GENERATION AND TRAPPING OF CHARGED SPECIES IN RARE-GAS MATRIX AT 4°K: ESR SPECTRA OF Cd^+, Cr^+, AND Mn^+

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Photoirradiation of a rare-gas matrix at 4°K containing both electron donating species and electron accepting species of suitable choice may lead to generation and trapping of charged species effectively isolated within the matrix lattice. Preliminary investigation conducted along this line using certain metal atoms (Cd, Cr, Mn, and Na) as electron donors and HI as an acceptor led to successful observation of the electron spin resonance spectra of Cd^+, Cr^+, and Mn^+.

Matrix isolation technique, trapping of unstable species inside a solid matrix of a rare gas at near liquid-helium temperature, is generally thought to be applicable only to neutral species. Recently we have found that, under a certain condition, charged species can be generated and kept trapped within the matrix. The process requires trapping of both electron-donating species and electron-accepting species of suitable choice within the same matrix, and then promoting an electron transfer between them by photoexcitation. Once the photoexcitation ceases, the return of the electron from the resulting anion to the cation is hampered by the local potential trap imposed by the electron affinity of the electrophilic species. Also the migration of the oppositely charged ions toward each other is prevented by the matrix lattice.

Following are the results of our preliminary investigation conducted along this line using certain metal atoms (Cd, Cr, Mn, and Na) as electron donors and HI as an electron acceptor. It has led to the observation of the ESR spectra of Cd^+, Cr^+, and Mn^+ ions as well as those of neutral Cr and Mn atoms. The net reaction that occurs within the matrix may be summarized as

$$M + HI \xrightarrow{h\nu} M^+ + I^- + H.$$

The design of the Dewar and ESR spectrometer system which allows the trapping of unstable species and the measurement of their ESR spectra has been described previously.[1] In the present series of experiments, the metal atoms were vaporized from a resistively heated tantalum cell and were trapped with argon containing 1% HI upon the surface of the cold finger. The matrices thus prepared were then examined for their ESR spectra before and after the photoexcitation. A high-pressure mercury lamp (GE AH-6) combined with uv filter (Corning 7-54 filter) was used as the light source unless mentioned otherwise.

Cd.—No ESR signal is observed prior to the photoexcitation. Figure 1 shows the spectrum obtained after photoexcitation. The strong doublet due to hydrogen atoms is easily recognized. The sharp signal near the center of the hydrogen doublet, and the two sharp, but weaker signals near 5000 G are assigned, respectively, to Cd^+ with nonmagnetic nuclei, $^{111}Cd^+$ (natural abundance = 12.86%, $I=\frac{1}{2}$) and $^{113}Cd^+$ (natural abundance = 12.34%, $I=\frac{1}{2}$). The ratio of the peak-to-peak intensities of the three signals is in reasonable agreement with the ratio of the natural abundances of the isotopes involved. The resonance spectrum can be interpreted in terms of an isotropic spin Hamiltonian (1) with $S=\frac{1}{2}$, and

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + A\vec{I}\cdot\vec{S}. \tag{1}$$

$I=0$ for Cd^+ with nonmagnetic nuclei, and $I=\frac{1}{2}$ for $^{111}Cd^+$ and $^{113}Cd^+$. Using the "Breit-Rabi formula" derived from the Hamiltonian (1), the following values were assessed:

$$g = 2.0006 \pm 0.0002,$$

$$A(^{111}Cd^+) = 5137 \pm 1 \text{ G or } 14.385 \text{ kMc/sec},$$

$$A(^{113}Cd^+) = 5374 \pm 1 \text{ G or } 15.048 \text{ kMc/sec}.$$

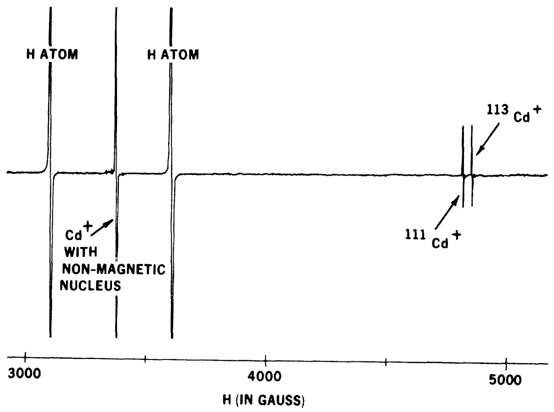

FIG. 1. ESR spectrum of Cd^+ in argon matrix at ~4°K.

The hfs constants obtained here give 1.0461 as the ratio of the magnetic moments of the two nuclei, ^{113}Cd and ^{111}Cd, in exact agreement with the known value. That these coupling constants are larger than the microwave frequency of the spectrometer (9.4 kMc/sec) accounts for the absence of the lower field component of the doublet normally expected from the hyperfine interaction with a nucleus of spin $\frac{1}{2}$. The closeness of the g value to the free spin value and the extremely large, isotropic hfs constants are consistent with the electronic configuration $4d^{10}5s^1(^2S_{1/2})$ expected of a singly ionized Cd atom. A reasonable estimate of the hfs constant of Cd$^+$ can be made from the known hfs constants of isoelectronic Ag atoms (^{107}Ag and ^{109}Ag)[2] using Goudsmit's relation.[3] The value so estimated, 15.7 kMc/sec, is very close to the observed ones. These features coupled with the fact that there is no evidence, in the observed spectrum, of any significant interaction with other nuclei such as hydrogen or iodine strongly support our expectation that, in their ground states, these charged species are effectively "isolated" within the matrix.

Cr.—The spectra observed before and after the photoexcitation are compared in Fig. 2. In each trace, the strong central signal is accompanied by a weak equally spaced quartet, a hyperfine structure due to ^{53}Cr (natural abundance = 9.55%, $I=\frac{3}{2}$). The ground-state electronic configurations of Cr^0 and Cr$^+$ are $3d^54s^1(^7S_3)$ and $3d^5(^6S_{5/2})$, respectively. The g values of both Cr^0 and Cr$^+$ are, therefore, expected to be very close to that of a free electron, and the spectra should be free of fine-structure interaction provided they are not subjected to a crystal field with a symmetry less than that of a cubic field. The fine-structure interactions are anisotropic, and the sharpness of the observed spectra clearly defies the possibility that diatomic molecular species such as CrH or CrI are responsible for the observed signals. The difference in the hfs spacing of the ^{53}Cr satellites before and after the photoexcitation is remarkable. Accordingly the spectra are assigned to Cr^0 and Cr$^+$ ions, respectively. The observed parameters are for Cr^0,

$$g=2.0006\pm 0.0002,$$

$$A(^{53}\mathrm{Cr})=33.8\pm 0.1 \text{ G or } 94.6 \text{ Mc/sec};$$

and for Cr$^+$,

$$g=2.0011\pm 0.0002,$$

$$A(^{53}\mathrm{Cr})=24.0\pm 0.1 \text{ G or } 67.2 \text{ Mc/sec}.$$

The coupling constant obtained for ^{53}Cr^0 is slightly larger than that determined by the atomic-beam magnetic resonance work.[4] The ESR spectrum of Cr$^+$ has been observed in many crystals.[5-7] Because of the covalent nature of the ligands involved, however, all of the hfs constants reported are much smaller (<50%) than the value observed here. Extrapolation of the spin-density calculation for Mn^{++} and Fe^{++} by Watson and Freeman[7] gives the hfs constant of ~27 G for Cr$^+$.

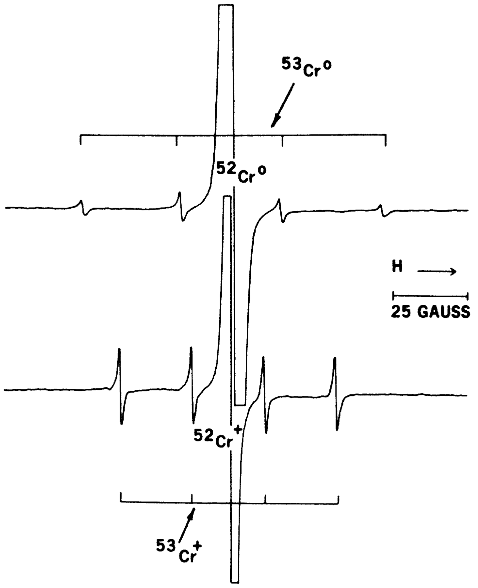

FIG. 2. ESR spectrum of Cr^0 (upper trace) and Cr$^+$ (lower trace) in argon matrix at ~4°K.

Mn.—Figure 3 shows the spectrum observed with Mn after the photoexcitation. It shows both the spectrum due to Mn^0 which, of course, was observed before the irradiation, and the spectrum attributed to Mn$^+$ which appeared only after the irradiation. The ground-state electronic configurations of Mn^0 and Mn$^+$ are $3d^54s^2(^6S_{5/2})$ and $3d^54s^1(^7S_3)$, respectively. The g values and hfs constants due to ^{55}Mn (natural abundance = 100%, $I=\frac{5}{2}$) are for Mn^0,

$$g=2.0013\pm 0.0002,$$

$$A(^{55}\mathrm{Mn})=27.9\pm 0.1 \text{ G or } 78.2 \text{ Mc/sec},$$

and for Mn$^+$,

$$g=2.0024\pm 0.0002,$$

$$A(^{55}\mathrm{Mn})=270.4\pm 0.5 \text{ G or } 757.9 \text{ Mc/sec}.$$

A very small coupling constant observed with Mn^0 is consistent with its electronic configuration. However the value determined here is

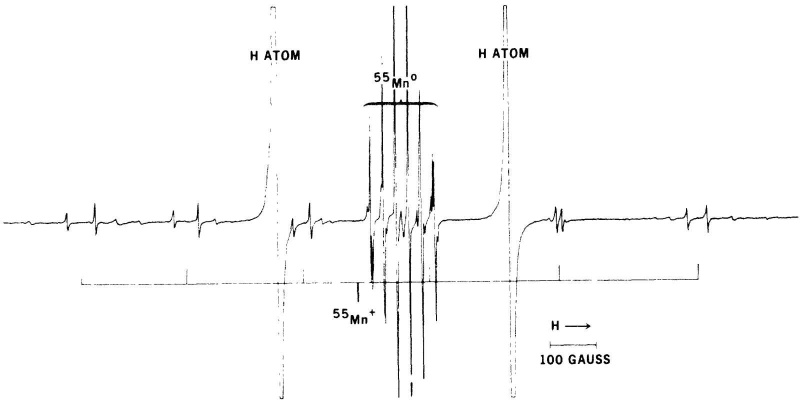

FIG. 3. ESR spectrum of Mn^0 and Mn^+ in argon matrix at ~4°K.

slightly larger than that reported by Woodgate and Martin[9] from an atomic-beam experiment. The hfs constant of Mn^+ may be estimated, using Goudsmit's relation, from that of the isoelectronic Cr^0 atom given in the preceding section. It gives 274 G almost in exact agreement with the value given above. A multiple structure within each hyperfine group is due to the extremely large second-order hyperfine interaction terms which include M_S, the magnetic quantum number of the total electronic angular momentum S of 3. A doublet appearance prominent in each group is due to the transitions $M_S = 1 \rightarrow 0$, and $M_S = 0 \rightarrow -1$.

Na.—Prior to the photoexcitation the spectrum observed was that of Na atoms.[10] Irradiation of the matrix using a sharp-cutoff filter (Corning 7-70) which cutoff all the light below 5000 Å resulted in a complete disappearance of the Na signals and an appearance of the strong doublet due to hydrogen. A matrix of argon containing HI but no Na atoms did not yield hydrogen atoms when irradiated with the same light, suggesting that, in a matrix containing Na, a HI molecule accepts an electron and then spontaneously decomposes into H atom and I^-. However it does not exclude the possibility that, under uv irradiation, an iodine atom formed by the photolysis of HI would also act as an electron acceptor. Both mechanisms are probably in effect under uv irradiation.

Details of the experiment and the analysis of the result will be reported shortly. The author wishes to express his sincere appreciation to W. D. Bird for his invaluable laboratory assistance.

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