MÖSSBAUER STUDY OF ^{57}Fe ISOLATED IN
NH$_3$ AND NH$_3$/Xe MATRICES

by

E. Baggio-Saitovitch[1], F.J. Litterst[2]

and

H. Micklitz[3]

1. Centro Brasileiro de Pesquisas Físicas/CNPq
   Av. Wenceslau Braz, 71, fundos
   22290 - Rio de Janeiro - R.J. - BRAZIL

2. Physik Department, Technische Universität München,
   D 8046 Garching, Fed. Rep. Germany

3. Institut für Experimentalphysik IV, Ruhruniversität,
   D 4630 Bochum, Fed. Rep. Germany

ABSTRACT

Mössbauer studies on ^{57}Fe isolated in solid ammonia and
ammonia/xenon mixtures were perfomed at 4.2 K and 77 K. They show
clearly that atomic iron reacts only with one ammonia molecule
forming $FeNH_3$ which is stable in an ammonia matrix up to 77K. In
addition a compound is formed which is attributed to an iron(II)
hexammine.

INTRODUCTION

Mössbauer spectroscopy was used in a series of experiments[1-4] for characterizing the products from cryochemical reactions of metal atoms or clusters trapped in frozen gas matrices. Barrett and co-workers, for example showed[1,2] that iron <u>atoms</u> do not react with nitrogen or methane, when they are co-deposited with these matrix gases onto substrates at 4.2 K. In contrast iron dimer <u>molecules</u> do react. In ammonia matrices, however, the iron <u>atoms</u> react[3], form ing a molecule of the form $Fe(NH_3)_n$. Photolysis experiments suggest that the reaction takes place between the iron atom and one ammonia molecule, i.e. that $FeNH_3$ is formed.

For a better understanding of the reaction between the iron atoms and ammonia molecules we have perfomed Mössbauer studies on isolated ^{57}Fe atoms in an ammonia matrix and in xenon matrices to which different amounts of ammonia had been added. Furthermore we have studied the stability of the reaction products by warming up the matrices from 4.2 K to 77 K.

EXPERIMENTAL

We have perfomed Mössbauer absorption experiments of ^{57}Fe isolated in ammonia and mixed xenon/ammonia matrices with 2 mole% and 10 mole% ammonia concentration. The cryostat used for the preparation of the gas matrix isolated species is similar to that described already in the literature[5]. The matrices were simultaneously condensed from an atomic beam of iron and the gas onto a Be disk kept at 7 K. The iron was evaporated from an alumina crucible. Its concentration was about 0.1 mole% for pure ammonia and about 0.5 mole% for the Xe/NH_3 matrices. The appropriate gas mixtures were prepared outside the cryostat.

RESULTS

The Mössbauer absorption spectra for ^{57}Fe isolated in xenon matrices containing 2% and 10% of ammonia obtained at 4.2 K (figure 1) are superpositions of a single absorption line and a quadrupole doublet (I). The single resonance line has an isomer shift S of -0.72 mm/s (relative to iron metal at room temperature) which is very close to the value measured for iron isolated in a pure xenon matrix[5/6]. It is thus attributed to monomeric iron which is surrounded only by xenon atoms as nearest neighbours. The dependence of the Mössbauer spectra on the ammonia content of the matrix is shown in figure 1: the relative intensity of the absorption associated with the doublet I increases with the ammonia concentration. The same doublet I appears also in the spectra of ^{57}Fe in the pure ammonia matrix. About 78% of the total absorption area is due to this quadrupole doublet. In addition we find a less intense second quadrupole doublet (II). On warming the pure ammonia matrix to 77 K the intensity of doublet II increases at the expense of doublet I (see figure 2).

The spectra of iron isolated in xenon containing 2% ammonia obtained at 4.2 K and 77 K are compared in figure 3: at 77 K the absorption lines of doublet II, already observed in the pure ammonia matrix, and a further doublet (III) are found; the monomer resonance and doublet I present in the spectrum at 4.2 K give no apparent contribution.

In table 1 we have collected all hyperfine parameters concerning the different studied matrices and temperatures. The isomer shift and the quadrupole interaction, for the doublet I, are nearly identical to those given in ref. 3 for the reaction product

of iron in ammonia. It should be noted that the doublets II and III were not observed in the photolysis experiments perfomed at 4.2 K. On the other hand, the reaction products formed there ($FeNH_2$ and FeNH) do not occur in the present experiments. Also complexes which are supposed to contain more than one iron atom as found[3] in ammonia matrices with higher iron concentration were not detected.

DISCUSSION

Ammonia is not an inert matrix and reacts chemically with iron atoms to form mainly a compound, associated with doublet I, which has a temperature independent quadrupole splitting. From the hyperfine parameters it is not possible to assign any high-spin $3d^6$ or $3d^7$ eletronic configuration to the iron. Its isomer shift is also too high to consider any strongly covalent bonding.

The observation of the same compound,when iron is isolated in xenon matrices with 2% and 10% ammonia concentration, suggests that even few ammonia molecules are sufficient to form the referred compound. We have calculated,for the xenon/ammonia matrices, the probabilities for the following nearest neighbour (nn) configurations for an iron atom in a substitutional site of the fcc matrix lattice,assuming a statistical distribution : a) iron with no NH_3 as nn; b) iron with one NH_3 as nn; c) iron with two NH_3 as nn. In table 2 we show the calculated and the experimentally determined ratios J_Q/J_M of the relative intensities of the doublet I (J_Q) and of the single resonance (J_M) of the monomer. The recoilfree absorbed fractions (Mössbauer - Lamb factors) for both,the monomer and the reaction product were assumed to be equal. A possibility higher recoilfree fraction

of the reaction product, would slightly increase the calculated ratios J_Q/J_M. The numbers of table 2 indicate that if two ammonia molecules were needed to form the iron compound, it should be impossible to observe doublet I in a xenon matrix with 2% of ammonia, as we did. Thus we propose the compound $FeNH_3$ to be formed in solid ammonia and in the xenon/ammonia mixtures which is in agreement with the conclusions from the photolysis experi-ments[3]. The fact that the experimental value of J_Q/J_M, found in the matrix with 10% ammonia, is smaller than expected for the $FeNH_3$ formation, can be attributed to some clustering of ammonia during deposition.

The hyperfine parameters of the quadrupole doublet II are close to those known for an iron (II) hexammine[7]. For the sta-bilization of such a compound, however, two negative ions are needed outside the ammonia octahedron. From the temperature de-pendence, of the relative intensity of doublet II, we see that this iron (II) hexammine complex is more easily formed in a $(NH_3)_{.02}Xe_{.98}$ matrix, at the expense of the monomeric iron, than in a pure ammonia matrix at 77 K. This result is consistent with a diffusion of the stabilizing negative ions previous to the reaction. The diffusion can more easily take place in a xenon matrix than in an ammonia matrix at 77 K, since the latter is more rigid at this temperature. In the pure ammonia matrix only the negative ion should diffuse, whereas in the xenon matrix also the ammonia should do it so as to achieve six ammonia as iron nearest neighbours. Indeed the size of an ammonia molecule should allow an unrestricted diffusion in a xenon matrix at 77K.

The presence of some iron (II) hexammine, even in the pure ammonia matrix at 4.2 K, could be due to stabilizing negative

negative impurity ions which are trapped to an iron (II) hexammine configuration, already during the condensation process. Tentative assignments for the negative ions would be O_2^- impurities or NH_2^- which can be formed during condensation.

The hyperfine parameters of the further reaction product, associated with doublet III found on heating in the xenon/ammonia matrix, can tentatively be attributed to ferric ions surrounded by distorted oxygen tetrahdra (like in several amorphous oxides[8]).

CONCLUSION

Atomic iron isolated in solid ammonia or xenon/ammonia, re acts with one ammonia molecula forming the compound $FeNH_3$. In an ammonia matrix this compound is quite stable even at 77 K. In addition a smaller contribution from another compound is found in the ammonia matrix at 4.2 K which can be assigned to some iron (II) hexammine. It can also be formed in the xenon/ammonia matrix at 77 K at expense of the iron monomer (and possibly also of the $FeNH_3$).

We propose that $FeNH_3$ is formed due to a reaction in the condensation zone of the matrix during deposition, where both iron and matrix gas are not yet completely thermalized down. The reactions occurring at 77 K, however, which need preliminar diffusion (production of hexammine from the iron monomer), can be termed as real low temperature reactions.

REFERENCES

1. P.H. Barrett and P.A. Montano, J.Chem.Soc.Faraday Trans.II 73
   (1977) 378.

2. P.H. Barrett, M. Pasternak and R.G. Pearson, J.Am.Chem. Soc.
   101 (1979) 222.

3. P.H. Barrett and M. Pasternak, J.Chem.Phys. 71 (1979) 3837.

4. M. Pasternak and P.H. Barrett, J.Physique 41 C1 (1980) 79.

5. T.K. McNab and P.H. Barrett, in: Mössbauer Effect Methodology,
   Vol.7, ed.I.J. Gruverman (Plenum, New York, 1971) p.59.

6. T.K. McNab, H. Micklitz and P.H. Barrett, Phys. Rev. B4 (1971)
   3781.

7. G.M. Bancroft, M.J. Mays and B.E. Prater, Chem. Phys. Lett. 4
   (1969) 248.

8. J.M.D. Coey, J.Physique 35 C6 (1974) 89

Table 1

Hiperfine parameters of ^{57}Fe isolated in solid ammonia and in xenon/ammonia mixtures, T(K) is temperature, s(mm/s) is the isomer shift rel. iron metal at room temperature, QS(mm/s) is the quadrupole splitting $1/2\ e^2qQ$, W(mm/s) is the experimental linewidth, J is the intensity of the respective component normalized to the total intensity of the absorption spectrum.

matrix	T	monomer			doublet I				doublet II				doublet III			
		S	W	J	S	QS	W	J	S	QS	W	J	S	QS	W	J
NH$_3$	4.2				.67	2.0	.47	.78	1.29	2.23	.99	.38				
	77				.65	2.0	.53	.64	1.17	2.42	.91	.36				
(NH$_3$)$_{.02}$Xe$_{.98}$	4.2	-.72	.72	.71	.60	1.89	1.50	.29								
	77								1.18	2.49	.99	.48	.32	1.0	.87	.52
(NH$_3$)$_{.10}$Xe$_{.90}$	4.2	-.72	.43	.53	.60	1.72	.67	.47								

typical errors: S: ± 0.02mm/s; QS: ± 0.02 mm/s; W: ± 0.02 mm/s; J: ± 5%

Table 2

Calculated and experimentally determined ratios of the intensity of the doublet I (J_Q) and of the single resonance (J_M) of the monomer. The calculated ratios are for one and two NH_3 nearest neighbours (nn) of the iron atom, respectively.

matrix	J_Q / J_M		experimental
	calculated		
	one NH_3 nn	two NH_3 nn	
$(NH_3)_{.02}Xe_{.98}$	.27	.05	.4
$(NH_3)_{.10}Xe_{.90}$	2.5	1.2	.9

FIGURE CAPTIONS

Figure 1: Mössbauer absorption spectra of 0.5 mole% ^{57}Fe ($\sim 0.02\,mg/cm^2$) in $(NH_3)_{.02}Xe_{.98}$ (a) and $(NH_3)_{.10}Xe_{.90}$ (b) at 4.2 K. Source: 20 mCi ^{57}CoRh at room temperature.

Figure 2: Mössbauer absorption spectra of 0.1 mole% ^{57}Fe ($\sim 0.02\,mg/cm^2$) in NH_3 at 4.2 K (a) and 77 K (b). Source: 20 mCi ^{57}CoRh at room temperature.

Figure 3. Mössbauer absorption spectra of 0.5 mole% ^{57}Fe ($\sim 0.02\,mg/cm^2$) in $(NH_3)_{.02}Xe_{.98}$ at 4.2 K (a) and 77 k(b). Source: 20 mCi ^{57}CoRh at room temperature.
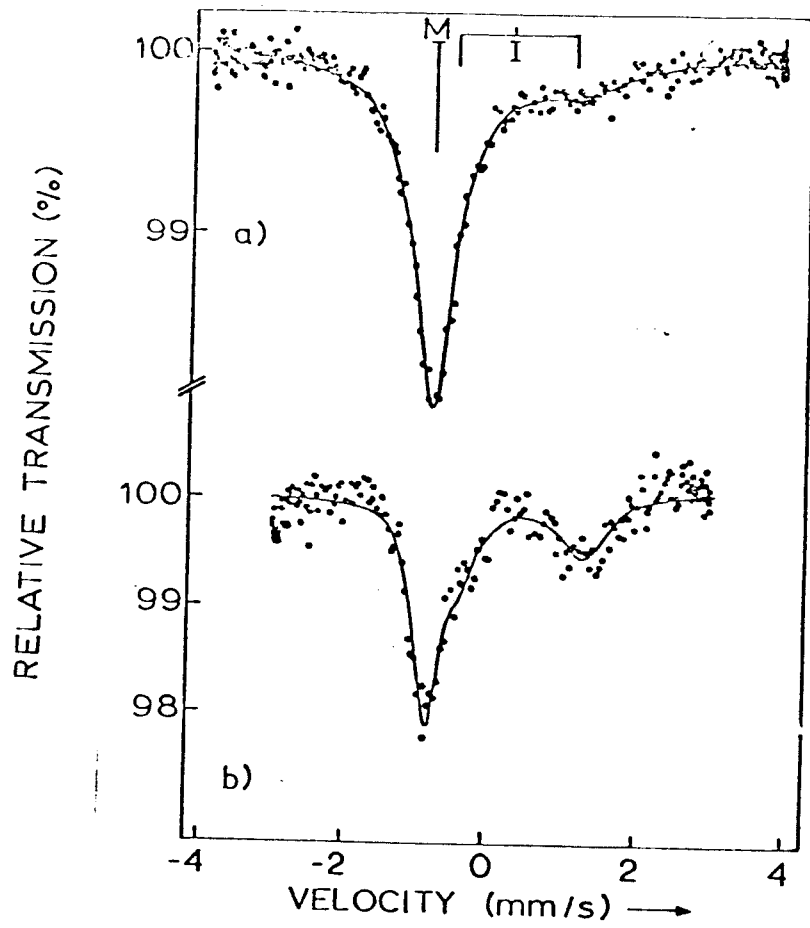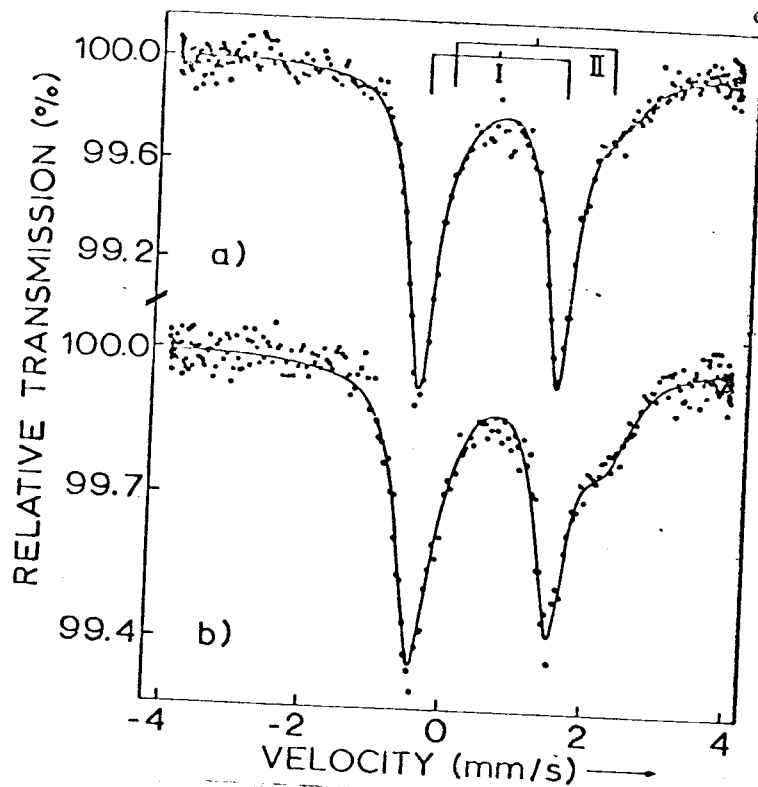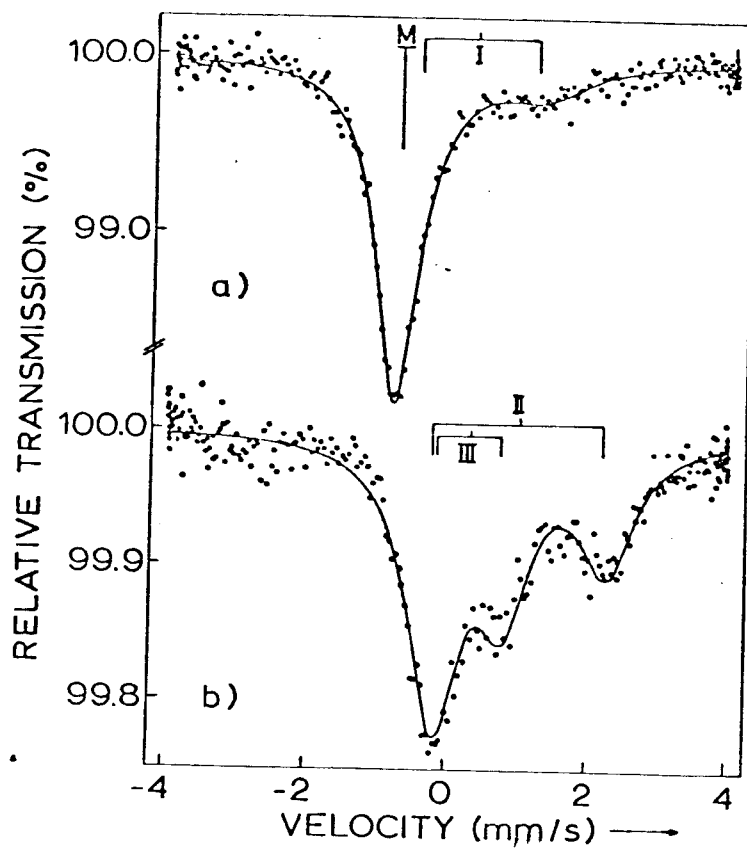
FIG. 1

FIG. 2

FIG. 3