Mössbauer Study of Matrix Isolated Iron Fluorides Produced by a Reaction of Laser-Evaporated Iron Atom and Sulfur Hexafluoride

Yasuhiro Yamada and Keiichi Katsumata

Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

(Received April 4, 2000; CL-000312)

The reaction-products of laser-evaporated iron atoms with sulfur hexafluoride SF_6 were isolated in a low-temperature matrix and their Mössbauer spectra obtained. Fe_2F_6 molecules were produced in a pure SF_6 matrix, whereas FeF_3 and Fe_2F_4 were also produced in a diluted SF_6/Ar matrix. A molecular orbital calculation supports the assignment of the species.

Laser-evaporated iron atoms are translationally and electronically high in energy and react with various gases to produce novel species that are not obtainable under normal conditions. We have studied the reaction of laser-evaporated iron atoms with oxygen or nitrogen molecules, and the novel iron oxide or iron nitride species trapped in low-temperature matrices were investigated by means of Mössbauer and infrared spectrscopies.[1,2] In this study, we investigate the reaction of laser-evaporated iron atoms with SF_6 gas. Though SF_6 gas is generally inert and stable, it releases F atoms by the reaction of highly-energetic iron atoms to produce iron fluoride particles. Mössbauer spectroscopy provides useful information about the electronic structures, such as valence and spin states of the novel iron fluoride species trapped in low-temperature matrices.

Details of the experimental setup are described elsewhere.[1] Briefly, laser-evaporated iron atoms were produced by the pulsed laser light (248 nm, 200 mJ/pulse, 20 ns) of a KrF excimer laser (Lambda Physik EMG101MSC) focused on a ^{57}Fe iron block. The iron atoms were mixed with the matrix gas that was introduced by a magnetic pulse valve and condensed onto an aluminum plate cooled to 17 K using a closed cycle helium refrigerator. Mössbauer spectra were measured in a transmission geometry using a ^{57}Co/Rh source. All the Mössbauer and infrared measurements were performed at 17 K.

In Figure 1, the Mössbauer spectrum of laser-evaporated iron atoms condensed with pure SF_6 gas on an Al plate (17K) is shown. The molar ratio of the sample was $^{57}Fe/SF_6 = 1/300$. A set of doublet absorption peaks (species **A**) was observed as the main product trapped in the SF_6 matrix, as well as a sextet set which has the same Mössbauer parameters as α-iron assigned to large metallic iron particles produced by the laser-ablation. Neither Fe atoms nor Fe_2 dimers were observed in the spectrum, indicating that most of the small Fe species reacted with SF_6 to form species **A**. The Mössbauer isomer shift δ of species **A** suggests that it is a trivalent iron species. The highly energetic iron atom breaks the SF_6 gas molecule to produce F atoms in the gas phase and to form iron fluorides that are trapped in the low-temperature SF_6 matrix. The temperature of this sample was increased to 60 K for 24 h and then lowered to 17 K in order to observe the effects of annealing. No change in the Mössbauer spectrum was observed, indicating that species **A** was stable even at 60 K. The Mössbauer parameters observed in this study, as well as other related iron–halide species vaporized by resistive heating reported in literature,[4] are summarized in Table 1. Species **A** has a larger ΔE_q than that of amorphous FeF_3 produced by the reaction of an Fe atom and HF reported in the literature[3] ($\delta = 0.45$ mm/s, $\Delta E_q = 0.60$ mm/s at 77 K), and thus it should be a small particle rather than amorphous. As vapor produced by the sublimation of solid $FeCl_3$ contains dimeric Fe_2Cl_6, dimeric Fe_2F_6 may also be stable in the gas phase. We assigned species **A** as Fe_2F_6 by analogy to Fe_2Cl_6.

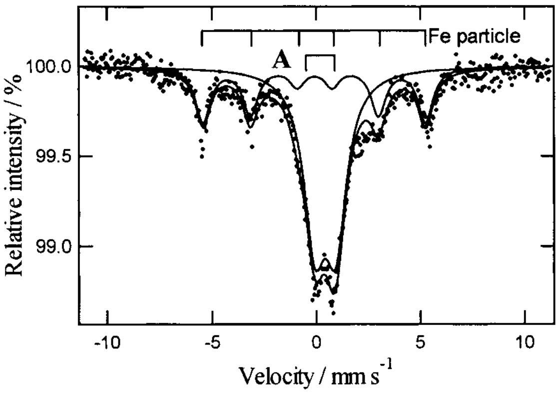

Figure 1. Mössbauer spectrum at 17 K of laser-evaporated iron atoms condensed in SF_6 matrix. Molar ratio is $^{57}Fe/SF_6 = 1/300$.

Table 1. Mössbauer parameters at 17 K of iron fluoride species observed in this study and other iron halide reported in literature, and calculated electronic properties using HF/6-311G

Species	Observed Mössbauer parameters mm s^{-1}		Calculated electronic properties a. u.	
	δ	ΔE_q	ρ(0) -1500	|EFG|
Fe_2F_6 **A**	0.53 ± 0.10	1.02 ± 0.10	92.03	1.87
FeF_3 **B**	0.68 ± 0.10	2.86 ± 0.10	92.44	2.89
Fe_2F_4 **C**	1.31 ± 0.10	2.72 ± 0.10	90.61	3.66
FeF_2			91.13	0.43
$FeCl_2$	0.88 ± 0.02[a]	0.63 ± 0.02[a]	91.32	0.73
Fe_2Cl_4	1.10 ± 0.05[a]	2.80 ± 0.10[a]	90.90	3.05
$FeBr_2$	0.81 ± 0.02[a]	0.86 ± 0.02[a]	91.67	0.90
Fe_2Br_4	0.99 ± 0.05[a]	3.10 ± 0.10[a]	91.25	2.97
Fe_2Cl_6	0.35 ± 0.01[a]	2.00 ± 0.01[a]	92.91	1.32

[a] Reported at 5 K in the literature.[4]

We also performed experiments using a diluted matrix gas: the SF_6 gas was diluted in Ar gas and introduced with laser-evaporated iron atoms to form a matrix-isolated sample. The Mössbauer spectrum of the sample is shown in Figure 2a. The molar ratio of the sample was $^{57}Fe/SF_6/Ar = 1/1/480$. Species

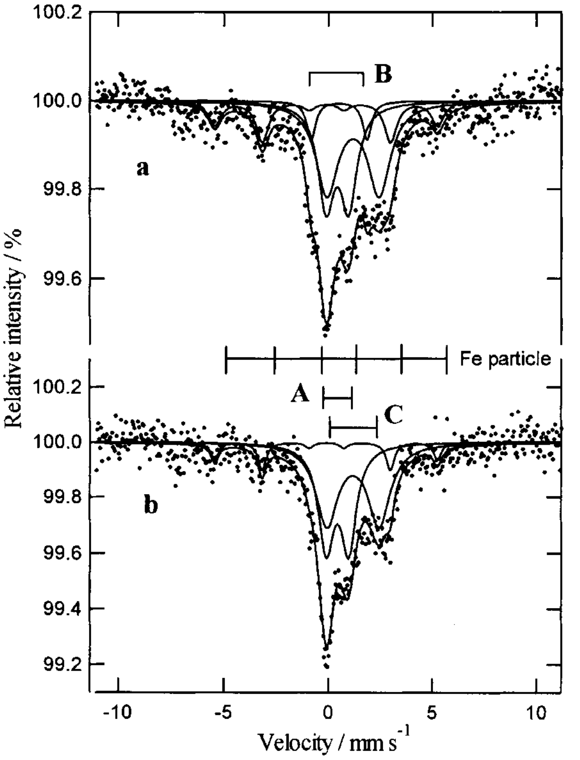

Figure 2. Mössbauer spectrum at 17 K of laser-evaporated iron atoms condensed with SF_6 in Ar matrix (a), and the spectrum obtained after annealing at 30 K for 30 h (b).
Molar ratio is $^{57}Fe/SF_6/Ar=1/1/480$.

A, as well as two other species (species **B** and species **C**), can be observed in the spectrum. Their Mössbauer isomer shifts δ suggest that species **B** is a trivalent iron species and species **C** is a high-spin divalent iron species. This sample was annealed at 30 K for 30 h and the Mössbauer spectrum again recorded at 17 K (Figure 2b). The intensity of species **B** decreased and that of species **A** increased, indicating that species **B** migrates in the matrix to form species **A** on annealing. The intensity of species **C** did not change. Species **B** was assigned as monomeric FeF_3, because it has a large ΔE_q value and formed Fe_2F_6 on annealing. When iron atoms and SF_6 are diluted in Ar, iron atoms have the opportunity to produce unstable monomeric FeF_3 (species **B**). For the divalent species, only one species **C** was observed in the experiment, and it was stable on annealing. In the diluted SF_6/Ar matrix, the concentration of released F atoms was low, and therefore divalent species were produced. Species **C** may be FeF_2 or Fe_2F_4 because it is produced under the condition in which FeF_3 and Fe_2F_6 are produced. The Mössbauer spectra of monomeric $FeCl_2$ or $FeBr_2$ in low-temperature matrices have been reported to possess small quadruple splittings[4] (Table 1) and thus species **C** may not be monomeric FeF_2. Though solid FeF_2 has a large quadrupole splitting (ΔE_q= 2.68 mm/s), species **C** did not show magnetic splitting at 17 K and is not a large particle: the Néel temperature of solid FeF_2 is 78 K.[6] We assigned species **C** as Fe_2F_4 from comparison with reported Fe_2Cl_4 and Fe_2Br_4, which are bridged-structured dimers. No sulfide species was found in this study.

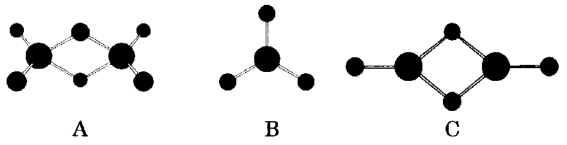

Figure 3. Structures of the species.

We performed ab initio molecular orbital calculations of the species using the Gaussian 98[7] program with HF/6-311G (Figure 3). We previously reported molecular orbital calculations of Mössbauer parameters for iron species isolated in low-temperature matrices,[5] and the procedure used in the present study was similar to that reported previously. The calculated ρ(0) and |EFG| at an iron nucleus should have a linear correlation with observed δ and ΔE_q, respectively. The calculated ρ(0) and |EFG| of the iron halide species are summarized in Table 1. The EFG value of the monomeric FeF_3 was calculated to be large, which is in agreement with the observed large ΔE_q value. Molecular orbital calculations suggest that dimeric Fe_2F_6 is more stable than monomeric FeF_3 by 67.8 kcal/mol from the comparison of ground states energies. The calculated EFG for monomeric FeF_2 was too small to interpret the observed species **C**; species **C** proved to be Fe_2F_4 with bridged F atoms. We obtained a good correlation of δ–ρ(0) and ΔE_q–EFG, listed in Table 1, which supports the assignments of species **A**, **B**, and **C**.

References

1 Y. Yamada, H. Sumino, Y. Okamura, H. Shimasaki, and T. Tominaga, *Appl. Radiat. and Isot.*, **52**, 49 (2000).

2 Y. Yamada and T. Tominaga, *Hyperfine Interact.*, **112**, 189 (1998).

3 S. F. Parker, C. H. F. Peden, P. H. Barrett, and R. G. Pearson, *J. Am. Chem. Soc.*, **106**, 1304 (1984).

4 F. J. Litterst, A. Schichl, and G. M. Kalvius, *Chem. Phys.*, **28**, 89 (1978).

5 Y. Yamada and T. Tominaga, *Radiochim. Acta*, **80**, 163 (1998).

6 G. K. Wertheim and D. N. E. Buchanan, *Phys. Rev.*, **161**, 478 (1967).

7 Gaussian 98, A.6., Gaussian Inc., Pittsburgh PA, U.S.A., 1998.