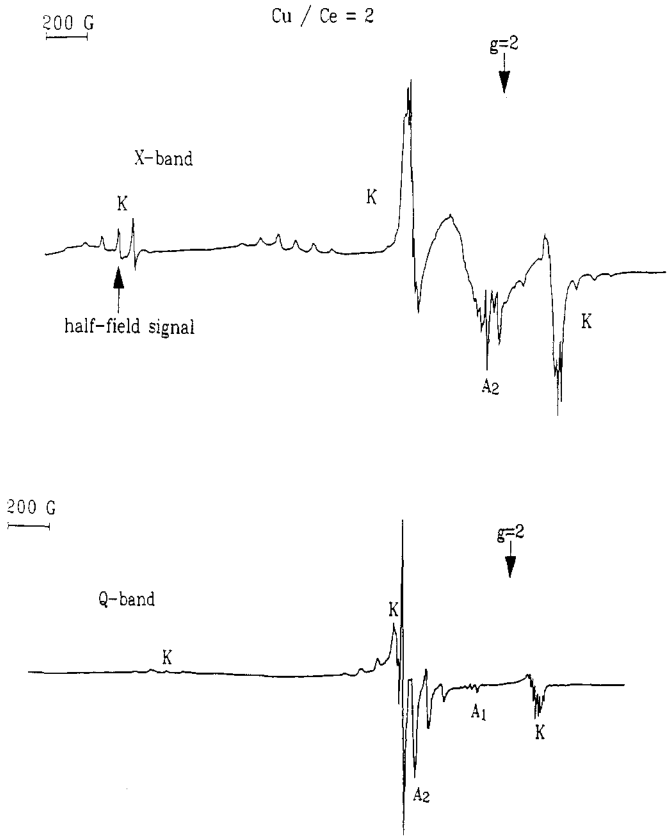

Figure 2. X and Q band EPR spectra of CuCe oxide (Cu/Ce = 2) recorded at 77 K.

signal obtained at half the normal magnetic field intensity, are characteristic of the existence of copper(II) ion pairs. From the intensities ratio measured by double integration of the signals observed at $\Delta m_s = 2$ and $\Delta m_s = 1$, the interion distance between the two Cu^{2+} ions, forming the pair, has been evaluated as 3.4 Å. From the separation of perpendicular and parallel components, directly deduced from spectra of the Figure 1, the zero-field constant D has been found to be equal to 0.066 cm^{-1}. The splitting between the singlet- and the triplet-state J has been also calculated either from the dipolar and pseudodipolar interaction or from the Boltzmann distribution and the Curie law. The value deduced ($J = 52.5$ cm^{-1}) was much larger than A_{iso} (0.0037 cm^{-1}) of the K signal.

Two signals, A_1 and A_2, correspond to isolated monomeric Cu^{2+} ions in CeO_2. The first one has been correlated with copper(II) species in octahedral sites with a tetragonal distorsion. From EPR parameters, it has been shown that these Cu^{2+} monomeric ions (A_1) are the precursors of the copper(II) ion pairs in ceria. The other one (A_2 signal) has been attributed to Cu^{2+} ions localized in surface substitutional sites with a square-pyramidal symmetry.

We have also noticed previously[2] that the A_2 signal has been obtained at both X- and Q-band frequencies, whereas the half-field signal has been observed only in the X-band spectrum (Figure 1).

When a CuCe oxide sample with an atomic ratio Cu/Ce = 2 was prepared and calcined at 1173 K as indicated previously, the X-band EPR spectrum is mainly formed of the K and A_2 signals, and apparently no trace of the A_1 signal is observed (Figure 2a). Contrary to that observed in CuCe oxide (Cu/Ce = 0.01) X-band spectrum, the relative intensity of the A_2 signal is weaker than K dimer signal. When the Q-band spectrum of this solid is recorded (Figure 2b), the intensity of the A_2 signal becomes larger than K and the A_1 signal is observed with a weak intensity. From these results it is obvious to deduce that the A_2(Q) signal, obtained at Q band, must not correspond to A_2(X) signal, obtained at X band, as was indicated previously[2] in the case of Cu/Ce = 0.01. To confirm this it has been demonstrated that the EPR parameters of A_2(X) and A_2(Q) are different, since the separation between A_1 and A_2(Q) is greater in comparison with that of A_1 and A_2(X) when the X band is replaced by the Q band. Since no signal in the X-band spectrum has the same shape and the same splitting constant as that of the A_2(Q) signal, we are then allowed to wonder about the origin of this signal and what happened to the A_2(X) signal in the Q band spectrum.

The direct comparison of EPR signal obtained in the X- and Q-band spectra allows us to notice that the half-field signal observed at the X band is the only one in the spectrum which can be considered as similar in shape and splitting constant (80 G) to that of the A_2(Q) signal. Are we then allowed to suppose that the A_2(Q) signal is the half-field signal of the Q-band spectrum? To answer this question, it is necessary to have recourse to some theoretical considerations and to the literature of the dimeric spectra.

It has been shown[4] that if the zero-field splittng D of a dimer is larger than $h\nu$, where ν is the microwave frequency of the spectrometer, it may be impossible to observe an EPR spectrum or only some of the allowed transitions may be observed. On the contrary, if D is less than $h\nu$, the resulting EPR spectrum ($\Delta m_s = 1$ and $\Delta m_s = 2$) shows considerably anisotropy. Since the zero-field splitting D previously calculated from EPR parameters of the copper(II) ion pairs signal (K) of CuCe oxide ($D = 0.066$ cm^{-1})[2] is less than the X-band frequency (0.3 cm^{-1}) and the Q-band frequency (1.1 cm^{-1}), the allowed and the

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forbidden transitions ought to be observed in the K signal and X- and Q-band spectra.

On the other side, it has been demonstrated[5] that the position of the low-field edge of the half-field signal in a powder spectrum is given by

$$H_{\min}(\Delta m_s = 2) = \frac{1}{2g\beta}\left[(h\nu)^2 - 4\left(\frac{D^2}{3} + E^2\right)\right]^{1/2} \qquad (1)$$

where ν is the spectrometer operating frequency and D and E are the zero-field splitting parameters. For axial symmetry, $E = 0$.

From eq 1, it is then possible to determine the $H_{\min}$ position of the half-field signal when the X-band frequency is replaced by the Q band. The value obtained ($H = 5813$ G) is shifted more than 250 G to a higher field from that directly obtained ($H = 5558$ G) by the usual equation of Zeeman effect ($h\nu = g\beta H$). Despite this shift, the value obtained corresponds to a magnetic field already recorded by Q band. Since no EPR signal has been observed, it is then possible to suppose that the intensity of this signal can be very weak. In fact, the relative intensity I_{rel} between the signal observed at $\Delta m_s = 2$ and that obtained at $\Delta m_s = 1$ is given by[5]

$$I_{\text{relative}} = \frac{I(\Delta m_s = 2)}{I(\Delta m_s = 1)} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2 \qquad (2)$$

A is a constant ($A = (21 \pm 2) \times 10^{-6}$), r is the interion distance, and ν is the microwave frequency. From eq 2, the I_{rel} will be decreased approximately 15 times less when the X band is replaced by the Q band. But, despite this decrease, the sensitivity of the EPR spectrometer remains able to detect such intensity of signal if this latter exists. Then, no trace of the half-field signal has been evidenced even with the highest gain on the spectrometer. The absence of the half-field signal in the Q-band spectrum, where should it exist, allows us to suppose that a shift has occurred.

To our knowledge, generally, no shift of the half-field signal does occur from the low magnetic field to the high field, when the X-band frequency has been replaced by the Q band. In fact, in the case of CuTh oxide,[6,7] a dimer and monomers have been evidenced by EPR. One of signals is similar to $A_2(X)$ obtained in CuCe oxide. Despite that the thoria and the ceria have the same crystallographic structure, the $A_2(Q)$ signal was not obtained in CuTh oxide when the X band was replaced by the Q band.

However, in one particular case, a significant case of one low-field signal had been obtained by Jones et al.[8] in copper acetate monohydrate. Indeed, this latter compound had been widely studied by Bleaney and Bowers.[9] The EPR spectrum of Cu^{2+} ion pairs coupled via an antiferromagnetic exchange interaction to form a singlet ground state and a thermally accessible ($J = -260$ cm^{-1}) triplet state. A signal at low magnetic field had been observed in the X-band EPR spectrum. When the experiment on copper acetate monohydrate was repeated at Q-band frequency by Jones et al., the low-field signal significantly shifted to a higher field with a concomitant splitting of the lines and significant increase of the signal intensity. But, in that case, the low-field signal observed at X-band frequency, in copper acetate, by Bleaney and Bowers is similar to that obtained from the superconducting oxides below T_c.[10] Therefore, the significant shift of this signal observed by Jones et al. at Q-band frequency has been explained by the superconductivity properties. However, this low-field signal is completely different from the half-field signal of the CuCe oxide samples, and then it is not allowed to suppose that the half-field signal, observed at the X-band spectrum, can shift with the microwave frequency.

In conclusion, the origin and the nature of the $A_2(Q)$ signal remain unresolved, and if we suppose that this signal is different than $A_2(X)$ signal, a particular theoretical work should be necessary to explain that. In addition, measurements have to be made at intermediate frequencies (between X and Q bands) and at low temperatures (4.2 K) to follow the behavior of the dimer spectrum and specifically the $A_2(Q)$ signal.

Registry No. Cu^{2+}, 15158-11-9; copper cerium oxide, 12525-67-6.

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[$CF_3Au(C{\equiv}NMe)$] as a Precursor for CVD of Gold

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Introduction

The high conductivity and stability to corrosion of gold have led to its widespread use in modern electronics and hence to interest in chemical vapor deposition (CVD) of gold.[1-5] Established precursors for CVD of gold include organogold(III) complexes such as [$AuMe_2(CF_3COCHCOCF_3)$][1] and [$AuMe_3L$],[2-4] where L = PMe_3 or PEt_3, and organogold(I) complexes such as [AuMeL],[2,4,5] where L = PMe_3, PEt_3, or MeNC. CVD of gold from these alkylgold(I) complexes can be carried out at low temperature but the compounds have poor thermal and photochemical stability and so are not easily stored.[2] Since trifluoromethylgold(I) complexes are more stable than the corresponding methylgold(I) complexes,[6] their use as precursors for CVD of gold has now been investigated.

The new organogold(I) complex [$CF_3AuCNMe$] was prepared according to

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