

Observation of Single-Crystal-Type EPR Spectra from Monolayers of Copper-Exchanged Zeolite Na-A Crystals Assembled on Glass Plates

Hyunsoo So,^{*,†,‡,§} Kwang Ha,[‡] Yun-Jo Lee,[‡] Kyung Byung Yoon,^{*,‡} and R. Linn Belford^{*,§}

Center for Microcrystal Assembly and Department of Chemistry, Sogang University, Seoul 121-742, Korea, and Illinois EPR Research Center and Department of Chemistry, University of Illinois at Urbana-Champaign, Illinois 61801

Received: February 11, 2003; In Final Form: May 1, 2003

Single-crystal-type EPR spectra were observed for microcrystals of copper(II)-exchanged zeolite Na-A assembled on glass plates when the magnetic field was perpendicular to the glass surface. Two copper species (H and D) were identified both in the powder sample and in the assembled crystals. The g_z direction of species H is parallel to [001] of the cubic crystal, while that of species D is tilted 9° away from [001]. Previously, other authors assumed the g_z directions of the two corresponding species to be parallel to [111]. On the basis of the g_z directions, we suggest that Cu^{2+} in species H is displaced 0.149 nm along [111] from the six-ring plane into the β cage and octahedrally coordinated to three zeolite oxygen atoms in the six-ring plane and three water molecules. The g_z direction of Cu^{2+} in species D is not compatible with site II in the six-ring plane. Species D is probably a trigonal complex with Cu^{2+} displaced into the β cage and coordinated to three zeolite oxygen atoms.

Introduction

Single-crystal EPR spectra can provide information on the orientation of paramagnetic species in a crystal. This information, which is vital in characterizing the paramagnetic species for many important systems, is lost for powder samples. Yet many EPR studies have been carried out with powder samples, for it is difficult to grow large crystals suitable for single-crystal EPR studies. Recently some of us have developed various methods to assemble micrometer-sized zeolite crystals on glass plates,¹ opening up the possibility to determine the orientation of paramagnetic species in crystals from EPR spectra of assembled microcrystals. Here we report single-crystal-type EPR spectra that were obtained for the first time from monolayers of zeolite microcrystals on glass plates.

For our initial study we have chosen copper(II)-exchanged zeolite Na-A (Cu/NaA), which can be easily synthesized in microcrystals² and is structurally quite simple compared to other zeolites.³ Several groups have studied this system using EPR and ESEEM (electron spin-echo envelope modulation) techniques.^{4–10} EPR studies have identified three copper(II) species in Cu/NaA.^{4–6} In freshly prepared and in rehydrated samples, there is only one copper species. When this sample is partially dehydrated, either by evacuation at room temperature or by drying in air at 110 °C, another species appears with reversed g values ($g_{\parallel} < g_{\perp}$). Finally, when the sample is fully dehydrated at 400 °C, the previous two species disappear and a third species is formed. In partially dehydrated samples, two or three species can coexist.

The sites and coordination of these copper species were discussed in the original papers and several review articles.^{11–13} All EPR studies, however, have been carried out with powder

samples, and g_z directions of the copper species have never been determined experimentally. In ESEEM studies the g_z directions of all species were assumed to be parallel to [111] of the cubic unit cell.^{5,7} In this paper we report the g_z directions of the hydrated and the fully dehydrated copper species determined by comparing the EPR spectrum of a powder sample with that of microcrystals assembled on glass plates. The g_z directions of these copper species are not parallel to [111], but one is parallel to [001] and the other is slightly tilted from [001]. Copper sites consistent with this new information are discussed.

Experimental Section

Materials. Zeolite Na-A crystals with an average size of 1 μm were synthesized according to the literature procedures.² Cu^{2+} was introduced by adding 10 mL of 1 mM $\text{Cu}(\text{NO}_3)_2$ and 1 g of zeolite to 100 mL of water.⁷ (When Cu^{2+} is completely exchanged, one Cu^{2+} ion is introduced per 40 unit cells of the zeolite.) The slurry was vigorously stirred for 20 min at room temperature, and the exchanged zeolite samples were then filtered and washed with deionized water and dried under vacuum at 105 °C for 2 h (sample 1–1) or at 300 °C for 5 h (sample 1–2).

3-Chloropropyltrimethoxysilane was attached to glass plates according to the procedure described elsewhere.^{1c} Then Cu/NaA crystals were allowed to react with and assemble on the surface of glass plates in boiling toluene for 3 h.^{1c} The glass plates were dried under vacuum at 105 °C.

Samples with a higher concentration of copper were also prepared by adding 20 mL of 1 mM $\text{Cu}(\text{NO}_3)_2$ per 1 g of zeolite. Samples dried at 105 and 300 °C are referred to as sample 2–1 and sample 2–2, respectively.

Measurements. EPR measurements were performed on a Varian E-122 X-band spectrometer (12 in. magnet). The microwave frequency was determined with an EIP frequency meter, and powdered DPPH was used as a g marker. EPR

* Corresponding author.

† E-mail: hyunso@sogang.ac.kr.

‡ Sogang University.

§ University of Illinois at Urbana-Champaign.

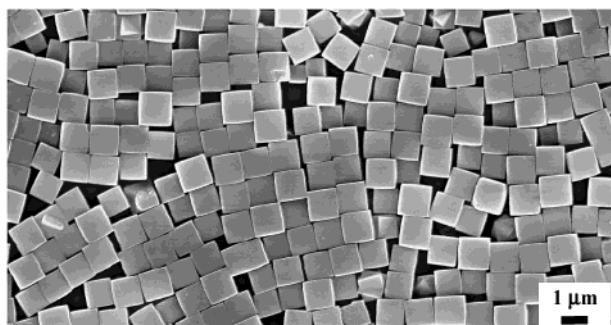


Figure 1. SEM image of a monolayer of copper-exchanged zeolite Na-A crystals covalently bound to a glass plate.

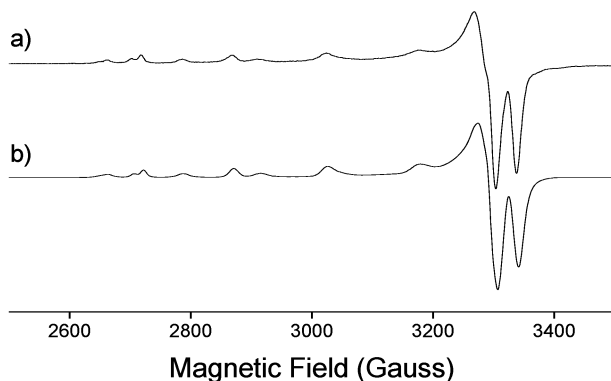


Figure 2. (a) Experimental and (b) simulated EPR spectra of a powder sample of copper-exchanged zeolite Na-A. The experimental spectrum was measured at room temperature.

spectra of powder samples and the crystals assembled on glass plates were measured at room temperature and at 77 K. Five thin glass plates ($3 \times 18 \text{ mm}^2$) were stacked up and attached to a quartz rod in a goniometer, and EPR signals were accumulated 40 times.

Scanning electron microscope (SEM) images of zeolite-coated glass plates were obtained with a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV.

Results

A typical SEM image of a Cu/NaA monolayer on a glass plate is shown in Figure 1. All crystals are aligned with a well-developed face parallel to the glass surface. X-ray diffraction (XRD) studies have shown that both zeolite Na-A and copper-exchanged zeolite Na-A crystals belong to the cubic crystal system.³ The XRD pattern of zeolite Na-A crystals assembled on glass plates revealed only (*h*00) reflections, indicating that the well-developed planes are {100} planes.^{1a,c} So the cubic crystals assemble with one of the three crystal axes normal to the glass surface. The Cu/NaA monolayer consists of small domains in which crystals are oriented in the same direction, but the domains are randomly oriented on the glass surface.

X-band EPR spectra of powder samples of Cu/NaA showed lines from two different copper species, H and D. Species H was predominant for the samples dried at 105 °C for 2 h, but the amounts of species H and D were comparable for the samples dried at 300 °C for 5 h. A powder EPR spectrum of sample 1–2 measured at room temperature is shown in Figure 2a. The spectrum exhibits two sets of four hyperfine features in the low field region, characteristic of the copper nucleus with $I = 3/2$. Additional splitting at the lowest field hyperfine components originates from two isotopes of copper, ⁶³Cu and ⁶⁵Cu (both $I = 3/2$), which are present with natural abundance

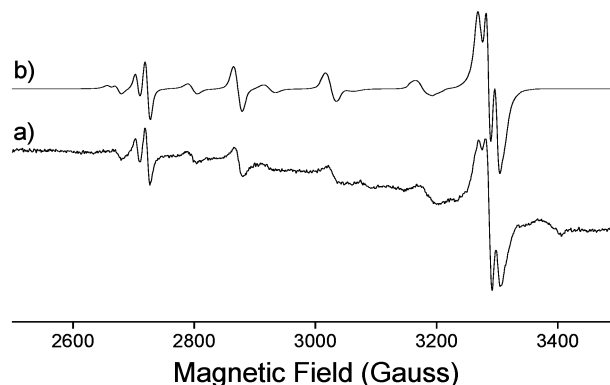


Figure 3. (a) EPR spectrum of copper-exchanged microcrystals of zeolite Na-A assembled on a glass plate with the magnetic field perpendicular to the glass surface measured at room temperature. (b) Simulated spectrum with $g_a = 2.060$, $g_b = 2.069$, $g_c = 2.311$, $A_a = 0.00025$, $A_b = 0.0002$, and $A_c = 0.0162 \text{ cm}^{-1}$ for species H and $g_a = 2.076$, $g_b = 2.079$, $g_c = 2.382$, $A_a = 0.0003$, $A_b = 0.0003$, and $A_c = 0.0138 \text{ cm}^{-1}$ for species D.

of 69.2 and 30.8%, respectively. Also noted is that the width of the parallel lines increases with increasing magnetic field. This was attributed to *g*- and *A*-strains, which are correlated because of linear relationships between the *g*- and *A*-components.^{14–16}

The spectrum was simulated with second-order perturbation equations that assumed coaxial **g** and **A** matrices. The effects of two isotopes of copper and the correlation in *g*- and *A*-strains were included in the simulation.¹⁷ The g_z and A_z values, which could be determined accurately by simulating the low field hyperfine components, are $g_z = 2.311$ and $A_z = 0.0162 \text{ cm}^{-1}$ for species H and $g_z = 2.389$ and $A_z = 0.0139 \text{ cm}^{-1}$ for species D. The individual g_x , g_y , A_x , and A_y values could not be determined accurately due to lack of resolution in the perpendicular region of the spectrum.¹⁸ The relative amount of species D to that of species H was 0.7:1.0 for this sample. This ratio varied for different samples.

EPR spectra of Cu/NaA on glass plates are dependent on the orientation of the magnetic field. When the magnetic field is normal to the glass surface, all crystals are oriented with [100], [010], or [001] parallel to the magnetic field, producing single-crystal-type EPR lines (Figure 3a).¹⁹ The spectrum was simulated by combining single-crystal spectra with the magnetic field parallel to [100], [010], and [001]. Again, the effects of two isotopes of copper and the correlation in *g*- and *A*-strains were included in the simulation.

We designate the three crystal axes as *a*, *b*, and *c* according to $g_a < g_b < g_c$. The *g* and *A* values of species H in the *c* direction ($g_c = 2.311$, $A_c = 0.0162 \text{ cm}^{-1}$) agree exactly with the g_z and A_z values determined from the powder spectrum, indicating that the g_z and A_z directions are parallel to the *c* axis. The *g* and *A* values of species D in the *c* direction ($g_c = 2.382$, $A_c = 0.0138 \text{ cm}^{-1}$) are a little smaller than the EPR parameters, $g_z = 2.389$ and $A_z = 0.0139 \text{ cm}^{-1}$. This indicates that the g_z direction is slightly tilted away from the *c* axis. g_c and A_c are given by

$$g_c^2 = g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \theta \sin^2 \phi + g_z^2 \cos^2 \theta \quad (1)$$

$$A_c^2 g_c^2 = A_x^2 g_x^2 \sin^2 \theta \cos^2 \phi + A_y^2 g_y^2 \sin^2 \theta \sin^2 \phi + A_z^2 g_z^2 \cos^2 \theta \quad (2)$$

where θ and ϕ are the polar and azimuthal angles of the *c* axis, respectively, in the principal frame of the **g** matrix. Since the

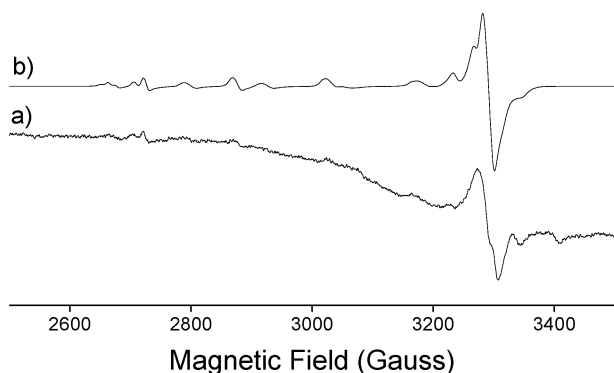


Figure 4. (a) Experimental and (b) simulated EPR spectra of copper-exchanged microcrystals of zeolite Na-A assembled on glass plates with the magnetic field parallel to the glass surface. The experimental spectrum was measured at room temperature.

system is nearly axial, the resulting θ value depends slightly on the ϕ value. Using the parameters determined from the powder spectrum, we get $\theta = 8.8 \pm 0.5^\circ$ for the whole range of ϕ . The relative amount of species D to that of species H is 0.4:1.0 for this sample.

When the magnetic field is parallel to the glass surface, a spectrum quite different from that in Figure 3a is obtained (Figure 4a).¹⁹ This spectrum could be simulated satisfactorily by combining spectra of single crystals randomly rotated around their *a*, *b*, or *c* axis (Figure 4b). The parameters used in the simulation are the same as those used for Figure 3b.

We have tried to generate the species with reversed *g* values by drying the assembled crystals of samples 1-1 and 2-1 in air at 110 °C for 67 h. No species with reversed *g* values were generated; instead, species H changed partly into species D.

Discussion

The EPR parameters of species H ($g_z = 2.311$, $A_z = 0.0162$ cm⁻¹) are very similar to those of the copper species in a hydrated sample reported by Herman ($g_z = 2.316$, $A_z = 0.0162$ cm⁻¹).⁴ However, Narayana and Kevan reported a considerably larger g_z value for the same species ($g_z = 2.352$, $A_z = 0.0157$ cm⁻¹).⁵ Nevertheless, we tentatively assume that species H is closely related with the hydrated species reported by Narayana and Kevan.⁴⁻⁶ The EPR parameters of species D ($g_z = 2.389$, $A_z = 0.0139$ cm⁻¹) agree with those of the copper species in fully dehydrated samples,^{5,6,8-10} and especially well with those of Schoonheydt ($g_z = 2.386$, $A_z = 0.0140$ cm⁻¹)⁸ and Pierloot et al. ($g_z = 2.38$, $A_z = 0.0139$ cm⁻¹).¹⁰

X-ray diffraction studies of highly loaded and dehydrated Cu/NaA samples showed that Cu²⁺ was located predominantly at the center of the plane of the six-ring (site II), coordinated to three O(3) atoms in the ring;³ see Figure 5. These are the oxygen atoms shared between a six- and a four-ring. The Cu–O(3) distance, 0.211 nm, is close to the sum (0.193–0.209 nm) of the ionic radii²⁰ of Cu²⁺ and O²⁻. Sites II* and II' are shifted from site II into the α cage and into the β cage along [111], respectively. All EPR and ESEEM studies located Cu²⁺ at one of these sites. There are three other oxygen atoms, O(2), in the six-ring. The Cu–O(2) distance, 0.296 nm, is too large for the O(2) atoms to bind directly to Cu²⁺ located on the 3-fold axis.

Kevan's group studied the hydrated species using EPR and ESEEM techniques.^{5,7} From analysis of deuterium modulation and aluminum modulation, they suggested that three water molecules are coordinated to Cu²⁺ and that Cu²⁺ is displaced ~ 0.2 nm from the six-ring plane.⁵ Later analysis of cesium modulation from Cs⁺ exchanged into Cu/NaA showed that Cu²⁺

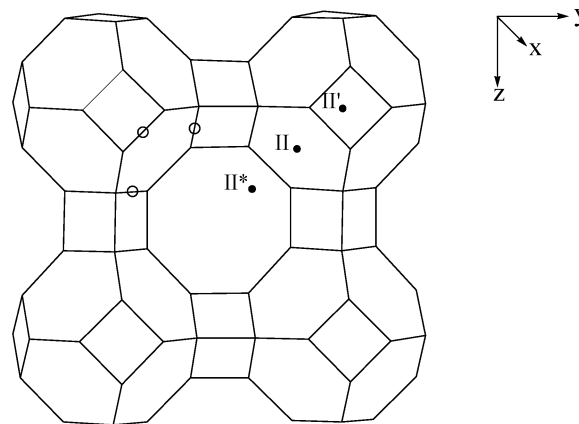


Figure 5. Crystal structure of zeolite A showing probable positions of Cu²⁺. Small circles represent zeolite oxygen atoms, O(3), that may be coordinated to Cu²⁺.

was displaced 0.09 nm from site II into the β cage.⁷ Since all ESEEM analyses were based on the assumption that the g_z direction was parallel to [111], a different g_z direction may produce somewhat different results. While ESEEM results do not agree on the extent of displacement of Cu²⁺ from the six-ring plane, X-ray diffraction studies on copper-exchanged zeolite Y showed consistently that Cu²⁺ is displaced from the six-ring plane to a position where the O(3)–Cu–O(3) angle is close to 90°.²¹

The copper site in the hydrated sample of zeolite Y suggests that Cu²⁺ may occupy a similar site in a hydrated sample of Cu/NaA. If Cu²⁺ is displaced 0.149 nm from the six-ring plane into the β cage along [111], Cu²⁺ and two O(3) atoms form a plane perpendicular to the *c* axis, and the bond between the remaining O(3) and Cu²⁺ is parallel to the *c* axis. If Cu²⁺ is further coordinated to two water molecules in the plane and one water molecule at the axial position located farther than the other aqua ligands, the singly occupied 3d_{x²-y²} orbital of Cu²⁺ will have the maximum probability amplitude at the plane perpendicular to the *c* axis. The g_z direction, determined by spin–orbit coupling, is perpendicular to this plane and thus parallel to the *c* axis.²²

Displacement of Cu²⁺ into the β cage by 0.149 nm would result in a Cu–O(3) distance of 0.258 nm, which is much larger than the sum (0.193–0.209 nm) of the ionic radii²⁰ of Cu²⁺ and O²⁻. However, long Cu–O bonds in the range 0.253–0.258 nm are characteristic of copper complexes in zeolites.²¹ It is interesting to note that a similar octahedral copper complex in the α cage cannot have the g_z direction parallel to the *c* axis because of the orientation of the six-ring plane.

EPR parameters for species D indicate that this species is identical with the fully dehydrated species reported previously by other authors.^{5,6,8-10} On the basis of the absence of deuterium modulation from D₂O and a weak interaction between Cu²⁺ and adsorbed ethylene (C₂D₄) in the ESEEM studies,^{5,23} Kevan's group suggested that Cu²⁺ was located at site II' displaced 0.12 nm from the six-ring plane into the β cage and coordinated to three O(3) atoms.^{11,23}

On the other hand, Schoonheydt located Cu²⁺ in the dehydrated species at site II on the basis of the diffuse reflectance spectrum.⁸ When Cu²⁺ is in a trigonal plane, the plane of maximum probability amplitude of the singly occupied 3d orbital coincides with the trigonal plane and the g_z direction invariably is perpendicular to this plane.²⁴ It is well-known that Cu²⁺ has a strong preference for a square planar coordination, and ab initio calculations on a copper complex in the six-ring

plane have suggested that Cu^{2+} is coordinated to three O(3) and one O(2), forming a distorted square plane.^{10,13} Still, as long as Cu^{2+} lies in the six-ring plane, the g_z direction should be parallel to [111], contrary to our finding that it is tilted only 9° away from the c axis.

A trigonal complex with Cu^{2+} displaced from the six-ring plane into the β cage is more compatible with our finding. When zeolite samples are fully dried, and all water molecules coordinated to Cu^{2+} in species H are removed, Cu^{2+} probably moves slightly toward the O(3) atoms. In the resulting trigonal complex with Cu^{2+} out of the trigonal plane, the plane of maximum probability amplitude of the singly occupied 3d orbital at copper may be closer to the plane spanned by Cu^{2+} and two ligand atoms than that spanned by three ligand atoms.²⁴ Then the trigonal copper complex can have the g_z direction slightly tilted from the c axis.

We have shown that single-crystal-type EPR spectra can be obtained from monolayers of micrometer-sized zeolite crystals assembled on glass plates. The g_z directions of two copper species in zeolite Na-A were determined experimentally for the first time. The g_z direction of species H is compatible with an octahedral complex in the β cage, and that of species D is compatible with a trigonal complex in the β cage, but not with a trigonal or square planar complex with Cu^{2+} in the six-ring plane. This new technique may be useful in characterizing paramagnetic species in other compounds whose microcrystals can be assembled on glass plates or other substrates.

Acknowledgment. We thank the U.S. NIH-Research Resources program for facilities and support (RR-01811, R.L.B.). H.S. thanks Sogang University for University Research Grant (2001) and financial support during a sabbatical leave. K.B.Y. thanks the Ministry of Science and Technology of Korea for financial support through the Creative Research Initiatives Program.

References and Notes

(1) (a) Kulak, A.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 950. (b) Choi, S. Y.; Lee, Y.-J.; Park, Y. S.; Ha, K.; Yoon, K. B. *J. Am. Chem. Soc.* **2000**, *122*, 5201. (c) Ha, K.; Lee, Y.-J.; Lee, H.-J.; Yoon, K. B. *Adv. Mater.* **2000**, *12*, 1114. (d) Lee, G. S.; Lee, Y.-J.; Ha, K.; Yoon, K. B. *Tetrahedron* **2000**, *56*, 6965. (e) Kulak, A.;

Park, Y. S.; Lee, Y.-J.; Chun, Y. S.; Ha, K.; Yoon, K. B. *J. Am. Chem. Soc.* **2000**, *122*, 9308. (f) Lee, G. S.; Lee, Y.-J.; Yoon, K. B. *J. Am. Chem. Soc.* **2001**, *123*, 9769.

(2) Zhu, G.; Qiu, S.; Yu, J.; Sakamoto, Y.; Xiao, F.; Xu, R.; Terasaki, O. *Chem. Mater.* **1998**, *10*, 1483.

(3) (a) Reed, T. B.; Breck, D. W. *J. Am. Chem. Soc.* **1956**, *78*, 5972. (b) Lee, H. S.; Seff, K. *J. Phys. Chem.* **1981**, *85*, 397.

(4) Herman, R. G. *Inorg. Chem.* **1979**, *18*, 995.

(5) (a) Kevan, L.; Narayana, M. In *Intrazeolite Chemistry*; Stucky, G. D., Dwyer, F. G., Eds.; ACS Symposium Series 218; American Chemical Society: Washington, DC, 1983; p 283. (b) Narayana, M.; Kevan, L. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 213.

(6) Packet, D.; Schoonheydt, R. A. In *Structure and Reactivity of Modified Zeolites*; Jacobs, P. A., Jaeger, N. I., Jiru, P., Kazanski, V. B., Schulz-Ekloff, G. Eds.; Elsevier: Amsterdam, 1984; p 41.

(7) Anderson, M. W.; Kevan, L. *J. Phys. Chem.* **1987**, *91*, 1850.

(8) Schoonheydt, R. A. *J. Phys. Chem. Solids* **1989**, *50*, 523.

(9) Matar, K.; Goldfarb, D. *J. Phys. Chem.* **1992**, *96*, 3100.

(10) Pierloot, K.; Delabie, A.; Groothaert, M. H.; Schoonheydt, R. A. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2174.

(11) Kevan, L. *Rev. Chem. Intermed.* **1987**, *8*, 53.

(12) Schoonheydt, R. A. *Catal. Rev.—Sci. Eng.* **1993**, *35*, 129.

(13) Delabie, A.; Pierloot, K.; Groothaert, M. H.; Schoonheydt, R. A.; Vanquickenborne, L. G. *Eur. J. Inorg. Chem.* **2002**, 515.

(14) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691.

(15) Froncisz, W.; Hyde, J. S. *J. Chem. Phys.* **1980**, *73*, 3123.

(16) Carl, P. J.; Larsen, S. C. *J. Phys. Chem. B* **2000**, *104*, 6568.

(17) The slope of the linear relationship for g_z and A_z , $\text{slope}_z = -0.039 \text{ cm}^{-1}$, was taken from ref 14, and $\text{slope}_{x \text{ or } y} = -0.075 \text{ cm}^{-1}$ was estimated from representative copper complexes. Then the strains in g_i and A_i can be expressed as $g_i = g_{i,\text{mean}} + \Delta g_i$ and $A_i = A_{i,\text{mean}} + \Delta g_i(\text{slope}_i)$.

(18) The parameters used in the simulation are $g_x = 2.062$, $g_y = 2.071$, $A_x = 0.00025$, and $A_y = 0.0002 \text{ cm}^{-1}$ for species H and $g_x = 2.068$, $g_y = 2.079$, $A_x = 0.0003$, and $A_y = 0.0003 \text{ cm}^{-1}$ for species D.

(19) A line at 3400 G comes from an unidentified impurity in sample 2–2. This line is much weaker for sample 1–2.

(20) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. The ionic radius depends on the coordination number of the ion.

(21) (a) Maxwell, I. E.; de Boer, J. J. *J. Phys. Chem.* **1975**, *79*, 1874. (b) Fowkes, A. J.; Ibberson, R. M.; Rosseinsky, M. J. *Chem. Mater.* **2002**, *14*, 590.

(22) A square planar or pyramidal complex with Cu^{2+} located on the 4-fold axis in the β cage and coordinated to the four oxygen atoms of the four-ring would have the g_z direction parallel to the c axis. Although the X-ray crystal structure of the copper-exchanged zeolite A revealed no such copper site (ref 3b), the existence of such a complex cannot be ruled out completely.

(23) Ichikawa, T.; Kevan, L. *J. Am. Chem. Soc.* **1981**, *103*, 5355.

(24) van Gastel, M.; Boulanger, M. J.; Canters, G. W.; Huber, M.; Murphy, M. E. P.; Verbeet, M. Ph.; Groenen, E. J. J. *J. Phys. Chem. B* **2001**, *105*, 2236.