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Matrix Isolation Study of FeMn Molecules

Sir

Recently the matrix isolation technique has been used in conjunction with the Mössbauer effect to study "almost free" atoms and molecules.^{1,2} The main purpose of those experiments was to determine the isomer shift (IS) calibrations. By modifying the matrix isolation technique so that poor isolation is obtained, one may produce dimer and higher aggregate species which are of great interest in areas such as nucleation, surface physics and chemistry, alloying, and heterogeneous catalysis.³ The first stage in these studies should be to examine the simplest molecules, the homonuclear diatomic molecules. There have been several studies of diatomic molecules both in the gas phase and isolated in rare gas solids.⁴ Several studies of heteronuclear diatomic molecules using different spectroscopic techniques have been published by various groups.⁵ In this work we want to report a Mössbauer study of matrix isolated iron-manganese molecules. From the Mössbauer parameters we are able to determine the electronic ground state of the FeMn molecule.

The samples were made in a liquid-helium cryostat evacuated to a pressure of $<10^{-7}$ Torr. The Mn and (90% enriched) ⁵⁷Fe atomic beams were produced in alumina crucibles contained in resistance heated tantalum furnaces and codeposited with a stream of Ar gas at ~ 4.2 K onto a Be disk; the rare gas deposition rate being monitored by the attenuation of the

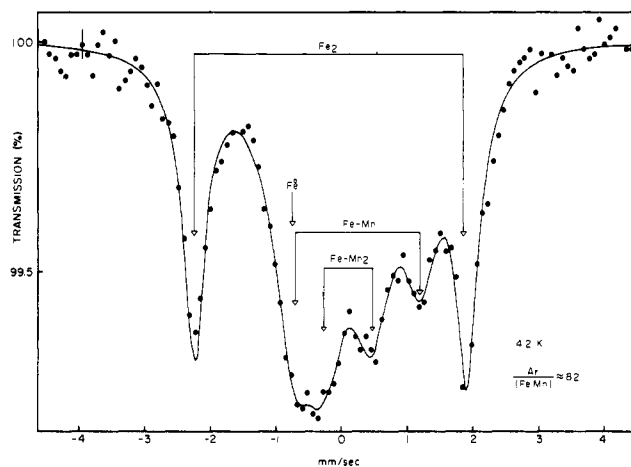


Figure 1. Mössbauer spectrum of (FeMn)-Ar at 4.2 K, 1.2 at. % metal concentration (continuous line is the fit to the experimental data).

6.3-keV X-ray of a ⁵⁷Co/Pd source, the metal deposition rates being calculated through previously determined collection efficiencies. Mössbauer spectra were obtained with a conventional constant acceleration spectrometer using the same source as above. An iron foil was used for calibration purposes and the zero velocity is given with respect to this absorber. Mössbauer spectra were taken for two different metal concentrations, 1.2 and 3 at. % metal in argon. The spectra were analyzed using a nonlinear least-squares fitting program and assuming Lorentzian line shapes.

The Mössbauer spectrum for the 1.2 at. % metal sample is shown in Figure 1. The Fe:Mn ratio for this sample was $\sim 1:1$. In this figure the presence of iron monomers and iron dimers (Fe₂) can be easily identified by their respective IS, -0.75 mm/s for Fe⁰ and -0.14 mm/s for Fe₂.¹ The iron dimer also has a characteristic quadrupole splitting (QS) of 4.09 ± 0.03 mm/s. The best fit to the spectrum is obtained when two extra doublets are considered. One has an IS of 0.24 ± 0.03 mm/s and a QS of 1.93 ± 0.03 mm/s and is indicated in Figure 1 as FeMn. The identification of this doublet as FeMn comes from its concentration dependence, the magnitude of the QS and IS, and its comparison with the values obtained for FeNi⁶ (QS = 1.95 ± 0.03 mm/s, IS = -0.54 ± 0.03 mm/s). One major difference between the FeNi and the FeMn molecules is that the latter has a more positive IS. The relative iron concentration in the argon matrix was 0.5 at. %, and no iron trimers are detectable using Mössbauer spectroscopy at this iron concentration.^{1,6}

There is another doublet in Figure 1 that we have tentatively identified as FeMn₂ (and/or Fe₂Mn). This doublet is characterized by an IS = 0.10 ± 0.03 mm/s and a QS = 0.74 ± 0.03 mm/s. The ratio of the areas of the two doublets was $\sim 1:1$, with the line width for the triatomic molecule equal to 0.76 mm/s, broader than that of FeMn and Fe₂. This broadening of the line suggests different geometrical configurations for the triatomic molecule. However, both Fe₂Mn and FeMn₂ are equally probable at the concentration used and the broadening of the lines could be produced by slightly different IS and QS for the two molecules.

In order to further study the concentration dependence of the iron-manganese molecules, we carried out measurements at a higher metal to argon ratio (metal/argon, 1:30). In this case the ratio of iron to manganese was 1:3 and consequently the only pure iron species we were able to observe were Fe⁰ and Fe₂; however, larger multimers of iron-manganese are possible. Trimers and higher multimers of iron become detectable by Mössbauer spectroscopy only at concentrations higher than 1.5 at. %; consequently the contribution of Fe₃ to the spectrum in Figure 2 is negligible. However, Fe₃ may appear after an

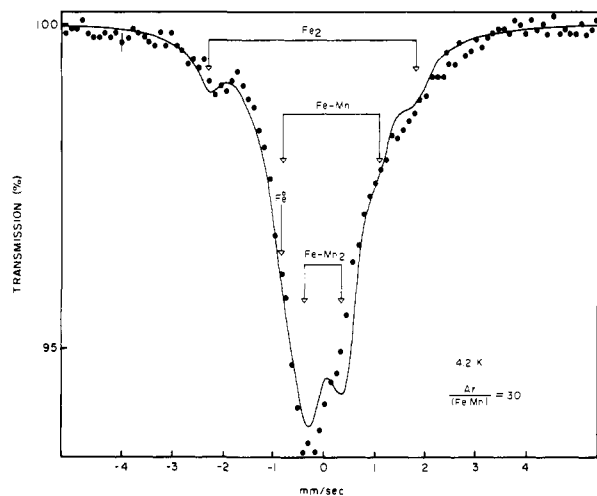


Figure 2. Mössbauer spectrum of (FeMn)-Ar at 4.2 K, 3 at. % metal concentration (before annealing).

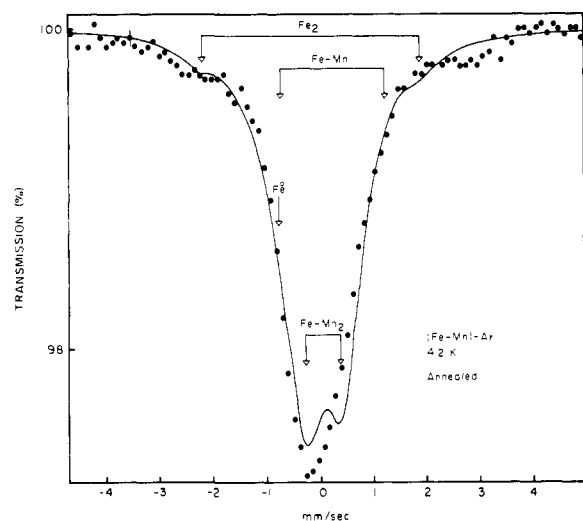


Figure 3. Mössbauer spectrum of (FeMn)-Ar at 4.2 K, 3 at. % metal concentration (after annealing).

nealing. The Mössbauer spectrum for this sample (before annealing) is shown in Figure 2. The positions of Fe^0 , Fe_2 , FeMn , and FeMn_2 (Fe_2Mn) are indicated in the figure. We observed a larger ratio of triatomic to diatomic heteronuclear molecules which is expected at this high concentration; it is also another indication that the FeMn molecule has been correctly identified. In order to completely fit all the points in the spectrum shown in Figure 2, one needs to consider also molecules like Mn_3Fe , Mn_2Fe_2 , and Mn_3Fe_2 . Since they represent <10% of the total spectral area, any attempt to resolve those species will have large errors. Consequently, the fit shown in Figure 2 ignored the presence of those compounds. However, from the analysis of the spectrum in Figure 2, one can infer that any small cluster (less than six atoms) of iron and manganese will have a positive IS. This is in a striking contrast to the results obtained in the FeMn alloys⁷ (where the IS is slightly negative), suggesting that, at least for the Fe-Mn system, small clusters are not representatives of the bulk alloy. This is an important point that should be considered if any "ab initio" calculations are used to describe the properties of Fe-Mn alloys.

In order to further confirm the identification of the FeMn molecules, the sample shown in Figure 2 was annealed for 30 min at ~ 35 K. At this temperature one can expect migration of iron and manganese atoms in the matrix. The spectrum obtained after annealing is shown in Figure 3. We observed an

Table I. Symmetry Type and Electric Field Gradient of d Orbitals in a $C_{\infty v}$ Symmetry.

orbital	symmetry type	electric field gradient
$d_{3z^2-r^2}$	$\Sigma^+, \Lambda = 0$	$-4/7 e \langle r^{-3} \rangle$
d_{xz} d_{yz}	$\Pi, \Lambda = 1$	$-2/7 e \langle r^{-3} \rangle$
$d_{x^2-y^2}$ d_{xy}	$\Delta, \Lambda = 2$	$4/7 e \langle r^{-3} \rangle$ $4/7 e \langle r^{-3} \rangle$

increase of the triatomic doublet, the disappearance of the monomer (Fe^0), and the decrease of Fe_2 . The results obtained from the analysis of Figure 3 are consistent with the identification of the FeMn molecule and the trimeric species. We can determine the ground state of the FeMn molecule from the observed value of the QS and the known electronic ground states of the homonuclear molecules, Fe_2 ⁸ and Mn_2 ^{5,9}. We find that the QS for FeMn is approximately one half the value measured for Fe_2 . From the magnitude of the QS and the sign of the electric field gradient at the ^{57}Fe nucleus in Fe_2 , one found that the atomic orbital ground state is $d_{3z^2-r^2}$.¹⁰ This is in complete agreement with the ground state of the Fe_2 molecule which is ${}^7\Sigma$. In Table I we show the splitting of the d orbitals under the symmetry group $C_{\infty v}$ of a diatomic molecule, along with the symmetry type and the electric field gradient produced by the atomic orbitals of the iron atom. From Table I it can be seen that only the doublet d_{xz}, d_{yz} of the symmetry type Π gives the correct magnitude of the electric field gradient (one half the value observed for Fe_2). From the known ground-state electronic configurations of Fe_2 (${}^7\Sigma, \sigma_g^2\pi_u^4\delta_g^4\sigma_g\delta_u^2\sigma_u^*\pi_g^*2$)⁸ and Mn_2 (${}^1\Sigma, \sigma_g^2\pi_u^4\sigma_g^2\delta_g^4\sigma_u^*2$)^{9,5} we suggest the following configuration for the FeMn molecule ${}^4\Pi: \sigma^2\pi^4\sigma^2\delta^4\delta^*2\pi^*$. This ground state is consistent with the Π symmetry type which gives the right magnitude for the electric field gradient. One interesting result of these measurements is that the FeMn molecule has a magnetic moment. Iron and manganese have different spin values and several combinations of the spins are possible; only one combination gives the right orbital symmetry (Π), total spin equal to $3/2$, indicating that the coupling in Fe-Mn is antiferromagnetic like in Mn_2 .⁹ We also observe a more positive IS value for FeMn (+0.24 mm/s) than for Fe_2 (-0.14 mm/s). The IS value for FeMn is closer to the values observed for FeCo and FeCu , suggesting a stronger bond between Fe and Mn than between Fe and Fe . This result is consistent with our proposed configuration for the FeMn molecule and the configurations of Fe_2 and Mn_2 . If one considers the bond orders of the three diatomic molecules, the bond order for FeMn falls between the values for Fe_2 and Mn_2 , implying stronger bonding in FeMn than in Fe_2 . From the difference in the IS between the iron monomer Fe^0 ($3d^64s^2$) and the value obtained for FeMn , one can infer that this difference corresponds to about one 4s electron less at the iron atom. This indicates that the 4s electrons are actively participating in the bonding between the two atoms.

We have shown that the combination of Mössbauer spectroscopy and matrix isolation techniques can be successfully used to study simple heteronuclear transition metal molecules. We applied these techniques to find the electronic ground state of the FeMn molecule. More measurements are necessary to better characterize the iron-manganese multimers, in particular, measurements in the presence of an external magnetic field so as to obtain more information about their electronic configurations from the magnetic hyperfine fields.¹⁰

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Apldiasphingosine, an Antimicrobial and Antitumor Terpenoid from an *Aplidium* sp. (Marine Tunicate)¹

Sir:

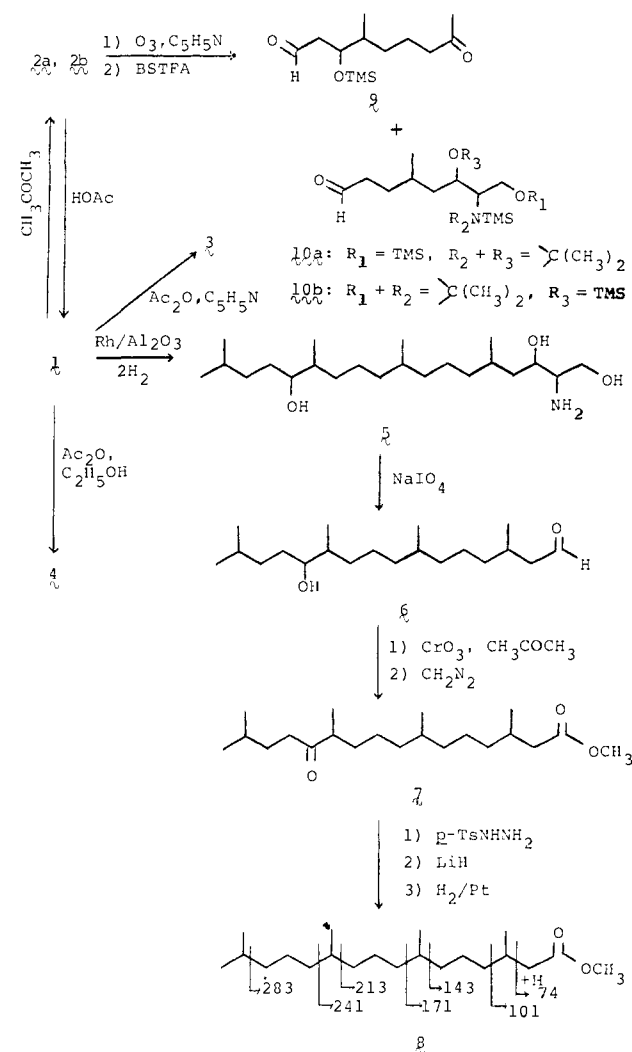
The orange-flecked compound tunicate identified as an *Aplidium* species² was originally collected from the Gulf of California during the Illini-Trojan Baja Expedition of June 1976 (ITBE 2-VI-76-1-3)³ and subsequently recollected in March 1977 (IBE 13-III-77-2-5). Extracts of the tunicate were shown in our mobile laboratory to possess inhibitory activity toward Gram-positive and Gram-negative bacteria and fungi and were subsequently shown to be cytotoxic to tumor cells (KB^{4a} and L1210^{4b}) and monkey kidney cells^{4c} and to inhibit Herpes virus type I.^{4c} Apldiasphingosine (**1**), isolated from the tunicate, gives the zones of inhibition indicated vs. the following microorganisms at 80 µg/12.7-mm disk:^{4d} *Bacillus subtilis* (24 mm), *Klebsiella pneumoniae* (21 mm), *Bacteroides fragilis* (21 mm), *Mycobacterium avium* (21 mm), *Sarcina lutea* (20 mm), *Clostridium perfringens* (14 mm), *Candida albicans* and *Penicillium oxalicum* (both, trace). Cytotoxicity toward KB^{4a} and L1210^{4b} tumor cells in tissue culture is also shown by **1** (ED₅₀ 8.3 µg/mL and ID₅₀ 1.9 µg/mL, respectively).

A sample (500 g) of the tunicate⁵ was homogenized in methanol-toluene (3:1) and the extract was partitioned by addition of 1 M sodium nitrate. Extraction of the aqueous phase with chloroform yielded 1.88 g of oil, which was subjected to repeated chromatography on silica gel developed with chloroform-acetone-methanol-concentrated ammonia (71:23:4.5:1.5) to give 400 mg of a mixture of the two acetone adducts, **2a** and **2b** (C₂₅H₄₇NO₃).^{6,7a} Treatment of the mixture of **2a** and **2b** with 50% aqueous acetic acid cleaved the acetonide, affording **1** (C₂₂H₄₃NO₃)^{7a} as an oil.

The oxygens and nitrogen of apldiasphingosine were shown to be present in three hydroxyl groups and a primary amine by the formation of its tetraacetyl derivative, **3** (C₃₀H₅₁NO₇),^{7b} whose IR spectrum (CHCl₃) contains bands corresponding to ester (1740 cm⁻¹) and secondary amide (1682, 1518 cm⁻¹) groups. A mono-*N*-acetyl derivative, **4** (C₂₄H₄₅NO₄),^{7a} IR (CHCl₃) 1665, 1521 cm⁻¹, was obtained by reaction of **1** with acetic anhydride in ethanol. The ¹³C NMR spectrum (CD₂Cl₂) of **4** clearly shows >CH-O- carbons at 76.5 (d) and 70.0 (d) ppm, a -CH₂O- carbon at 64.6 (t), and a >CH-N < carbon at 54.7 ppm (d).

The two elements of unsaturation required by the molecular

Scheme I. Derivatives and Degradation Products of Apldiasphingosine (**1**)



formula of **1** were determined to be double bonds from the four olefinic carbon absorptions in the ¹³C NMR spectrum of **4** (CD₂Cl₂) at 135.6 (s), 135.0 (s), 125.5 (d), and 121.8 (d) ppm, and by formation of a tetrahydro derivative, **5** (C₂₂H₄₇NO₃),^{7b} upon catalytic hydrogenation of **1** (Scheme I). Periodate oxidation⁸ of **5** gave aldehyde **6** (C₂₀H₄₀O₂),^{7b} which was converted to the phytanic acid methyl ester **8**⁹ by the reactions shown in Scheme I. The characteristic series of fragment ions observed in the spectrum of **8** (Scheme I) identify it as methyl 3,7,11,15-tetramethylhexadecanoate, a conclusion confirmed by comparison with the published mass spectrum.^{9a}

The loss of C₂H₆NO from **5** during periodate oxidation, taken with the ¹³C NMR data for **4**, indicated hydroxyl or amino substitution at C-1, C-2, and C-3 of **5** (and **1**), i.e., -CHX-CHY-CH₂OH, where X = OH, Y = NH₂, or vice versa. The formation of two acetone adducts (**2a**, **2b**) involving adjacent hydroxyl and amino groups argues for the former arrangement, and this was confirmed by the abundant C₅H₁₀NO peak in the mass spectrum of **2b**, as shown.¹⁰ In addition, the ions at *m/e* 340 and 310 locate the third hydroxyl at C-14 and restrict one double bond to the C-15-C-18 region, argued also by the *m/e* 69 ion.

It was noted above that **1** contains two =CH- and two =C < carbons. Of the five methyl groups observed in the ¹H NMR spectrum of **1**, three are olefinic methyl singlets, at 1.73, 1.63 and 1.58 ppm, requiring a Δ^{16,17} double bond. The position of the Δ^{16,17} unsaturation was confirmed and the position of the other olefinic bond was established as Δ^{8,9} by ozonolysis