PARAMAGNETIC RESONANCE OF SILVER ATOMS TRAPPED IN POLAR MEDIA AT 77°K

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Free silver atoms were trapped in polar media (distilled water, absolute ethanol) at the temperature of liquid nitrogen by the condensation method. The paramagnetic resonance spectra of these atoms were obtained and investigated.

IN previous work[1] free silver atoms were trapped in nonpolar media at the temperature of liquid nitrogen and their paramagnetic resonance spectra investigated. It was of interest to investigate the possibility of trapping the same atoms in polar media and likewise study the paramagnetic resonance of such trapped atoms. This study is the subject of the present paper.

Up to this time the paramagnetic resonance of atoms trapped in polar media has been observed only for hydrogen atoms obtained by irradiation of aqueous solutions of acids frozen at liquid-nitrogen temperatures.[2,3]

In the present work, water and ethanol were chosen as the polar matrices, and the trapping was accomplished, as in [1], by the simultaneous condensation of the free atoms and the vapors of the matrix substance on a surface cooled by liquid nitrogen.

EXPERIMENTAL METHOD

As before,[1] the samples containing the trapped neutral atoms were obtained at the temperature of liquid nitrogen directly in the cavity of the spectrometer used to study their paramagnetic resonance spectra. The apparatus for obtaining the samples is basically the same as that shown in Fig. 1 of [1]. In distinction to earlier work, in which the substances used for the matrix were solid at room temperature, this time the matrices had to be formed from substances that are liquid at this temperature and required cooling to lower their vapor pressure. This required a number of changes in the apparatus. The vessel containing the matrix substance was removed from the apparatus and placed in a dewar full of alcohol. The alcohol in the dewar was chilled to a low temperature with liquid nitrogen. The temperature of the alcohol bath was measured with a thermocouple. The vapors of the matrix substance were conducted by a special tube straight to the bottom of the dewar in which the sample was condensed. In addition, in the present work vaporization of the silver with a molybdenum coil was replaced by vaporization from a tungsten boat heated by an electric current.

The same X-band spectrometer with high-frequency modulation used in [1] was also used for these experiments. The cylindrical transmission-type cavity had 15 mm holes in the end plates, through which passed the quartz tube of the sample-preparation apparatus (see [1]).

The dc magnetic field was measured to one part in 10^4 by nuclear magnetic resonance. Field markers were introduced in the recorded traces. The frequency of the klystron was measured with a heterodyne wavemeter with an accuracy of 5×10^{-5}.

EXPERIMENTAL RESULTS

The ground state of the silver atom is $^2S_{1/2}$. Hence the energies of the Zeeman levels of the hyperfine structure of the ground state of free silver atoms are given by the following Breit-Rabi formula[4]:

$$W_{I\pm 1/2} = -\frac{\Delta W}{2(2I+1)} + g_I\beta Hm \pm \frac{\Delta W}{2}\left(1 + \frac{4m}{2I+1}x + x^2\right)^{1/2}. \quad (1)$$

Here ΔW is the energy of the hyperfine splitting of the ground state in zero magnetic field; I is the nuclear spin; $g_I = -\mu_I/\beta I$ is the nuclear gyromagnetic ratio; μ_I is the nuclear magnetic moment; β is the Bohr magneton; H is the dc magnetic field in which the atom is placed; m is the magnetic quantum number of the total moment of the atom; $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where J and I are the moments of the shell and nucleus, respectively; $x = (g_J - g_I)\beta H/\Delta W$ is a dimension-less quantity proportional to the magnetic field H; g_J is the electronic gyromagnetic ratio of the atom (Landé factor).

In accordance with the considerations presented in [1], the Zeeman levels of atoms trapped in passive media and remaining neutral within them can also be described by Eq. (1), but with different values of ΔW and g_J. Deviations in the values of these quantities from their values for free atoms depend on the interaction of the matrix with the trapped atom. Therefore, having determined from paramagnetic resonance experiments the quantities ΔW and g_J for trapped atoms through the use of Eq. (1) and comparing them with the analogous quantities for free atoms, one can judge the nature of the perturbation of the shell of the trapped atom by the matrix.

Silver has two stable isotopes, Ag^{107} and Ag^{109}, which exist in nature in almost equal proportion. The spins of the nuclei of both isotopes $I = {}^1/_2$, and the nuclear magnetic moments are negative and close in magnitude. Therefore, four Zeeman levels of the hyperfine structure appear in a magnetic field for each isotope; in strong fields it is possible to observe two resonance transitions among them [1]:

$$(F = 1,\ m = -1) \rightarrow (F = 0,\ m = 0)$$
$$\text{and } (F = 1,\ m = 0) \rightarrow (F = 1,\ m = 1).$$

Consequently, the paramagnetic resonance spectrum of each silver isotope consists in strong fields of two lines lying on either side of and at equal distances from the line for the free electron at g = 2.0. Since the nuclear moments and the quantities ΔW of the silver isotopes differ somewhat, the complete paramagnetic resonance spectrum of the silver atoms will have a characteristic form of four lines, distributed in pairs on either side of the free electron line.[1]

In paramagnetic resonance experiments the resonance frequency ν is usually kept constant while the magnetic field H is varied. Taking this into consideration, we obtain from Eq. (1) the following expressions for the aforementioned two transitions for each silver isotope:

$$\nu = -\Delta\nu\left\{\frac{1}{2}(1 + x_1^2)^{1/2} + \frac{1}{2}(1 - x_1) - \frac{g_I\beta H_1}{h\Delta\nu}\right\},$$
$$\nu = -\Delta\nu\left\{\frac{1}{2}(1 + x_2^2)^{1/2} - \frac{1}{2}(1 + x_2) - \frac{g_I\beta H_2}{h\Delta\nu}\right\}, \quad (2)$$

where

$$x_1 = (g_J - g_I)\beta H_1/h\Delta\nu, \qquad x_2 = (g_J - g_I)\beta H_2/h\Delta\nu,$$

H_1 and H_2 are the values of the magnetic field for the first and second transitions; $\Delta\nu = \Delta W/h$, where h is Planck's constant. The nuclear gyromagnetic ratios are $g_I(Ag^{107}) = 1.237 \times 10^{-4}$ and $g_I(Ag^{109}) = 1.422 \times 10^{-4}$.

In what follows we shall determine the values of $\Delta\nu$ and g_J from the paramagnetic resonance experiments, using Eq. (2), and then compare them with the analogous values for free atoms.

1. Silver atoms trapped in water at 77°K. Doubly-distilled water was used as the matrix source in these experiments. To obtain samples with trapped atoms, the ampule containing the water was submerged in the alcohol bath and kept at a temperature of about −60°C. The vapor pressure of water over ice under these conditions is about 8×10^{-3} mm Hg. Water vaporized in vacuum from the solid at this temperature undergoes an additional distillation and becomes extremely pure. Hence the matrix obtained from such vapors was very clean.

Figure 1a shows the paramagnetic resonance spectrum of silver atoms trapped in such a matrix. (All the spectra presented here are differential absorption spectra.)

All the experiments described here were carried out at liquid-nitrogen temperature.

The spectrum in Fig. 1a consists of the four lines characteristic of silver atoms. Between the pairs of silver lines there occurs a relatively weak line in the center of the spectrum at g = 2.0. This line is due to a free radical created during the capture of the silver atoms in the water. We have not investigated the nature of this radical. It is possibly the OH radical, formed by hydrogen atoms knocked off the water molecules by silver atoms in the condensation process.

Figure 1b shows the low-field pair of lines at slow sweep. The high-field pair is similarly shown in Fig. 1c. The field markers can be seen in these traces. The resonance field values derived from these markers, together with the resonance frequency indicated, suffice to determine the quantities $\Delta\nu$ and g_J for the trapped silver atoms.

These quantities for silver atoms trapped in water are presented in the table. Data such as those shown in Fig. 1 are obtained rather easily, and we repeated these experiments many times. The table gives the mean values obtained from a series of 11 runs. The table also gives the values for free silver atoms. For comparison of these with the values for the trapped atoms, the table gives the quantity $\delta(\Delta\nu)/\Delta\nu$, where $\delta(\Delta\nu) = \Delta\nu - \Delta\nu_{free}$, expressed as a percentage. The limits of error indicated in the table represent the maximum deviations from the mean for each series of runs.

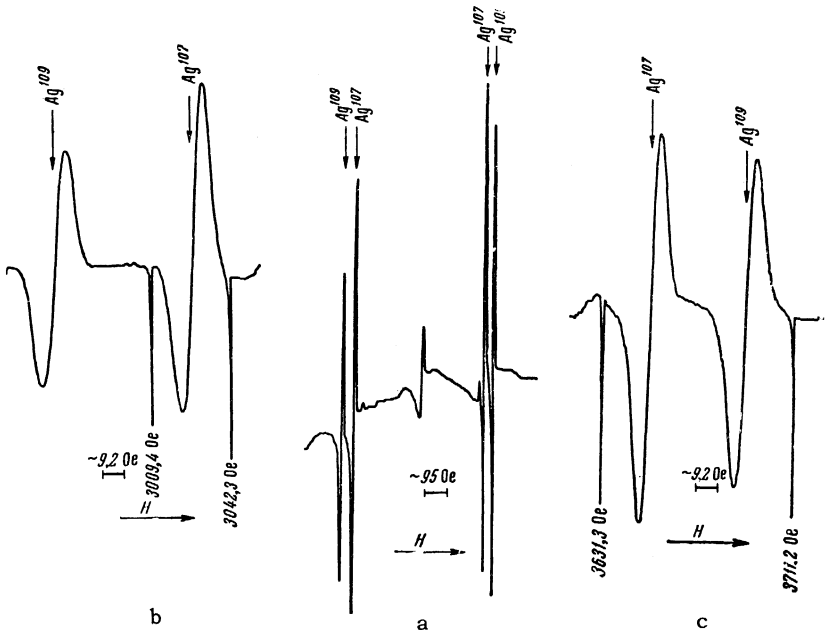

FIG. 1. Paramagnetic resonance spectrum of silver atoms trapped in H_2O; the frequency is 9435.8 Mc/sec.

Atom	Matrix	Number of runs	$\Delta\nu$, Mc/sec	$\delta(\Delta\nu)/\Delta\nu$, %	g_J
Ag^{107}	Free atom		1712.56±0.04		2.00224±0.00020
Ag^{109}	Free atom		1976.94±0.04		2.00224±0.00020
Ag^{107}	H_2O	11	1736.9 ±3.1	+1.42	2.0021±0.0005
Ag^{109}	H_2O	11	2004.7 ±2.9	+1.40	2.0020±0.0006
Ag^{107}	C_2H_5OH	6	1500.3 ±2.4	−12.39	2.0003±0.0008
Ag^{109}	C_2H_5OH	6	1733.0 ±2.3	−12.36	2.0004±0.0009

The traces shown in Fig. 1 are typical of the experiments on trapped silver atoms in water.

As can be seen from the table, the relative shift in $\Delta\nu$ (i.e., $\delta(\Delta\nu)/\Delta\nu$) for silver atoms in water turns out to be positive and equals ~1.4%. Aside from the demonstration that neutral silver atoms can be trapped and stabilized in water at 77°K, this is the most important result of these experiments.

The width of the line, defined as the separation between the maximum values of the first derivative of the absorption line, varied between the limits 6.5 and 10.5 Oe.

2. Silver atoms trapped in ethanol at 77°K. The matrix source was 99.5% absolute ethanol. The source was kept at a temperature of approximately − 80°C during sample preparation. Such a low-temperature distillation in vacuum provided an additional effective purification of the ethanol, removing dissolved impurities and possible incidental traces of water, the vapor pressure of which at this temperature is several times lower than that of ethanol.

The paramagnetic resonance of silver atoms trapped in an ethanol matrix is shown in Fig. 2a. The characteristic four-line spectrum of silver atoms is again seen. Between the pairs, in the center of the spectrum, appears a much weaker line (g = 2.0) from a free radical created by the silver atoms in the ethanol. We have not investigated this radical.

Figures 2b and 2c show the left and right pairs of Fig. 2a at slow scan and with field markers.

Figure 2 is typical of the many runs that were made on this system. The mean values of $\Delta\nu$ and g_J for a series of 6 runs are given in the table.

The significant result is the relative shift in $\Delta\nu$, which in distinction to the case of the water matrix is negative and larger in absolute magnitude, − 12.4%. This difference can be traced directly in Fig. 2a, in which the splitting in magnetic field between the two lines of each isotope is noticeably less than the analogous splitting in Fig. 1a.

The line widths varied within the limits 8—14 Oe and for the same lines were noticeably greater than in the case of water.

Our method did not permit measurements of the concentration of the trapped neutral atoms. However, the total number of isolated atoms in the matrix was determined from the EPR signal

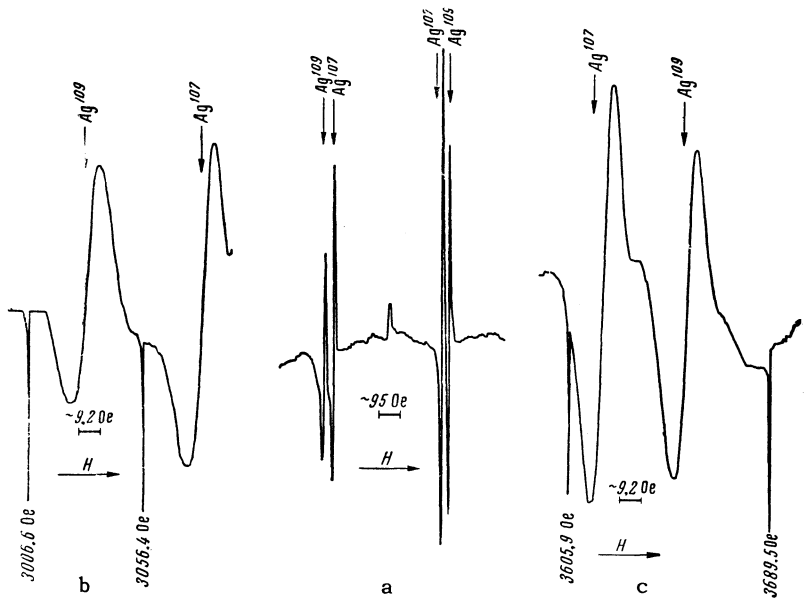

FIG. 2. Paramagnetic resonance spectrum of silver atoms trapped in C_2H_5OH; the frequency is 9441.2 Mc/sec.

intensity by means of a sample of DPPH. In the majority of the runs with water and ethanol this number exceeded 10^{15}.

The EPR spectra of silver atoms in water and alcohol at liquid-nitrogen temperatures were stable and did not change with time; this is evidence that the trapped atoms are immobile at this temperature.

CONCLUSION

The results presented above demonstrate the possibility of trapping and stabilizing isolated silver atoms in matrices of distilled water and ethanol at 77°K.

The most important results of the experiments with water are the smallness of the shift in $\Delta\nu$ and the positive sign of this shift. The latter is evidence that in this case the Pauli forces [5] prevail over the electric dipole-dipole forces in the atom-matrix interaction. It is strange that in a matrix of such a polar substance as water, which has a dipole moment of 1.94 D, the shift in $\Delta\nu$ for trapped silver atoms (+1.4%) is almost the same as the shift of +1.15% for silver atoms in paraffin, [1] which has a molecular dipole moment of zero.

The experiments on trapped silver atoms in ethanol also gave extremely interesting results. In a matrix of ethanol, i.e., of a polar substance whose dipole moment is 1.7 D, the shift turned out to be −12.4%, i.e., not only negative, but also greater in absolute value by about an order of magnitude than in water and paraffin. It can therefore be assumed that in ethyl alcohol the electric dipole-dipole interactions between the trapped atoms and the matrix predominate. [5]

Thus, in matrices of such similar polar substances as water and ethanol, the shifts in hyperfine splitting for trapped silver atoms were found to be different in sign and completely different in absolute magnitude. On the other hand, for matrices of such different substances as polar water and nonpolar paraffin, these shifts agree in sign and are almost equal in magnitude. At the present time, it is evidently impossible to give an explanation for all these facts since we have as yet no information about the structure of the deposits of water and ethanol condensed in vacuum at 77°K, and consequently nothing is known about the nature of the surroundings of the atoms trapped in such matrices. Besides, no theory has yet been developed to the describe the interactions with the matrix and their effect on the EPR spectra of atoms trapped in polar media.

As has been mentioned, the width of the silver lines in alcohol were usually somewhat greater than the width of the same lines in water. Besides, the lines on the low-field side were as a rule somewhat wider than those on the high-field side in the same run.

It should be noted that the matrices were of a high degree of purity. This was achieved by the use of pure starting materials and by the low-temperature distillation in vacuum. The trapping of silver atoms in a matrix obtained by the above-described method from ordinary technical 96% ethanol (rectified) was investigated. In this case a shift of −12.1% (average of three runs) was obtained, i.e., the water impurity in the starting material gave a deviation from the value of −12.4% obtained using absolute alcohol.

The weakness of the free radical signals in Figs. 1a and 2a is evidence that extraneous paramagnetic impurities were present in extremely small amounts in the investigated samples.

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